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去る11月10日から３日間、京都会館にて標題の国際シンポジウムが、当研究所の共催のもとに開催されました。

内外から127件の講演発表と、273名の参加者を得、成功裡に終了しました。

ここに、このシンポジウムの Abstract を再録いたします。

S1-01

INTERFERENCE OF IODIDE FOR THE USUAL MERCURY DETERMINATION BY ATOMIC ABSORPTION SPECTROMETRY

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The most widely used method for the determination of mercury is the cold-vapor atomic absorption analysis after the reduction of mercury with tin(II) chloride in acidic solution (Method 1), cited as a Japan Industrial Standard(JIS). However, it was found that iodide in the sample solution interfered with the determination of mercury by this method even after digestion. Recently, waste waters discharged from university and industry often contain a large amounts of iodide, so a new analytical method of mercury without the interference of iodide is necessary. In the present study, the interfernce of iodide was discussed from the standpoint of redox reaction and atomic absorption determination of mercury in samples containing iodide by a combined copper(II)-tin(II) chloride reduction reagent in alkaline solution (Method 2) and that by a combined iron(III)-sodium borohydride($NaBH_4$) reduction reagent in acidic solution (Method 3) were presented. These methods were applied to the determination of mercury in waste water samples containing iodide with satisfactory results.

1. INTERFERENCE OF IODIDE FOR THE MERCURY DETERMINATION BY METHOD 1

The effect of potassium iodide and potassium iodate on the determination of mercury by Method 1 was examined. These results obtained are shown in Table 1.

Table 1. Influence of iodide additions to mercury standard solutions before digestion (Hg; 0.5μg/100ml)

I^- added (mg)	Mercury recovery (%)	
	KI	KIO_3
0.1	100	98
0.5	99	98
1.0	96	94
5.0	89	31
10	61	9
50	9	
100	5	

Even after digestion with acidic permanganate, the presence of iodide more than 1.0mg/100ml interfered with reduction of mercury. In the wet digestion with acidic permanganate at 95°C, the iodide is oxidized to iodine(I_2), which is easily released from sample solution, but iodine is further oxidized to iodate or an ion pair, I_3^- is formed at high concentration of iodide. Hence, mercury complexes with iodide such as HgI_4^{2-} would be formed because iodide in sample solution could not be released completely in the digestion. Since the stadard reduction potential for HgI_4^{2-} system is -0.038 V vs. NHE and the standard potential for tin(II) chloride is 0.15 V in acidic solution, the formation of mercury complexes with iodide would make reduction to elemental mercury with tin(II) chloride in acidic solution impossible. From these results, it became apparent that the reducing reagent more powerful than tin(II) chloride in acidic solution is necessary for the mercury determination in the sample containing iodide.

2. DETERMINATION OF MERCURY IN THE SAMPLE SOLUTION CONTAINING IODIDE

We investigated various reducing reagents. As a result, it was found that a combined copper(II)-tin(II) chloride reduction reagent in alkaline solution[1)] or a combined iron(III)-$NaBH_4$ reduction reagent in acidic solution[2,3)] may be available as a reducing reagent for the mercury determination in the sample containing iodide.

The reducing power of tin(II) in alkaline solution is stronger than that in acidic solution because the standard potential for tin(II) is -0.93V vs. NHE at pH 14. By Method 2, iodide up to 500mg did not interfere with the determination of mercury. However, in the samples of coexisting silver with iodide, silver more than 0.5mg interfered with the determination of mercury. We found that potassium zinc cyanide($K_2Zn(CN)_4$) is available as a masking reagent for silver. The determination procedures are as follows: An aliquot (100ml) of sample solution was taken into a reaction vessel after digestion with potassium peroxodisulfate in a sulfuric acid solution heated at 95°C for 2hr. To the solution 10ml of 5N sodium hydroxide, 1ml of 5% $K_2Zn(CN)_4$, 2ml of 1000ppm Cu(II) and 2ml of 10% tin(II) chloride were added, and the evolved mercury was measured with an atomic absorption spectrophotometer. Furthermore, sodium borohydride is known to be more powerful reducing reagent than tin(II) chloride. Iodide up to 100mg did not interfere with the determination of mercury by Method 3. These methods were applied to the determination of mercury in waste water samples containing iodide with satisfactory results.

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S1-02

ION-EXCHANGER ABSORPTIOMETRY --- APPLICATION TO FLOW ANALYSIS OF TRACES OF CHROMIUM(VI) IN RIVER WATER

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Ion-exchanger colorimetry is based on the direct measurement of the degree of light-absorption by an ion-exchange resin phase which has sorbed a sample component. Direct application of the method makes it possible to determine trace elements in natural water samples without preconcentration.1,2)

The purpose of this study is to show how this method used for chromium(VI)3) can be extended to flow analysis.

PROCEDURE The reaction product of chromium(VI) with 1,5-diphenylcarbazide3) is introduced into a sulfuric acid-acetone solution stream (Fig. 1). The flow-through cell was supplied by Nippon Quartz Glass Co; it was black-sided and had a 10-mm path length and a 1.5-mm diameter. The cell was filled with 5 - 10 mm^3 of a cation-exchange resin: Bio-Rad AG 50W-X2 (100-200 mesh). The increase in the attenuance by the colored complex sorbed in the resin phase was monitored at 550 nm with a double-beam Nippon Bunko spectrophotometer, Model UVIDEC-320. The colored species in the resin phase was easily desorbed with a nitric acid solution.

RESULTS AND DISCUSSION To compare the present method sensitivity and the corresponding solution absorptiometry sensitivity the ratio of the two absorbances for sample solutions of the same chromium concentration can be measured. If all the colored species injected is retained in the resin phase in the flow-through cell, the sensitivity ratio (SR) is closely related to:

$$SR = (\bar{\varepsilon}\ V)/(\varepsilon\ S\ l) \qquad (1)$$

where ε is the molar absorptivity, V the sample volume injected in cm^3, S the diameter of the flow-through cell in cm^2, and l the light path length in cm.4) The bar over the ε refers to the ion-exchanger phase. In the case of the chromium(VI)-1,5-diphenylcarbazide system, the distribution ratio of the colored species is sufficiently high (D = 1.2 x 10^4 cm^3/g), and $\varepsilon \approx \bar{\varepsilon}$. The present system ($V$ = 4.41 cm^3, S = 0.0177 cm^2) is expected to yield a sensitivity about 250 times greater than that of the solution method (l = 1 cm), which is in fairly good agreement with the results obtained. Equation (1) implies that the cross section of a flow-through cell and the sample volume injected are very important factors for obtaining high sensitivity, provided that the photo-cell of the instrument is in proportional detection to the light intensity in spite of the tremendous light loss due to scattering and/or absorption. An inside mirror quartz tube was placed between the cell holder and the light-detector window to recover partly the light scattered from the cell. This reduced the attenuance by 1.

After the sample injection, the attenuance in the range of 2.5 to 2.8 increased, because the colored species sorbed in the cation-exchange resin phase. It was not necessary to desorb the colored species after each injection (Fig. 2). The change of flow rate from 0.66 to 2.12 cm^3 /min decreased the sensitivity by 75 %, but there was a strictly linear relationship between measured absorbance and chromium concentration at a constant flow rate. A variation in the sample volume ranging from 0.2 to 8.7 cm^3 resulted in a proportional increase in absorbance. Much higher sensitivities can be obtained by employing larger amounts of sample solution.

The present method was applied to the analysis of fresh water samples. THe results obtained for river and underground water were in the range of 0.1 to 1 μg Cr(VI)/dm^3.

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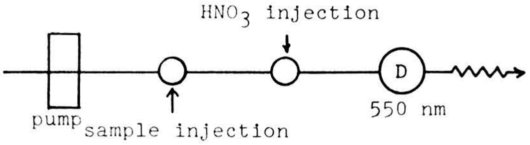

Fig. 1. Schematic flow analysis diagram.

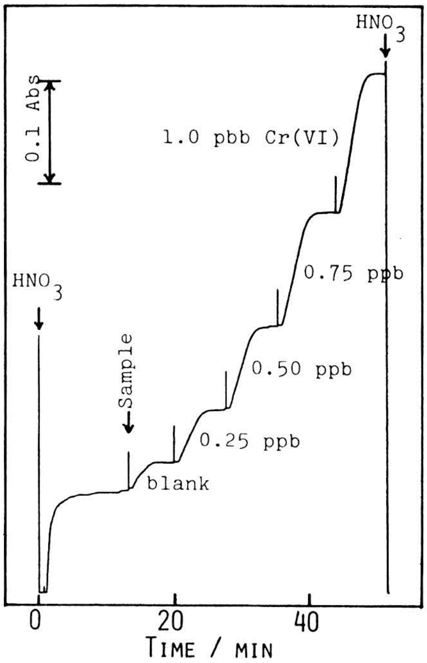

Fig. 2. Color-developing profile for chromium by the flow system of ion-exchanger absorptiometry.

Sample volume: 4.41 cm^3
Resin: AG 50W-X2 (100-200 mesh)
Flow-through cell: 1.5 mm in diameter
Carrier solution: 0.06 mol/dm^3 H_2SO_4 (2 % acetone)
Flow rate: 1.17 cm^3/min
Wavelength: 550 nm

S1-03

DETERMINATION OF TRACE VANADIUM IN AIR SAMPLES WITH AZO-DYE REAGENTS BY REVERSED-PHASE HPLC

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A highly sensitive method for the determination of trace vanadium(80 ppt) was developed.

Vanadium is one of the most important elements in environmental chemistry because it may be an indicator for an estimate of air pollution from fossile-fuel and petroleum products, especially fuel oil, coal fly ash, and asphalt. Vanadium in air is usually present at very low concentration, 2-10 ng/m^3 in the presence of various elements such as iron and aluminum. So sensitive and selective method for vanadium is desired.

Recently, high performance liquid chromatography(HPLC)-photometric detection system has been accepted as a powerful alternative to conventional colorimetry for trace metal analysis. In this work, metal ions are determined by the pre-column derivatization method, in which metal ions are converted into colred metal chelates in off-line system and the chelates are separated and selectively decomposed on a column by using eluent containing no chelating agent. Highly sensitive reagents for vanadium, some azo dye compounds have been investigated in this HPLC system. Among these reagents, 2-(8-quinolylazo)-5-N,N-diethylaminophenol(QADAP) has been chosen because of its excellent selectivity. With QADAP, only vanadium(V) ion gave a well-resolved peak on a propylcyano bonded phase column using an aqueous acetonitrile mobile phase, among 16 kinds of metal ions of Al, Ba, Ca, Cr(III), Cu(II), Fe(III), Ga, Mg, Hg(II),Mn(II), Ni, Pb(II), V(V), Cd, Co(II), and Zn. The proposed method has been successfully applied to the detremination of vanadium in airborn particulates and in rain water.

EXPERIMENTAL

Apparatus and reagents: The HPLC system consisted of a conventional pumping system and spectrophotometric detector(Shimazu LC-5A, and Shmazu SPD-2A) and a u-Bondapack-CN(3.9mm x 300 mm, Waters Assoc. Inc.) or ZORBAX CN(4.6 mm x 150 mm, Du Pont) column. QADAP(0.012 %) was prepared by dissolving in 0.02 M HCl and 4 % PONPE-20 aqueous solution. The surfactant, PONPE-20, was used for solubilization of QADAP and its metal chelates. A mobile phase was 32 % acetonitrile-water solution containing 5x10^{-3}molal sodium acetate and 10^{-4} molal EDTA.

Procedure: To a sample solution containing less than 342 ng of vanadium, 5 cm^3 of QADAP solution and acetate buffer solution(pH 5.4) were added.

A masking agent, if required, was added prior to addition of QADAP solution. The mixture was heated on a water bath at 85 - 90°C for 60 min and then was made up to 25 cm^3 with water after cooling. An aliquot of the solution was injected with a 100 mm^3 loop injector. The detecor settings of 0.005 or 0.001 absorbance unit full-scale(AUFS) range at 540 nm were used for 1 mv or 10 mv recorder out-put. Flow rate of the eluent was 1.0 cm^3/min.

RESULTS AND DISCUSSION

Vanadium(V) quantitatively reacts with QADAP over the pH renge of 4 - 8 to form colored chelate which has absorption maximum at 544 nm in PONPE-20 solution and at 540 nm in the eluent solution, respectively. Figure shows a typical chlomatogram of QADAP system in the presence of varoius cations. Only Vanadium(V) gave a peak on the chromatogram. Many metal ions in 100 fold (wt/wt) excess did not interfere, however, iron(III) in more than 60 fold did interfere with the determination. Iron(III) could be masked with cyclohexanediaminetetraacetic acid(CDTA). The peak height calibration curve was linear over the range 0 - 342 ng/25 cm^3 of vanadium. The relative standerd deviation at 228 ng/25 cm^3 of vanadium was 3.0 %. The detection limit(twice peak-to-peak noise) for vanadium at 0.005 AUFS was down to 80 ppt.

The QADAP method was applied for the determination of ultra trace amoints of vanadium in air samples. A 10 cm^3 of rain water was directry analyzed. Airborn particulates have been collected on a quartz fiber filter(Dylec 2500-QAST, 47 mm) attached to low-volume air sampler(20 dm^3/min) in 30 days. The sample together with the filter was treated with nitric acid and hydrogen peroxide. The solution obtained was made up to 20 cm^3. From this solution, 0.5cm^3 of sample was taken and vanadium was determined by the recommended procedure. The results are listed in Table. With atomic absorption method, no vanadium was detected in these samples.

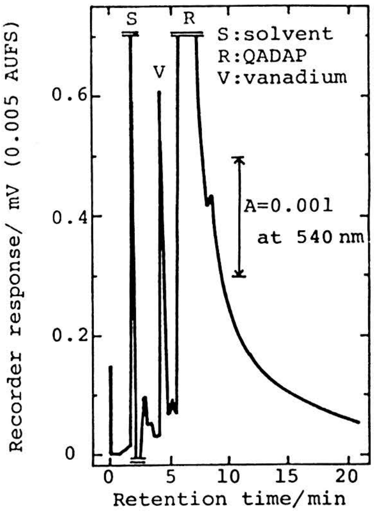

Fig. Separation of V(V)-QADAP chelate on a ZORBAX CN column

V:1.79 x 10^{-7} M, Each foreign metal ion(Fe,Zn, Al,Co,Ni,Cu,Ga and Mn): 2 x 10^{-6} M,

Table Determination of vanadium in air samples

Rain water (1985.9.7.)

Precipitation/ mm	V found/ µg dm^{-3}
0 - 1	2.4
1 - 2	0.76
6 - 7	N.D.*

* not detected

Airborne particulates

Season / Locality	V found/ ng m^{-3}	
	1984.7.	1985.2.
A	2.7 3.4**	1.7 2.0**
B	3.1 3.5**	2.8 2.8**
C	3.6	2.0

** CDTA was added.

S1-04 SIMPLE AND RAPID SEMIQUANTITATIVE DETERMINATION OF METAL SPECIES ON POLYMER REAGENT MATRIX.

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ABSTRACT

Polymeric (or resin-immobilized) reagents were synthesized for use as hydrogen-ion concentration buffer agent. The acid dissociation properties were studied by potentiometric method. Semiquantitative solid-phase colorimetry1) for metal ions was attempted by useing these polymeric pH-buffers.

INTRODUCTION

The use of pH buffer reagents are usually limited to a homogeneous system. However, if solid polymers are endowed with a pH-buffering function such polymers may be used to construct a solid-phase chemical detecting system with a built-in pH adjustment capability. Since a sensing reagent can also be immobilized onto a solid polymer matrix, the combinations of polymeric pH-buffers and sensing reagents are expected to give a new generation of solid phase chemical detecting devices. From this point of view, we synthesized some polymeric pH-buffer reagents and studied their acid dissociation properties. The polymers were used to make pM detecting film or pad.

1. Synthesis of polymeric reagents.

Polymeric pH buffer reagents 1 - 7 were synthesized. Only in case of compound 1 and 2, the polymerization of the corresponding monomeric reagent (p-substituted styrenes) was performed. The preparation of other reagents involved the reaction of appropriate proton-dissociating reagents with polymers; poly(4-vinylpyridine) and chloromethylated styrene-divinylbenzene copolymer (macroreticular type resin) were used for the synthesis of 3 and 4 - 7 respectively. Proton-dissociating groups were selected as such that only small complexing interactions were expected between the conjugate bases and metal ions in general.

2. Acid dissociation properties of polymeric pH buffer reagents.

Acid dissociation property was studied potentiometriccally by titrating the conjugate acids with standard potassium hydroxide solution. In case of compound 1 to 3, pH titration was carried out in a usual way. The titration curves are analyzed according to the modified Henderson-Hasselblacn's equation proposed by Kern.2) Titration graphs are indicated in Fig. 1.(a) together with the acid dissociation constants obtained. It can be seen in Fig. 1. (a), that compound 2 shows considerable deviation from the calculated curve. It may be pointed out that while 1 and 3 have fixed (permanent) charges which are independent of ordinary pH variation, 2 does not have such a structural feature.

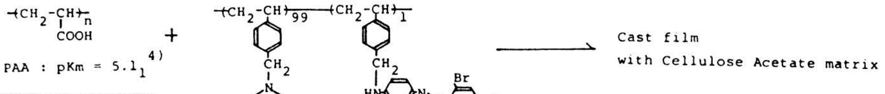
For resin-immobilized reagents, pH titration was carried out as described by Helfferich.$^{3)}$ The titration graphs are indicated in Fig. 1.(b) and (c). As is evident from the figure, it is possible to cover a wide range of pH-buffer regions (pH 2 - 9) by properly selecting the structure of the proton-dissociating groups.

3. Application as pH testing polymer film

A resin-type reagent which carries both pH-buffering and metal detecting functions was synthesized according to Scheme 1. The loading of the metal-indicator reagent amounted to only 1% of the total chloromethyl group content, the rest being reacted with a large excess of morpholine. The compound in a free base form was blended with an equivalent amount of polyacrylic acid to give a film with a "self buffer" action.$^{5)}$ The film obtained was unfortunately relatively hydrophobic and did not sorb aqueous solutions readily. It took 30 min at room temperature to obtain a fully-developed color when an aqueous solution containing Cu(II) was spotted on the film. Therefore, it is not convenient for the purpose of quick pM testing.

A different version of pM testing paper, i.e., a dry reagent pad with resin-immobilized pH buffer, metal indicator, and related reagents is now being studied.

Scheme 1



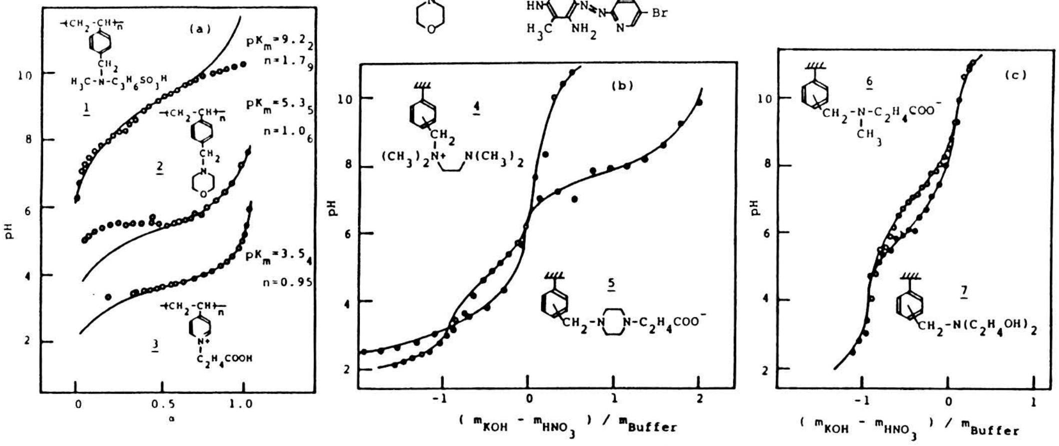


Fig. 1 Potentiometric titration graphs. Ionic strength, 0.1 ; Temperature 25 °C.
The solid lines in (a) represent theoretical curves,and α represents degree of neutralization.

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S1-05

APPLICATION OF ORGANIC SOLVENT-SOLUBLE MEMBRANE FILTERS TO THE PRECONCENTRATION AND SPECTROPHOTOMERIC DETERMINATION OF TRACES OF PHOSPHORUS IN WATER

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INTRODUCTION

The determination of traces of phosphorus in water is very important, because it is generally believed that a P concentration between 0.01 and 0.1 mg/L is sufficient to promote accelerated eutrophication in lakes, ponds and estuaries.

The most commonly employed method for the determination of traces of phosphorus in water is solvent extraction of the phosphomolybdenum blue, followed by measurement of the absorbance. However, extraction is very tedious and time-consuming.

In the present paper, a simple and rapid preconcentration-spectrophotometric method is proposed. This method is based on forming phosphomolybdenum blue, collecting the blue complex on an organic solvent-soluble membrane in the presence of cationic surfactant, and dissolving the membrane in a small volume of water-miscible organic solvent, and measuring the absorbance of the solution. A few micrograms per L levels of phosphorus in water can be determined with sufficient precision by the proposed method.

EXPERIMENTAL

Reagents

Ammonium molybdate solution: Dissolve 6 g of ammonium heptamolybdate tetrahydrate and 0.24 g of potassium antimonyl tartrate hemihydrate in 500 mL of 3 N sulfuric acid.

L-Ascorbic acid solution: Dissolve 7.2 g of L-ascorbic acid in 100 mL of water.

Mixed reagent: Mix 50 mL of the ammonium molybdate solution and 10 mL of the L-ascorbic acid solution.

Standard phosphorus solution: Prepare by dissolving an appropriate amount of potassium dihydrogen phosphate in water.

n-Dodecyltrimethylammonium bromide(C_{12}-TMAB) solution: Dissolve 0.08 g of C_{12}-TMAB in 100 mL of water. If necessary, remove any phosphate in this solution by coprecipitation with aluminium hydroxide in the following manner: add 0.5 mL of 10% aluminium sulphate solution to 100 mL of C_{12}-TMAB solution, adjust the pH to 8.5 with aqueous ammonia, and filter off the aluminium hydroxide formed.

Reducing agent for As(V): Mix 20 mL of 1.75 N sulfuric acid, 40 mL of 14% sodium metabisulphite solution and 40 mL of 1.4% sodium thiosulphate solution. Prepare fresh daily.

Membrane filters: Most of the data presented in this paper were obtained with Toyo TM-2 membranes(25 mm in diameter, 0.45 μm pore size, nitrocellulose), but other membranes can be used equally satisfactorily as long as they are made of nitrocellulose or acetylcellulose.

Procedure

Take 100 mL of sample solution, containing less than 7 μg of phosphorus, add 8 mL of the mixed reagent, set aside for at least 15 min in a water-bath controlled at 20-40 °C, then add 1 mL of C_{12}-TMAB solution. Filter off the phosphomolybdenum blue on the membrane filter, and wash the membrane with about 20 mL of water. Dissolve the filter in 5 mL of DMSO, and measure the absorbance of the DMSO solution at 710 nm against a reagent blank.

RESULTS AND DISCUSSION

Optimum conditions for color development

The conditions for the formation of the phosphomolybdenum blue are similar to those reported by earlier workers. The volume of reagent added are varied in proportion to the sample volume.

Cationic surfactant

Hiiro et al. collected phosphorus on a membrane filter as phosphomolybdenum blue, and determined phosphorus from the reflectance of the colored membrane. This method is very rapid and sensitive. However, collection is never quantitative and efficiency of collection varies depending on the manufacturer and the pore size of the membranes used. In preliminary experiments, we found that the addition of a cationic surfactant greatly enhances the adsorption of phosphomolybdenum blue on membranes. Several cationic surfactants of different molecular weight were tested. Of these surfactants, C_{12}-TMAB gave the most satisfactory results. The absorbance of the DMSO solution increases with increasing amount of C_{12}-TMAB added and reaches a constant value with at least 0.5 mL of 0.08% solution per 100 mL of sample.

Membrane filter for collection

Several filters of different sorts and pore-sizes were examined for usefulness for collecting phosphomolybdenum blue. Nitrocellulose and acetylcellulose membrane filters are suitable because they readily dissolve in DMSO. Any nitrocellulose and acetylcellulose membrane filter with pore-size between 0.2 and 0.45 μm can be used.

Solvent for dissolving the membrane filter

Several water-miscible organic solvents were tested as solvents for the wet membranes. DMSO, DMF and acetone readily dissolve the nitrocellulose and acetylcellulose membranes, but acetone is not recommended, because of its high volatility. The color intensity decreased with time in DMF, but only very slowly in DMSO. If the membrane is washed with water before being dissolved in DMSO the color intensity is stable for at least 3 hr.

Sensitivity and precision

Microgram quantities of phosphorus in 50-500 mL of sample can be determined with satisfactory precision. Beer's law is obeyed for 0.5-7 μg of phosphorus in 5 mL of DMSO at 710 nm.

Effect of foreign substances

Moderate concentrations of silicate and anionic and nonionic surfactants, and high concentrations of sodium chloride, do not interfere with the determination. Interference from As(V) can be eliminated by addition of 1 mL of the reducing agent before color development.

Application to river water and seawater

The phosphorus in river water and seawater samples were determined with satisfactory precision. The phosphorus in spiked samples were recovered quantitatively.

CONCLUSION

The preconcentration technique proposed in the present paper is simple and very rapid and can be used in place of the conventional solvent extraction. This technique may find many other applications for the determination of trace elements in water samples.

S1-06

ELECTROCHEMICAL STRIPPING ANALYSIS OF VITAMINS EMPLOYING ADSORPTION PRECONCENTRATION

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INTRODUCTION

Anodic stripping analysis employing amalgam formation in the preconcentration step is a very sensitive method and used widely in the trace analysis of heavy metals in the environment (1).

In order to extend the application of the stripping analysis attempts have been reported which employ film formation reactions on the electrode (2) or adsorption on the electrode (3) in the preconcentration step instead of amalgam formation. Film formation or adsorption preconcentration made it possible to determine organic compounds which cannot be determined by amalgam formation preconcentration. It is considered that adsorption preconcentration is especially important in the determination of organic compounds because film formation preconcentration is considered to be applied to the limited groups of organic compounds. The purpose of this work is to establish the method to determine trace amount of vitamins. Vitamins investigated were riboflavin, vitamin B_{12} and thioctic acid.

EXPERIMENTAL

DC and differential pulse polarograms were measured by a Princeton Applied Research Model 174A. Square wave polarograms were measured by Fuso Models 311 and 333. Differential capacity was measured by a phase-selective ac polarograph (Fuso Models 312 and 332). The hanging mercury drop electrode used was a Metrohm EA 290, the area of which was 1.49 mm^2. In the stripping analysis with adsorption preconcentration, at first the electrode potential was kept at the potential where the vitamin or its reduced form is adsorbed while stirring the solution. After 1 min rest period the potential was scanned to the negative (cathodic stripping) or positive (anodic stripping) and the resulting current was measured.

RESULTS

From the depression of the differential capacity - potential curves it is clear that both riboflavin and its reduced form (leucoflavin) are adsorbed on mercury electrodes. Cyclic voltammograms of riboflavin show cathodic peaks and anodic peaks at around -0.55 V. Therefore it is expected that two electrochemical stripping methods of analysis of riboflavin are possible in which preconcentration is achieved by the adsorption of riboflavin (cathodic stripping) or leucoflavin (anodic stripping) (4). Experimental conditions, such as preconcentration time, preconcentration potential, potential scan rate and temperature, were studied by a dc polarograph in 0.1 M ammonium acetate. With the optimum conditions the detection limits were 10 nM (cathodic) and 5 nM (anodic). The calibration curves were linear up to 100 nM. To improve the sensitivity of this method 0.1 M sodium acetate was used as the supporting electrolyte and a square wave polarograph was used in the stripping step. Experimental conditions including square wave polarographic measurements were studied. With the optimum conditions the detection limit was 0.5 nM and the calibration curve was linear up to 100 nM. The relative standard deviation was 5.5 % with 50 nM riboflavin. 1 μM dodecyl lauryl sulfate, 2 μM Cd(II), 1 μM Pb(II), 0.1 μM Zn(II), 20 μM Co(II), 0.01 μM Ni(II) and 0.01 μM Cu(II) did not interfere with the determination of 0.05 μM riboflavin.

Vitamin B_{12} is adsorbed on a mercury electrode in the potential region between 0 and -1.5 V and yields a polarographic catalytic wave at ca. -1.6 V. Cathodic stripping analysis with adsorption preconcentration is possible (5). A concentration of 0.3 M ammonium acetate was used as the supporting electrolyte and a dc polarograph was used in the stripping step. The calibration curve was linear up to 100 nM and the detection limit was 2 nM. To improve the sensitivity of this method 0.01 M disodium hydrogenphosphate with 0.01 M sodium dihydrogenphosphate was used as the supporting electrolyte and a differential pulse polarograph was used in the stripping step. With the optimum experimental conditions the detection limit was 0.5 nM. The relative standard deviation was 5.8 % with 50 nM vitamin B_{12}. Effect of interfering substances on the determination was also studied.

Thioctic acid also can be determined by the stripping analysis with adsorption preconcentration. A concentration of 0.1 M ammonium acetate was used as the supporting electrolyte and a dc polarograph was used in the stripping step. After studying experimental conditions, the detection limit was 0.1 μM and calibration curve was linear up to 1.6 μM. The relative standard deviation was 7.7 % with 1 μM thioctic acid. Effect of interfering substances on the determination was also studied.

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S1-07

CHEMILUMINESCENT TECHNIQUE FOR THE ENVIRONMENTAL ANALYSIS

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A great interest to practical application of chemiluminescent (CL) reactions has recently arisen, it has largely originated from the great need for determining of pollutants in environmental samples. Chemiluminescent methods attract attention of analytical chemists by its potentiality to analyse a lot of inorganic and organic substances with high sensitivity without requiring expensive instrumentation. These methods are notable for rapidness in analysis and may be applied in field.

THE DEVELOPMENT OF CL ANALYSIS IN THE UKRAINE

Chemiluminescent reactions in liquid phase have been studied for analytical purpose at A.V.Dumansky Institute of Colloid and Water Chemistry of the Ukrainian Academy of Sciences for many years. Investigation of luminol reactions as well as CL reactions of its derivatives, lucigenin, lophine, some non-cyclic hydrazides have shown their great potentiality for determination of variety of inorganic and organic substances on μg/l and ng/l level. Highly selective methods for copper, cobalt, iron, manganese, platinum metals, silver, gold and others have been developed. Chemiluminescence resulting from luminol oxidation by heteropolyacids has been used for phosphorus, silicon, arsenic, germanium determination, detection limit is 0.01-0.001 ng/ml. CL methods for different classes of organic compounds have been developed, detection limit is 10^{-5} - 10^{-10} mol/l. The methods are based upon inhibition of CL reactions, catalyst activation in L-H_2O_2-Mn(II) and L-H_2O_2-Ag(I) systems or vanadium (V) reduction with subsequent V (IV) determination via its reaction with luminol and oxygen. There is an opinion that lack of selectivity is a major limitation of CL based determination. But it has been shown in our papers that the choice of suitable CL system, optimal conditions for analysis, application of masking reagents permit to achieve the high selectivity of CL methods. The examples of CL methods free from interferences are given.

CL METHODS FOR Fe, Mn, Co, Si, Ag DETERMINATION IN NATURAL WATERS

CL technique has not found a wide application in environmental analysis despite of a wide range of analytical possibilities. There are only a few examples. Chemiluminescent reactions in solution are used for determination of H_2O_2, O_3, adenosine triphosphate, chromium, cobalt, chlorine in waters. CL-analysers based on gas-phase reactions reveal more wide practical application, especially for SO_2, H_2S, NO_2, NO detection in air and N-nitrosoamines in waters.

In this report the examples of iron, cobalt, manganese, silver, silicon CL determination in river, ground and potable water are presented [1-4]. For iron and manganese determination the reaction of luminol oxidation with hydrogen peroxide has been used, triethanolamine (for iron) and phenanthroline-citrate mixture (for manganese) have been used as activators; detection limit is 0.5-1.0 μg/l. Cobalt is determined via reaction of luminol with dissolved oxygen, detection limit is 1 μg/l, the method is remarkable for high selectivity. For silicon determination the reaction of luminol with silicomolybdate acid has been used, detection limit is 0.01 mg/l. Effect of micro- and macrocomponents of natural waters on determination of the abovementioned elements has been studied, the ways of elimination of interference action of dissolved organic substances and hardness salts have been discussed. Analysis of river and ground waters has been done by chemiluminescent method, the results are in good agreement with the data of standard analytical methods. Advantages of chemiluminescent methods in environmental analysis are discussed.

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S1-08

TRACE MULTIELEMENT ANALYSIS IN ENVIRONMENTAL SAMPLES BY CAPILLARY GAS CHROMATOGRAPHY

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Numerous researches on gas chromatographic separation and determination of metal chelates of β-diketones have been reported since Lederer first suggested the possibility of the separation of lanthanide as acetylacetone complexes by gas chromatography (1,2). Most of these works utilized packed columns and only a single element was determined. Recently developed silica capillary columns offer the advantages of enhanced efficiency and increased inertness, which might reinforce and extent the application of inorganic analysis.

The authors have studied the capillary column chromatographic behaviour of several β-diketone metal chelates. The results of the investigation showed that these chelates can be separated on capillary columns with quite good resolution and multielement analysis is possible (3). In the present work, the separation of Be, Cr, Al, Ga and In chelates of β-diktones on several capillary columns have been investigated. On the basis of optimum chromatographic conditions a method for the determination of Be, Al and Cr in natural waters has been developed by capillary gas chromatography.

RESULTS AND DISCUSSION

SEPARATIONS

The Be, Al and Cr chelates of trifluoroacetylacetone (TFA) have been studied with fused silica WCOT OV-101, SE-30, SE-54 columns, and glass WCOT OV-17 column. These chelates can be well separated at the column temperatures of 140 or 160°C. The peak shapes are very sharp and symmetrical and the resolution is much better than that obtained with packed columns.

The group IIIA metals Al, Ga and In as TFA, trifluoroacetylpivaloylmethane (TPM) and dipivaloylmethane (DPM) chelates have been separated with fused silica WCOT OV-101 and SE-54 columns, the peak shapes of these chelates obtained were broader and unsymmetrical. However, Al and Ga chelates can be eluted from a short silica WCOT SE-30 column, at a column temperature of 140°C, giving sharp and symmetrical peaks. Indium can be eluted at a column temperature of 180°C and the peak shape is better than all other columns. It seems that short SE-30 column is most suitable for the separation of Al, Ga and In chelates.

DETERMINATION

According to the results of the separation mentioned above, a method of simultaneous determination of Be, Al and Cr as TFA chelates by capillary gas chromatography has been established.

1. General procedure

A 10 ml solution containing 0.01 – 0.1μg each of Be, Al and Cr was placed in an extraction flask. Add 0.5 ml of pH 5.6 NaAc-HAc buffer solution and 5 drops of 1 M sodium sulfite solution. Then add 2 ml of 0.15 M TFA-benzene solution. Place the flask in a water bath of 70°C and heat for 15 min. Shake for one minute. Let stand until the organic layer remains clear. Discard the aqueous phase and wash the organic phase with 4 ml of 0.1 M NaOH solution. Discard the washing solution. Pipette 2 μl of organic layer with a microsyringe and inject into the chromatographic column, detect the signal by electron capture detector. Measure the peak height for quantitative analysis.

2. Conditions for gas chromatographic analysis

Column: Fused silica WCOT OV-101, 25 m x 0.2 mm
Column temperature: 140°C
Detector and injector temperature: 200°C
Carrier gas: nitrogen, flow rate: 50 ml/min
Split ratio: 1 : 8, Sample size: 2 μl, Detector: ECD

3. Application to real samples

The method was applied to the determination of Be, Al and Cr at sub-ppb levels in natural waters, such as mineral water, snow water, esturine water and sea water collected from different depths. The results for the determination of samples are listed in table I. The method is sensitive and rapid. The detection limits of Be, Al, Cr are 5×10^{-13}g, 1×10^{-12}g, 1.6×10^{-12}g respectively.

Table I

Samples	Concentration of the element (μg/l)		
	Be	Al	Cr
Esturine water R-1	0.06	11.2	0.27
R-3	< 0.05	11.7	0.20
R-7	0.10	12.0	0.55
Sea water C-2-A	< 0.05	1.5	0.44
C-2-B	< 0.05	7.0	0.32
C-2-C	0.05	11.0	0.06
C-2-D	0.06	172	< 0.05
Mineral water	< 0.05	< 0.1	< 0.05
Snow water(6000m)	< 0.05	156	0.84

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S1-09

TRACE ANALYSIS FOR METAL HYDRIDE-AsH3,PH3,B2H6-BY MEANS OF FLAME PHOTOMETRIC METHOD AND CHEMILUMUNESCENT METHOD

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Due to the rapid production increase of semiconductor, the treating amounts of arsine(AsH3), phosphine(PH3) and diborane(B2H6) etc. has increased. As these gases have high toxicity, high sensitive and high reliable analyzer for low concentration range has been and will also be needed to insure a safe operation of semicinductor manufacturing process.

Authors developed the utility alarm systems with the function of safety monitoring, which applies a flame photometric method (FPD) for low concentration range and a chemiluminescent method(CLD) for compact type.

The function of each utility alarm system is explained.

1. UTILITY ALARM SYSTEM WITH A FLAME PHOTOMETRIC METHOD

(1) Principle

In case of popular FPD, as sample gas is introduced into the fuel gas line, the sensitivity is not sufficient to detect at the threshold limit value(TLV). In case of this system, the sample gas is introduced into the air line, therefore, it is found that this system is about 100 times as sensitive as the former FPD.

It is concluded that the sample gas is burned in oxidizing flame and intensity of emission due to combustion is large in comparision with those in reducing flame.

(2) Performance obtained

a) High sensitivity

This system have a minimum detectable concentration of 0.004 ppm for AsH3, 0.002 ppm for PH3 and 0.024 ppm for B2H6 which is below each TLV.

b) Rapid response time

Response time (90% response) is within 3 seconds typically. This is important in order to monitor quickly gas leakage in the workshop.

c) Selectivity

Influence by other gas contained in normal workshop must be minimized, and very small. However, in case of leakage of high concentration of organic solvent, this system have not a sufficient signal to give warning. In order to eliminate this problem, the complex detector with flame ionization detector is equipped with this system, and then the signal on FPD by organic solvent is cancelled electrically.

d) Stability

Stability of zero point is maintained within ± 1%/FS/day. Furthermore, as the auto zero calibrator is prepared, the stability is kept within ± 2%/GS/month.

e) Others

Two alarm points are set every measuring point at will, and the alarm is done by warning lamp and sound. In addition multi-sampling unit is also available and measuring points are up to sixteen.

2. UTILITY ALARM SYSTEM WITH A CHEMILUMINESCENT METHOD

(1) Principle

Atmospheric pressure type chemiluminescent method is adopted to this system. Sample gas is passed through defumidifier, and then is devided into two streams. One stream is introduced reaction chamber at adequate flow rate, and other is introduced into reaction chamber after through the ozonizer. Chemiluminescence emission caused by the reaction between metal hydride and ozone is detected and ampliphied by photomultiplier. So as to increase the chemiluminescence emission, the reaction chamber is wormed .

(2) Performance obtained

a) High sensitivity

The limit detectable concentration are as follows;

AsH3 : 0.004 ppm, PH3 : 0.02 ppm, B2H6 : 0.06 ppm

b) Response time

Response time(90% response) is within 20 seconds typically, therefore, this system shall apply to continuous monitoring.

c) Selectivity

Influence by other gases except metal hydride is very small. Especially, in case of high concentration of organic solvent is coexisted in the sample gas, it causes actually no signal.

d) Stability

Stability of zero point for this system is maintained within ± 3%/FS/W.

e) Others

Two alarm points (low,high) are set at will, and the alarm is done by warning lamp and sound.

S1-10

HIGH-PEFORMANCE LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL AND SPECTROPHOTOMETRIC DETECTION FOR DETERMINATION OF COPPER AND IRON IN ENVIRONMENTAL SAMPLES

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In recent years, considerable attention has been focused on the use of high-performance liquid chromatography(HPLC) for the separation and simultaneous determination of metals as chelated complexes on analytical columns [1,2]. Particularly, the dithiocarbamate ion is an extensively used ligand in reversed-phase HPLC because it reacts rapidly with many heavy metals which are then extractable into organic solvents [3,4]. In a recent article [5], the present authors noted that copper(II) and iron(III) complexes of 8-quinolinol were separatable under the conditions of reversed-phase HPLC and could be determined simultaneously by electrochemical(amperometric) detection monitoring the reduction of the complexes with glassy carbon electrode. It is the aim of this work to explore the possibility of separating copper(II) and iron(III) as cupferronates using reversed-phase HPLC and determining simultaneously the metal ions at the ng/mL levels using electrochemical and/or spectrophotometric detection.

EXPERIMENTAL

Liquid chromatography was performed using a Toyo Soda CCPD pump connected to a shorter column(4.6mm i.d. x 150mm, 5μm) packed with TSKGEL ODS-80 TM and fitted with a Rheodyne 7125 valve injector with a 10 μL loop. The complex formation of metal ions with cupferron was carried out before injection as follows: procedure(A) 1.0mL of aqueous sample solution was mixed with 1.0mL of 0.02M acetate buffer(pH 3.5) and 2.0mL of 0.02M cupferron solution in acetonitrile; procedure(B) 40mL of aqueous sample solution was transferred to a 100mL glass separatory funnel followed by addition of 5.0mL of 0.02M acetate buffer(pH 3.5), 5.0mL of 0.10M cupferron solution in water and 6.0mL of ethylacetate. After shaking the contents for 3min, a 10-μL of the pretreated samples was injected into the ODS column. Chromatographic separations were made with (A) 7:3 acetonitrile/water solvent containing 10^{-3}M cupferron, 0.2M potassium nitrate and 0.02M acetate buffer(pH 3.5); (B)45:20:5:30 acetonitrile/methanol/ethylacetate/water solvent. The moble phase reservior was cooled in an ice bath and degassed with nitrogen during the runs. The column temperature was kept at (20 ± 0.1)°C,and the flow rate was 1.0mL/min. The eluates were detected using a Toyo Soda UV-8000 spectrophotometric detector and a PAR 174A polarographic analyzer with a BAS TL-5 thin layer flow cell(glassy carbon

RESULTS AND DISCUSSION

The chromatographic behaviour of Cu(II) and Fe(III) cupferronates was investigated by changing the composition of mobile phase. It was found that the procedure(A) gave good separation and simultaneous determination of the two metals. The eluates were monitored by electrochemical detection at -0.40V vs. Ag/AgCl and by spectrophotometric detection at 375nm. The limits of detection were 0.2ng Cu(II) and 1.0ng Fe(III) by both detection methods. Above sub-μg/mL Cu(II) and Fe(III) can be determined after direct injection of the cupferron complexes pre-formed according to the procedure(A) onto the column. This method was applied to the HPLC determination of the two metals in Bovine liver(NBS 1577) and Oyster tissue(NBS 1566)[see Fig.1]. In order to increase the sensitivity of determination, we attempted the preconcentration of the metals by extraction of the cupferron complexes with ethylacetate as a suitable solvent followed by HPLC determination(procedure B). Data indicated that this technique could offer good potential for the determination of Cu and Fe in drinking water, river and waste water[see Table 1].

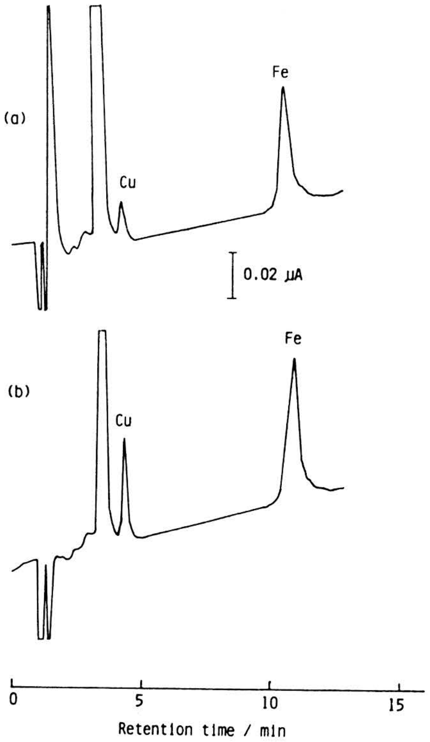

Fig.1 HPLC determination of Cu and Fe in oyster tissue(a) and bovine liver(b)

Table 1

Determination of Cu and Fe in environmental samples

Sample	Analytical result E.C.	S.P.	Remark
a Oyster tissue	Cu 62.8 ±6.5 Fe 199 ±6.6		Cu 63.0 ±3.5 Fe 195 ±34
Bovine liver	Cu 186 ± 4.0 Fe 279 ±16		Cu 193 ±10 Fe 268 ± 8
b Drinking water	Cu 12 ± 1.4 Fe 170 ± 7.5	170 ±15	Cu 10.1(AAS) Fe 201(phn method)
Kuzuryu river	Cu * Fe 8.7 ±0.4	6.5 ±0.4	Cu 2.0(AAS)
Asuwa river	Cu * Fe 157 ±7.8	165 ±7.9	
Waste water	Cu 6.0 ± 0.6 Fe 195 ±15		Fe 216 ±38 (phn method)

*: Non detectable, a: μg/g , b: ng/ml

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S1-11

LIQUID CHROMATOGRAPHIC DETERMINATION OF TRACES OF PHENOLS IN AIR

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Several convenient methods [1-4] have been so far developed for determination of aldehydes, amines and alkylthiols using Sep-PAK C_{18} (SP-18) sampling cartridges in the course of our analytical study on reactive compounds in field research. In this report, a convenient method is presented to sample traces of phenols in ambient air by the use of a SP-18 cartridge impregnated with sodium hydroxide and to determine them by liquid chromatography (LC) via derivatization with p-nitrobenzenediazonium tetrafluoroborate (NBDTFB).

EXPERIMENTAL

Analytical Procedure. A 2-100-L volume of air sample was sampled at 0.2-1.0 L/min through a SP-18 cartridge impregnated with 1.0-1.2 mg of NaOH. The adsorbed substances were eluted with 3 mL of methanol. The eluate was adjusted to pH 11.5 with a $Na_2CO_3/NaHCO_3$ buffer, mixed with 0.5 mL of 0.1% NBDTFB solution and allowed to stand for 30 min. The sample was mixed with 0.5 mL of 1% NaOH solution, and the volume was adjusted to 5 mL. A 2-10 μL aliquot of the sample was analyzed by LC with a 15 cm X 4 mm i.d. column packed with Develosil ODS-3 and a mobile phase of 85/15 methanol/water at 1.0 mL/min.

RESULTS AND DISCUSSION

Phenols reacts with NBDTFB to form the red nitrobenzeneazo (NBA) derivatives in a weak alkaline solution [5]. The reaction proceeded much more rapidly in the methanol-rich solution than in the aqueous solution. The reaction was completed within 15 min. **Figure 1** shows a liquid chromatogram where the NBA derivatives were excellently separated. The detection limits were 0.05, 0.1, 0.1 and 0.5 ng for phenol, m-cresol, o-cresol and p-cresol, respectively. To investigate collection efficiency and analytical accuracy for phenol vapors, 100 L of an air sample containing 2-50 μg of the phenols was sampled with two coated SP-18 cartridges in series. The phenols are detected on the first cartridge only and no phenols were found on the second. **Table** indicates the recovery of the phenol vapors trapped on the first cartridge. The recovery was 65.5-102% with 1.2-4.7% standard deviation. The estimated detection limits of the phenol vapors were 0.02-0.03 ppb for 100 L of air sample. Phenols placed on the cartridge were recovered without loss after the cartridge was stored for more than 10 days in the cool place (3-5 ^{o}C) in the dark. The NBA derivatives were stable at least for 2 weeks in the sample solution. The method was applied to determination of phenol in industrial emission and in ambient air around emission sources. **Figure 2** shows typical chromatograms of phenol in environmental samples. Low parts-per-billion levels of phenol were easily determined without any effects of coexistent substances.

The proposed method may be useful for determination of trace levels of the phenols in ambient air especially in the area of field research.

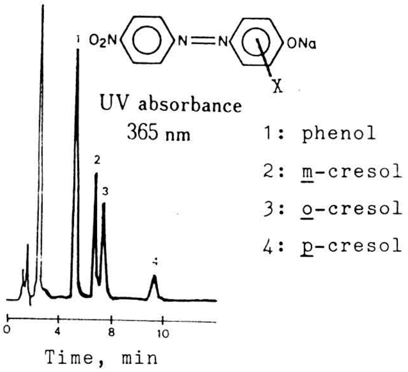

Figure 1. NBD Derivatives of Phenols.

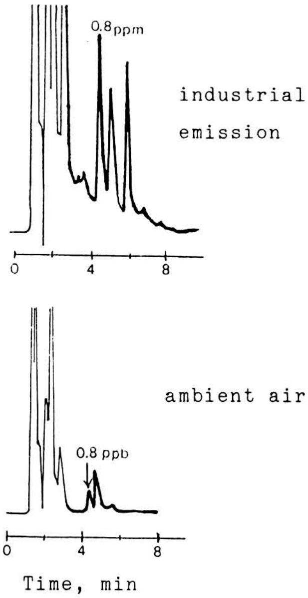

Figure 2. Phenol in Environmental Samples.

Table Recovery of the Phenol Vapors.

phenol vapor,*ug	recovery, aver** ± SD,*** %			
	phenol	o-cres.	m-cres.	p-cres.
2	93.9±2.5	102 ±1.7	102 ±1.3	89.4±3.7
10	85.8±1.3	97.7±1.4	96.1±1.8	65.1±2.2
50	71.3±1.2	88.4±3.7	91.3±3.5	69.5±4.3

* Phenols were vaporized at 150 °C in a nitrogen stream and introduced into 1.0 L/mL of air stream. ** Average in 6 runs. *** Standard deviation.

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S1-12

USE OF GREEN TEA AS AN ADSORBENT OF Au^{III}, Mo^{VI}, AND V^{V} IONS IN AN AQUEOUS ACID SOLUTION

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A feature of tea is to contain a relatively large amount of tannin components which are composing of polyphenols. Such phenolic-aromatic compounds can act as an ideal adsorbent not only for the aromatic compounds, but also for the metal ions. Our previous study has shown that the tea treated with formalin can quantitatively accumulate and remove Ag^{+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Fe^{2+} in an aqueous solution [Ref.1].

In the present study we examined the uptake of Au^{III}, Mo^{VI}, and V^{V} ions from an aqueous acidic solution using the Japanese green tea as an adsorbent. The tea powder was treated with formalin in a dilute sulfuric acid. A 100 ml sample containing Au^{III}, Mo^{VI}, and V^{V} ions was mixed with 0.1 – 0.5 g of the treated tea under stirring for 30 min at room temperature. The suspension was then centrifuged and concentrations of the metal ions in the supernatant liquid were determined by using the graphite-furnace AAS with Zeeman-background correction. The Au^{III}, Mo^{VI}, and V^{V} ions of 0.04 – 1.2 ppm in total concentrations were uptaken by the tea over 90% from solutions at pH 3 – 6 (see Table 1).

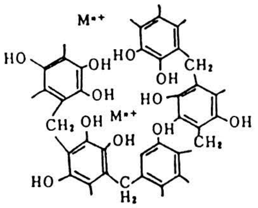

Fig.1. Schematic sketch for metal ion (M^{n+}) adsorbed on the formalin-treated tea.

TREATED TEA

To prevent the dissolution of some components in the tea, and to improve the adsorption ability (see Fig.1) and the physical characteristics, the green tea was treated with formalin. Some tannin compounds could be polymerized and insolubilized by this treatment: 7 g of the tea powder was treated with 35 ml of 40% formalin and 140 ml of 0.1 mol dm^{-3} H_2SO_4 for 2 hr at 60 °C. The mixture was centrifuged and washed with distilled water and with 0.02 mol dm^{-3} NaOH solution until the pH was 6 – 7. The residue was dried at 110 °C for 6 – 8 hr. The treated tea was then screened to get 80 mesh particles.

Table 1. Effect of pH on adsorption[a)]

pH Initial	pH Final	Adsorption % Au	Mo	V
1.3 —	1.3	72	94	30
3.4 —	3.5	86	97	96
5.4 —	5.3	100	96	100
6.2 —	6.3	100	79	100
6.5 —	6.6	96	98	100
9.4 —	8.1	61	3	81
11.5 —	11.4	28	0	41

a) The pH was adjusted to the desired values by adding NaOH, HCl, and/or CH_3COONa.

EFFECT OF pH ON ADSORPTION

Table 1 shows the effect of pH on the adsorption% of three ions. The initial pH was measured immediately after mixing adsorbent with solution, and the final pH after removal

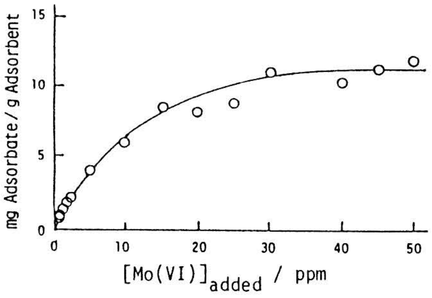

Fig.2. Adsorption isotherm. 0.1 g tea; pH 3.5 – 3.9; room temp.

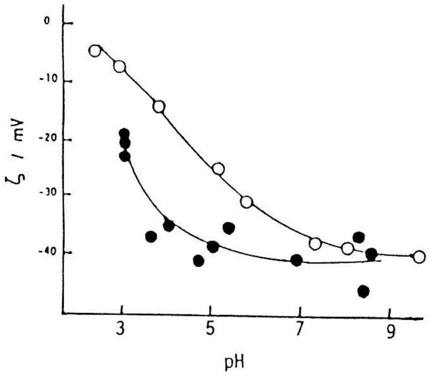

Fig.3. Zeta potentials ζ of the treated tea (○) and the Mo(VI)-adsorbed tea (●) at various pH values.

of adsorbent from solution at 30 min after the mixing.

ADSORPTION ISOTHERM

The adsorption isotherm for the molybdate adsorption onto the treated tea is shown in Fig.2. For such a system the Langmuir equaton can be written as follows.

$$\frac{1}{q} = \frac{1}{b} + \frac{1}{bKc} \qquad \text{[Langmuir equation]}$$

where q represents the moles of adsorbed solute per gram of adsorbent; b is a maximum number of moles adsorbable per gram of adsorbent; K is equilibrium constant between solute adsorbed and solute in solution; c is the molar concentration of solute at equilibrium in solution. When the adsorbed species is assumed as $[Mo_7O_{24}]^{6-}$ in the case of Mo^{VI} ion, the b and K values are 2×10^{-5} mol g^{-1} and 2×10^5 dm^3 mol^{-1}, respectively. In the poster session, the b and K values for Au^{III}, Mo^{VI}, and V^V will be presented to compare one another.

ZETA POTENTIAL OF ADSORBENT

For the purpose of getting some informations concerning the surface charges of the adsorbent particles, the zeta potentials ζ of the treated tea and the molybdate(VI)-adsorbed tea were measured for aqueous suspension of their particles of 0.1 g dm^{-3} in 0.001 mol dm^{-3} KCl (Fig.3). The zeta potential of the molybdate(VI)-adsorbed tea is more negative at pH 3 – 7 than that of the tea alone, and becomes almost equal at pH 7 – 9 (see Fig.3). Therefore, some molybdate(VI) ions may be adsorbed as negative species such as $[Mo_7O_{24}]^{6-}$ or $[H_nMo_7O_{24}]^{(6-n)-}$, and the molybdate adsorption may not occur at pH over 7 (refer to Table 1, comparing results in Fig.3). It is to be noted that the molybdate(VI) anion in weak acid solution forms different species, e.g. $[MoO_4]^{2-}$, $[Mo_2O_7]^{2-}$, $[Mo_7O_{24}]^{6-}$, $[Mo_8O_{26}]^{4-}$ etc., depending on the pH values in solution, and that the $[Mo_7O_{24}]^{6-}$ may dominate in solutions at pH's less than 6.

EFFECT OF COMPLEX FORMING AGENTS

Addition of ethylenediaminetetraacetate or oxalate ion leaded to the less adsorption of any metal ions, whereas that of 8-quinolinol or 1,10-phenanthroline leaded to the better adsorption over 90% for Au^{III}, Mo^{VI}, and V^V. Thus, it is assumed that the metal chelate complexes with 8-quinolinol and 1,10-phenanthroline are attracted by π-electron interactions at the aromatic sites of tea.

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S1-13

DETERMINATION OF CHROMIUM(III), TITANIUM AND VANADIUM BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY WITH AN ON-LINE PRECONCENTRATING ION-EXCHANGE COLUMN

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A method utilizing a miniature ion-exchange column of Muromac A-1 (Muromachi Chemicals, Tokyo) has been developed to increase the sensitivity for chromium(III), titanium and vanadium measurements by inductively coupled plasma-atomic emission spectrometry (ICP). This method gave signal enhancements which were 66-113 times better than for a conventional continuously aspirated system for the metals studied here. A precision of the technique is better than 5% RSD at the 10 $\mu g L^{-1}$ level for aqueous standards, and the sampling rate is 17 samples h^{-1}.

1. Inductively coupled plasma-atomic emission spectrometry(ICP) is widely used for the determination of trace metals in environmental samples. Although it is very sensitive, we sometimes suffer from the lack of sensitivity for the determination of trace metals. Recently one-line ion exchange preconcentrating methods for flame atomic absorption spectrometry (AAS)(1-3) or ICP(4-5) have been reported and those are capable of improving the detection limit by one or two orders of magnitude, with additional advantage of being rapid and separating the analyte from an interfering matrix.

In this paper, we investigated sensitivity enhancements of the the elements which form hydroxides easily in the alkaline pH region, e.g., chromium (III), titanium and vanadium for ICP with an on-line preconcentrating ion-exchange column.

2. EXPERIMENTAL SECTION

Apparatus. Simadzu Model ICPQ-100 inductively coupled plasma-atomic emission spectrometer and a Japan Spectroscopic Co., Model RP-4F plunger pump were employed. Operating conditions of ICP and flow injection analysis(FIA) are shown in Table I.

Reagents. Muromac A-1(100-200 mesh) is a chelating resin and a styrene divinylbenzene copolymer containing iminodiacetic groups.

Table I. Operating Conditions for ICP and FIA

ICP system		
coolant argon flow rate	$10.5\ L\ min^{-1}$	
plasma argon flow rate	$1.5\ L\ min^{-1}$	
carrier argon flow rate	$1.0\ L\ min^{-1}$	
rf incident power	1.3-1.4 kW	
rf reflected power	<10 W	
nebulizer	concentric	
observation height above load coil	16 mm	
FIA system		
sample flow rate	$6.0\ mL\ min^{-1}$	
buffer flow rate	$1.5\ mL\ min^{-1}$	0.5M CH_3COONH_4-HCl(pH3.8)
eluant flow rate	$3.0\ mL\ min^{-1}$	2M HNO_3 (about 160 μL)

Procedure. Sample loading times ranged from 30 to 180s depending upon the sensitivity enhancements required for an analysis. After merging with buffer stream, samples were loaded onto a column. Loaded samples were eluted for 20 or 25s with about 160 μL of 2M nitric acid.

3. RESULTS AND DISCUSSION

A manifold of FIA-ICP system studied here is shown in Fig. 1. The majority of elements studied showed increased sensitivities in the pH ranges from 2.5 to 5. Therefore, the pH of the sample and buffer solution was chosen to pH 3.8. The concentration efficiency for the elements studied are shown in Table II and Fig. 2. The relative standard deviations (%RSD) for five replicates of 10 μgL^{-1} standard of chromium(III), titanium and vanadium were 2.3-4.0% and signal enhancements were 66-113 times better than for a conventional continuously aspirated method.

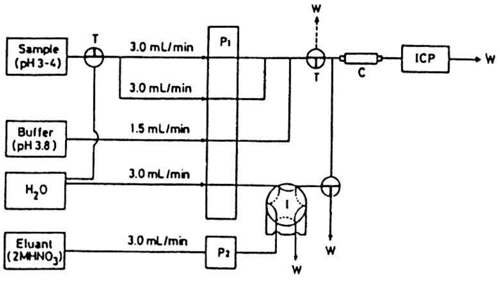

Figure 1. Flow diagram.

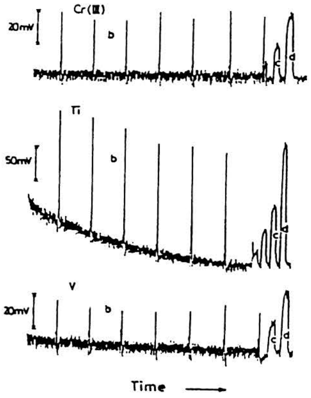

Figure 2. Cr(III), Ti, and V responses for (b) 1 ppb standards using Muromac A-1 column (2 mmI.D., 8 mm) with preconcentrating FIA-ICP system for 210-s column loading times and both (c) 50 ppb and (d) 100 ppb standards using conventional continuous aspiration ICP.

In the FIA-ICP system, effect of co-existing foreign ions is a result of summation of competitive reeaction between analyte and foreign ions and spectrointerference by foreign ions at the analytical wavelength of the element. A portion of magnesium is chelated the resin and eluted magnesium interfered with the measurement at the 267.72 nm chromium line. Among metals (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+} and Fe^{3+}), manganese showed positive interference. Anionic ions (NO_3^-, NO_2^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-}) did not interefere with the determination of chromium(III).

Table II. Precision and Signal Enhancement for the on-Line Preconcentrating FIA-ICP System

element	conc, μgL^{-1}	%RSD (n=5)	signal enhancement (fold increase) peak height
Cr(III)	10	4.0	113
Ti	10	2.3	68
V	10	3.4	66

a Sample rate = 17 samples h^{-1} with 180-s load times.

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S1-15

SPECTROPHOTOMETRIC DETERMINATION OF TRACE PHOSPHATE AND ARSENATE WITH THE PRECONCENTRATION OF MOLYBDOPHOSPHATE- AND MOLYBDOARSENATE-MALACHITE GREEN AGGREGATES USING MEMBRANE FILTER

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Because of toxicity and possible carcinogenicity of arsenate, and biological pollution of environmental water enriched with phosphate, the levels of phosphate and arsenate in environmental monitoring were widly measured. Most of the procedures for the spectrophotometric determination of ortphosphate are based on the formation of 12-molybdophosphate. In general, 12-molybdophosphate formed is determined after reduction to a heteropolyblue species, or after extraction into an organic solvent as an aggregate with a bulky cationic dye. However, when the phosphate concentration in the sample solution is too low, the methods are troublesome in routine work because of the necessity of solvent extraction for preconcentration.

In this work, a simple and rapid method for the determination of trace amounts of phosphate and arsenate in water sample was proposed. Molybdophosphate- and molybdoarsenate-Malachite Green aggregates were collected on a membrane filter and dissolved in a small volume of methylcellosolve together with the membrane filter. The absorbance at 627 nm was proportional to both the concentrations of phosphate and arsenate with the molar absorptivity of $2.7\times10^{5}M^{-1}cm^{-1}$. The present method made it possible to determine phosphate and arsenate in amount ranging from 0.3 to 30 ppb as phosporus and arsenic.

1. EXPERIMENTAL SECTION

Reagent. The Mo-MG reagent was prepared by mixing 300 ml of 0.68 M ammonium molybdate, 250 ml of 2 mM malachite green(oxalate) and 47 ml of concentrated sulfuric acid. About 30 min after mixing, the solution was filtered through a 0.45 µm pore size mmbrane filter. The filtrate used as the Mo-MG reagent.

Procedure for the determination. First, 1 ml of 7.5 M sulfuric acid and 3 ml of the Mo-MG reagent were added to 20 ml of water sample containing phosphate and arsenate ranging to 2 nM from 20 µM in total concentration. The solution was filtered through a 3 µm pore size membrane filter(made of nitro cellulose-acetyl cellulose or nitrocellulose) to collect the aggregates of 12-molybdophosphate, and arsenate with malachite green on the filter. The membrane filter including the aggregates was dissolved in 4 ml methylcellosolve. The absorbance, A(P+As), was measured at 627 nm using a reagent blank as a reference. The signal thus obtained corresponds to the sum of the concentrations of both phosphate and arsenate in the sample. Second, 0.3ml of

20 mM sodium thiosulfate, as a reducing agent for arsenate to arsenite,was added to 20 ml of the sample, and the solution was allowed to stand for 5 min at roomtemperature. The absorbance, A(P), of the solution was measured in the same way as described above. The signal obtained corresponds to that of phosphate alone, because arsenite forms no aggregate with malachite green. Then the difference in A(P+As) and A(P) corresponds to the arsenate concentration in the sample. When the concentration of phosphorus and arsenic in water sample was below 3ppb, 200 ml of sample water was needed.

2. RESULTS AND DISCUSSION

The absorbance at 627 nm was proportional to the concentration of both phosphate and arsenate aggregates in methylcellosolve with the molar absorptivity; $2.7\times10^{5} M^{-1}cm^{-1}$. A constant absorbance was obtained in the range from 0.25 to 0.75 M sulfuric acid in the final solution, so that the final concentration was adjusted to about 0.45 M sulfuric acid. As being obtained the constant and highest absorbance, the final concentrations of molybdate and malachite green in solution before filtration was fixed at levels of 40 mM and 0.1 mM, respectively. Asthe aggregates were collected quantitatively on the membrane filters of pore size in the wide range from 0.3 to 8 µm, 3 µm pore size was usually used. On the basis of the experimental results, the conditions for determination were decided as described above.

The absorbance determined with the standard phosphate and arsenate solutions were plotted against to give a linear relation in the concentration ranging from 2 nM to 20 µM (r=0.999). The coefficient of variation was less than 2.0 % at 0.2 µM in concentration.

The following experiments were performed to apply for the determination of phosphate and arsenate in water samples. The results obtained are shown in Table I.

Arsenic species can now be determined at low levels in water sample with flameless atomic absorption spectrophotometry coupled with analytical separations, however, the procedure is time-comsuming and equipment required is expensive. In the present paper, a simple and rapid method without pretreatment was provided for the determination of trace amounts of phosphate and arsenate in water sample.

Table I Detemination of Phosphate and Arsenate

Sample		P (ppb)	As (ppb)
Natural water	A	7.2	10.7
	B	18.1	7.6
	C	81.5	1.5
	D	44.3	9.1
	E	19.3	9.3
Tap water	A	11.8	2.0
	B	6.5	3.4
River water			
Hayato river		9.7	6.2
Mizusawa river		13.2	3.6
Hot well water	A	52.1	74.0
	B	40.9	36.1

S1-16

GAS CHROMATOGRAPHIC ANALYSIS OF POLYCYCLIC AROMATIC COMPOUNDS CONCENTRATED ON WATER SOLUBLE METAL PHTHALOCYANINES

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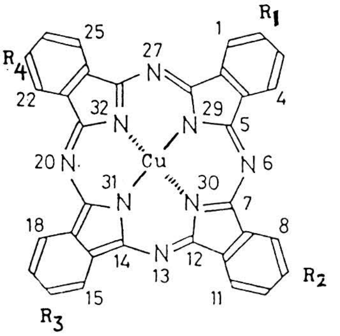
Many kind of carcinogenic polycyclic aromatic compounds have been found in the environment or in foods. There have been developed several methods to analyze these compounds in the environment.1) It is quite difficult to analyze trace amount of the compounds directly, so, they must be concentrated before detection or structural characterization. Solvent extractions and adsorption on special adsorbents are ofted used.2) Polycyclic aromatic compounds have been known to be adsorbed specifically on copper phthalocyanines. This finding is technically condensed on the blue cotton method for a screaning test of mutagenic compounds.3) This method is excellent in convenience and in time saving. But, structural characterization of the compounds adsorbed on the blue cotton is difficult because of their low concentration.

To overcome this difficulty, we have investigated a method of concentration and gas chromatographic analysis of polycyclic aromatic compounds based on adsorption on water soluble copper 2,9,16,23-tetrasulfophthalocyanine(CuPc(SO$_3$H)$_4$:I), copper monosulfophthalocyanine(CuPcSO$_3$H:II) and copper 2,9,16,23-tetracarboxyphthalocyanine(CuPc(COOH)$_4$:III) (Fig. 1) and deposition as a metal salt.

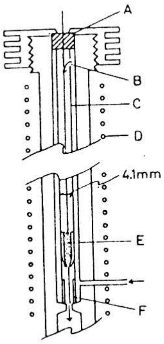


I $R_1=R_2=R_3=R_4=SO_3H$
II $R_1=SO_3H$ $R_2=R_3=R_4=H$
III $R_1=R_2=R_3=R_4=COOH$

Fig. 1

For the present purpose, compound I is better in solubility in water and in the rate of precipitation as a balium salt. Therefore, most experiments were carried out with compound I. Typical experiment is as follows.

To a sample solution(ca.50ml) was added a water solution of I(2mg) and balium nitrate(58mg) solution, the blue solution was kept for a while to complete precipitation. The precipitate was separated, washed with purified water, and collected finally in a glass tube(ca.15mm dia.4mm) by centrifugation, then water was removed with pipet and cotton rod as possible as can. The precipitate could be extracted with ammonia alkaline methanol or was directly introduced into a modified injection port of a gas chromatograph instrument(Hitachi Model 263-30: FID) (Fig.2). Conditions of gas chromatography: 5% Silicon OV-101; Glass column 4mmX2m; Column temp.:180-330°, programing rate: 7.5°C/min; Carrier gas:N_2. By direct method, 1.44×10^{-7}g of benz(a)pyrene in a 50ml of aqueous solution was quantitativly adsorbed and detected easily(GC sensitivity:10X 4;Peak height:3.9 cm, Peak area:0.98cm^2). Active carbon, instead of compound I, gave only 10% of the peak area.



A: Byton Stopper
B: Hole
C: Aluminum Insert
D: Heater
E: Sample
F: Glass Stopper

Fig. 2: Modified Injection Port

Fig. 3 shows a direct method gas chromatogram obtained from a water solution that absorbed smoke from a cigarett. For comparison, a water solution from a cigarett was treated with active carbon powder(2mg), which was examined by gas chromatography under the same conditions. But, only three small peaks were detected. It is not clear whether the failure of the peaks with active carbon is due to the adsorption process or desorption process.

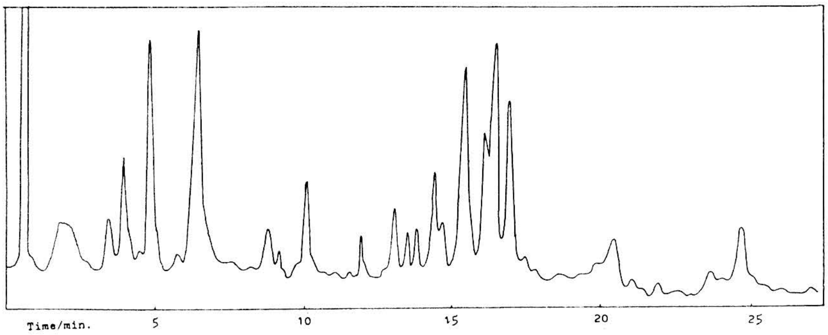


Fig. 3 Direct Method Gas Chromatogram of CuPc($SO_3\frac{1}{2}Ba)_4$ precipitated from a water solution that absorbed smoke from a cigarett.

Assignment of each peak will be the subject of future study.

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S1-17

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE IN WATER WITH MOLYBDATE AND MALACHITE GREEN

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INTRODUCTION

Determination of phosphorus is of importance, particularly in the fields of environmental science, agriculture and biochemistry. Most spectrophotometric methods for phosphorus are based on the formation of hetropolyacids with molybdate. Molar absorptivities of heteropolyacids and their reduced products (molybdenum blues) are about 2×10^4 l mol^{-1} cm^{-} or less. Now, more sensitive methods for determination of phosphorus are required in environmental science. In this work, we report very sensitive methods for phosphorus based on the formation of ion associate, and also we report the methods of the flow injection analysis (FIA) for phosphorus.

EXPERIMENTAL

Apparatus Absorption measurements were made on a Hitachi Perkin-Elmer Model 139 spectrophotometer and a Hitachi EPS-3T recording spectrophotometer in a glass cells of 10 mm and 20 mm path length. The FIA system was assembled from a double plunger micro pump (Sanuki DM-2M-1024), a 6-way injection valve, a Shimadzu UV-140-02 double beam spectrophotometer with a 10 mm micro flow cell (18 μl), a Toa Dempa FBR-251A recorder, Daiflon connectors and Teflon tubing.

Reagents All Chemicals used were of analytical reagent grade.

RESULTS AND DISCUSSION

Spectrophotometric determination of phosphate with molybdate and Malachite Green

In an acidic medium, molybdophosphate reacts with Malachite Green (yellow protonated type:HMG^{2+}) to form a green ion-associate as follows,

$$H_3PMo_{12}O_{40} + HMG^{2+} \longrightarrow (MG^+)(H_2PMo_{12}O_{40}^-)$$

An apparent molar absorptivity was 8×10^4 l mol^{-1} cm^{-1} at 650 nm. The absorbance of the reagent blank was about 0.02 (20 mm cell). The recommended concentration range of phosphorus was 0.1 - 5 μg and the limit of detection was 0.01 µg of phosphorus.

Solvent extraction-spectrophotometric determination of phosphate with molybdate and Malachite Green

Molybdophosphate, formed in sulfuric acid solution, was extracted into a mixture of toluene and 4-methylpentane-2-one (1:3 v/v) with Malachite Green as counter ion. A single extraction with equal phase volumes gives an apparent molar absorptivity for phosphate of 2.3×10^5 l mol^{-1} cm^{-1} at 630 nm. The absorbance of the reagent blank was about 0.03. With an organic to aqueous phase-volume ratio of 1:10, the molar absorptivity was 2.5×10^5 l mol^{-1} cm^{-1}. By the proposed method, ng/ml levels of phosphorus can be determined, and the detection limit is about 0.1 ng/ml.

Determination of phosphate by flow injection analysis

The coloration formed with molybdate and Malachite Green in aqueous solution was applied to FIA for phosphorus determination. Phosphorus (as inorganic phosphate) can be determined at the level of several ng/ml in water. Analyses can be done at a rate of up to 40 per hour.

Determination of phosphate by solvent extraction-flow injection analysis

Solvent extraction-spectrophotometry for phosphate with molybdate and Malachite Green was applied to solvent extraction-FIA. The extracting solvent was a mixture of benzene and 4-methylpentane-2-one (1:2 v/v). Newly designed phase separator was used to separate the organic phase. The calibration curves were linear below 30 ng/ml of phosphorus and below 1 µg/ml of phosphorus by injecting 300 µl and 10 µl of samples, respectively. The detection limit was 0.1 ng/ml of phosphorus. Analyses can be done at a rate of up to 40 per hour.

CONCLUSION

Sensitive spectrophotometric methods for determination of phosphorus were developed, and the methods were applied to FIA. The proposed FIA methods were very sensitive, simple and rapid procedures for determination of phosphorus.

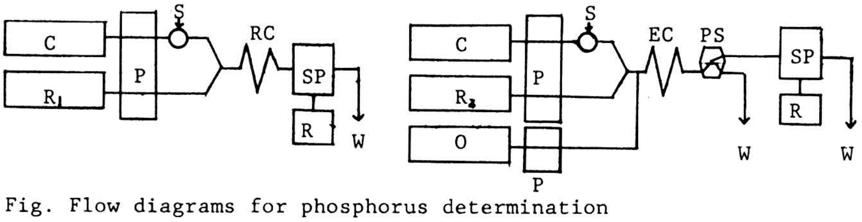

Fig. Flow diagrams for phosphorus determination
C:carrier solution(dilute H_2SO_4); $R_1$and R_2:reagent solution,R_1:molybdate +Malachite Green+H_2SO_4+ethanol,R_2:without ethanol; O:organic solvent; S:sample:RC:reaction coil(0.5mmx5m); EC:extraction coil(0.5mmx4m); PS: phase separator; SP:spectrophotometer; R:recorder; W:waste.

S1-18

SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF CATIONIC SURFACTANTS IN WASTE WATER BY TERNARY ION PAIR FORMATION

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Most of the procedures proposed for the extraction-spectrophotometric determination of onium compounds depend on the formation of ion associates between an onium cation and a dye anion. With monoprotic acid dyes such as tetrabromophenolphthalein ethyl ester(TBPE) and potassium picrate, the optimum pH range for the extraction was found to be wide. TBPE is an excellent reagent for the determination of trace amounts of tertiary amines, alkaloids and quaternary ammonium salts, but it is not selective enough for the determination of onium compounds in the complicated samples because the absorption spectra of those associates and the optimum pH range overlap. On the other hand, with multi-protic acid dyes such as bromophenol blue(BPB) and bromocresol green(BCG), the extraction behaiviour is very complicated because the ion associates formed between onium cations and dye anions depending on the pH level in the aqueous solutions.

For example, BPB reacts with both bulky amines and quaternary ammonium compounds in a pH 3.8 medium and forms yellow colored salts. The associates [$HBPB^-.HR_3N^+$, $HBPB^-.R_4N^+$] are readily extracted from acidic aqueous solutions with organic solvents. In alkaline media only quaternary ammonium compounds form blue colored salts with BPB and the associate [$(BPB^{2-})(R_4N^+)_2$] can be extracted into organic solvents. In the former associates, the extractability is good, but the selectivity is not satisfactory. In the case of the latter, the selectivity for amines is sufficient, but the extractability of the associates and the linearity of the calibration curves are poor.

In the present investigation, we found that a quaternary ammonium salt was successfully co-extracted with diprotic acid dyes such as BPB^{2-}, BCG^{2-} and $BCPB^{2-}$(bromochlorophenol blue) anions into organic solvents in a neutral medium, but only in the presence of quinine(tertiary amine, pK_1 : 4.1, pK_2 : 8.0). Extraction of quaternary ammonium salts was not possible in the absence of quinine and also amines did not form the ion pair in the media. Therefore, a trace amount of quaternary ammonium compound can be determined spectrophotometrically without interference of some quaternary ammonium compounds and various amines.

1. EXTRACTION MECHANISM OF ION ASSOCIATES WITH BROMOPHENOL BLUE

The continuous variation plots as shown in Fig. 1 seem to indicate that the extraction mechanism of ion associates with BPB in the different media can be represented as follows.

$pH < 3.8$

$$2HBPB^- + H_2Quinine^{2+} \rightleftarrows (HBPB^-)_2(H_2Quinine^{2+})$$
$$HBPB^- + R_4N^+ \rightleftarrows (HBPB^-)(R_4N^+)$$

$3.8 < pH < 4.1$

$$HBPB^- + HQuinine^+ \rightleftarrows (HBPB^-)(HQuinine^+)$$
$$HBPB^- + R_4N^+ \rightleftarrows (HBPB^-)(R_4N^+)$$

$4.1 < pH < 8.0$

$$BPB^{2-} + 2HQuinine^+ \rightleftarrows (BPB^{2-})(HQuinine^+)_2$$
$$BPB^{2-} + 2R_4N^+ \text{ ...... not extractable}$$

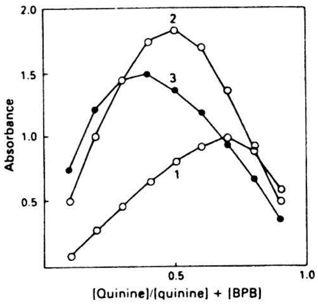
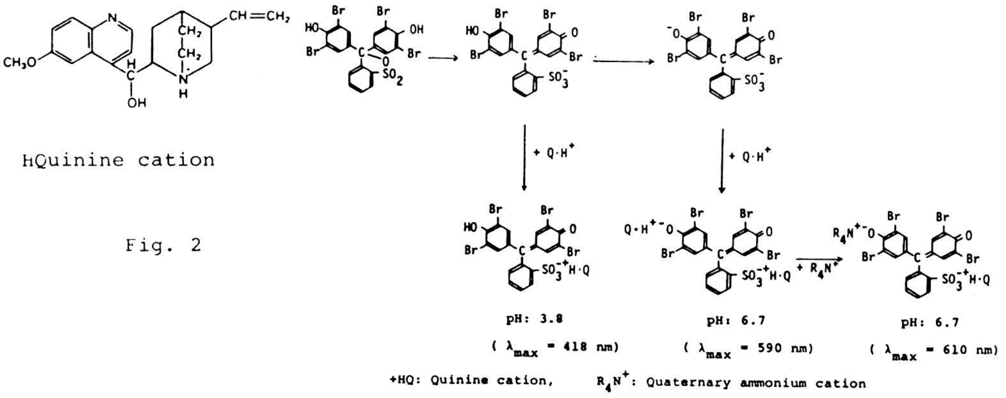


Fig. 1 Continuous variation plots
1 : pH 6.7 2 : pH 3.8
3 : pH 2.8

At the following pH media, $4.1 < pH < 8.0$, $(BPB^{2-})(HQuinine^+)_2$ associate was extracted into organic solvents, but $(BPB^{2-})(R_4N^+)_2$ associate was not extractable in the above media. However, in the presence of an adequate amount of quinine, several kinds of quaternary ammonium compounds could be extracted into organic solvents such as nitrobenzene, 1,2-dichloroethane and chloroform. Fig. 2 shows the extraction scheme by ternary ion pair formation. The extractability of a quaternary ammonium compound can be enhanced by the formation of bulky ion associates.



HQuinine cation

Fig. 2

2. RECOVERY OF QUATERNARY AMMONIUM SURFACTANTS IN WASTE WATER

Waste water containing known amounts of trimethylstearylammonium(TMSA) was determined by the recommended method. The result is shown in Table 1.

Table 1 Analysis of cationic surfactant in waste water

Methods	with BPB		with BCG	
	Found(mg)	Recovery(%)	Found(mg)	Recovery(%)
Sample	33.8	96	33.6	96

TMSA:35 mg/100ml

S1-19

FLUOROMETRY OF NANOGRAM AMOUNTS OF SELENIUM IN BIOLOGICAL SAMPLES

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INTRODUCTION

Selenium has been recognized as an essential trace element for humans and animals, and the metabolism and function of selenium such as in glutathion peroxidase have been reported. For biological and clinical research on selenium, an accurate and sensitive method is needed for routine assay of selenium in biological materials. Fluorometry of microgram or smaller amounts of selenium in blood, liver, and food have been reported. Because the selenium content of these samples is generally low (e.g.,ppm), a few grams of sample must be used for the fluorometric assay. Co-existing materials such as large amounts of iron and trace amounts of organic compounds remaining after the wet-ashing decomposition of the biological samples may interfer, producing considerable negative and positive error, respectively, in the fluorometric measurement of selenium. Accordingly, one tries to assay only small amounts of the sample to minimize the interferences. Therefore, a highly sensitive, accurate, and precise fluorometric assay for nanogram amounts of selenium is needed.

In this paper, the procedure for fluorometry of selenium in biological materials has been made more nearly accurate by our detailed considerations of methods for removing these sources of interference. Our method is highly sensitive (detection limit for selenium: 0.05 ng, 5 ng/L), accurate (as judged by comparison with analytical results by non-destructive neutron activation analysis), precise [e.g., 47.1 (SD 0.72, CV 1.5%) ng of Se per gram of animal bone], convenient, and suitable for use in routine analyses (about 2 h required for analyses of 10 samples).

METHODS

For fluorometry of selenium in biological materials (hair:0.05 g; liver and animal bone:0.5 g; blood: 0.5 g), we wet-ashed the samples with conventional nitric and perchloric acids, and then extracted piazselenol (complex of Se and 2,3-diaminonaphthalene) incyclohexane. Selenium was back-extracted from the cyclohexane into nitric acid to remove the fluorometric interferences of trace amounts of organic compounds. After removing the nitrate ions, the selenium was re-extracted with the diaminonaphthalene into cyclohexane. Then, we measure the relative fluorescence intensity of piazselenol in the sample and in the standard at the 520 nm, which is the peak for piazselenol fluorescence.

RESULTS AND DISCUSSION

1. EFFECT OF TRACE ORGANIC COMPOUNDS ON THE FLUOROMETRY OF SELENIUM

Figure 1 shows the effect of various acid treatments on the decomposition of organic compounds in a 1-mL plasma sample. The 2,3-diaminonaphthalene (DAN) reagent reacted not only with selenium but also with trace organic compounds, if a biological sample was not completely destroyed in the wet-ashing step.

2. EFFECT OF VARYING THE VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE IN THE BACK-EXTRACTION OF SELENIUM

Table 1 shows the result of this examination. We used a volume ratio 2/1.

3. EFFECT OF NITRATE AND IRON IONS ON THE FLUOROMETRY OF SELENIUM.

We removed nitrate from selenium by heating them with perchloric acid, and we masked iron interference by adding EDTA-NaF.

4. ANALYTICAL RECOVERY

The recovery of selenium was 87.3 (SD 1.6)% for three standard solutions containing 10 ng of selenium. This recovery percentage is not high, but is sufficient for our purpose; 100% recovery is not required for nanogram quantification, if the analytical precision is good (as shown by the SD of 1.6%).

5. ANALYTICAL RESULTS AND COMPARISON OF RESULTS

Table 2 lists the analytical values for selenium as determined by the present method for standard reference materials SRM-1577 bovine liver and SRM-1571 orchard leaves from The U.S. National Bureau of Standards, Washington, DC, and animal bone from the International Atomic Anergy Agency, Vienna, Austria. Fairly good agreement was obtained for selenium content.

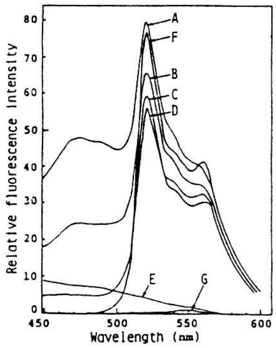

Fig.1. Fluorescence spectra

A,B,C: Se determined without back-extraction
D: With back-extraction
E: Without wet-ashing
F: Standard Se (100 ng Se)
G: Reagent blank

Table 1. Percentage of selenium obtained in back-extraction

Organic/ aqueous vol ratio	Organic vol, mL	Aqueous vol mL	Aqueous Se ng	% extracted
20	20	1	14.6	73.2
10	20	2	18.0	90.1
4	20	5	18.8	93.8
2	20	10	18.8	94.1
1	20	20	19.1	95.5

Table 2. Analytical values of selenium

	Se content, µg/g This method	Se content, µg/g NAA method	Se content, µg/g NBS data
NBS SRM-1577	1.18	0.9-1.3	1.1(SD0.1)
NBS SRM-1571	0.0646	0.05-0.09	0.08(SD 0.01)
IAEA animal bone (n=4)	0.0471 (SD 0.00072)	0.05-0.06	
Human plasma			
10 men	120(SD 16.7)		
10 women	112(SD 23.0)		

S1-20

DETERMINATION OF TRACE AMOUNTS OF IRON BY MEASURING COLOR INTENSITY OF ION-EXCHANGER COLUMN

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INTRODUCTION

For the purpose of the establishment of forecast technique of occurrence of red tide in natural waters, automatic monitoring technique of eutrophic substances, such as phosphorus and nitrogen compounds, were being studied$^{1)}$. The present paper describes the determination of trace amounts of iron, which is seemed as one of the substances caused the red tide in natural waters. To determine soluble iron in natural water, an appropriate preconcentration is necessary. Trace amounts of iron in natural water was determined by direct measurement of light absorption of ion-exchanger resin phase colored by sorption of red 1,10-phenanthroline-iron(II) complex in sample solution$^{2)}$ (Ion-exchanger colorimetry$^{3)}$). In this study, the colorimetry was applied to the determination of trace amounts of iron by using the ion-exchanger column. The intensity of the colored band on the ion-exchanger column was measured. The colored band on the column was produced by passing the purple TPTZ(2,4,6-tris(2-pyridyl)-s-triazine)-iron(II) complex solution, which formed by the addition of TPTZ to sample water contained ferrous iron.

PROCEDURE

TPTZ and sodium acetate buffer (pH 3.4 ~5.8) solutions were added to sample solution after the reduction of iron(III) to iron(II) with hydroxylamine. The colored solution contained TPTZ-iron(II) was passed through the cation-exchanger column (3mmx5mmx70mm). The color intensity of the band on the column was measured (light path; 3mm) by the spectrophotometer moved along the column (Fig.1). The iron concentration in sample solution was determined from the peak height or the area of intensity of colored band on the column.

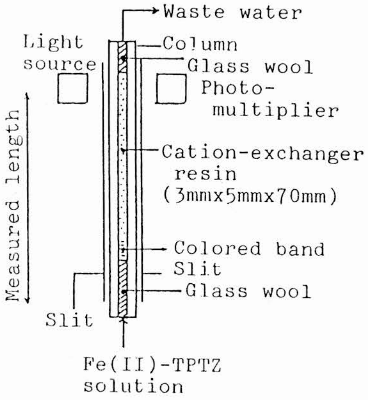

Fig. 1 Schematic diagram of color measurement system of column

RESULTS AND DISCUSSION

The cationic TPTZ-iron(II) complex was sorbed effectively on the cation-exchanger resin. The particle size of the resin in the column affected on the sorption of the colored complex. When 20 to 50mesh of the resin was used, the complex was insufficiently sorbed on the column, and the color intensity of the resin phase (without the treatment by the sample solution) was not constant (Fig. 2). Weakly acidic cation-exchanger resin (Na$^+$ form, 50~100mesh) was suitable for the method, and was usable repeatedly with regeneration using 1M hydrochloric acid and 2M sodium chloride solutions.

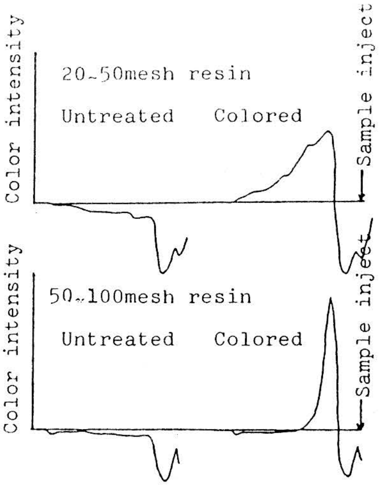

Fig.2 Color intensity of columns before and after coloring

When 10ml of the colored sample solution contained 1μg of iron was passed through the column at a rate of 2.5ml/min, the colored complex was sorbed on 0.2 to 0.3cc of the resin (the length of the colored band; in 1~2cm). Then the enrichment ratio of the complex was 30 to 40 times. Up to 1~2μg of iron was determined by this method, and ten ppb of iron was detectable in 10ml of the sample solution. Low concentration of iron was able to determine by taking large amounts of sample water. Detection limit and precision of the method was affected by the iron concentration of the reagent blank. Muximum error of the method was ±15% for 5 samples contained 1μg of iron in 10ml of sample solution.

Sulfate, phosphate, nitrate and nitrite of 100ppm, and chloride of 1,000 ppm did not interfere the determination.

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S1-21

RADIO-ACTIVATION ION CHROMATOGRAPHY ON TRACE AMOUNT OF MN IN CHALYBEATE WATER

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An ion chromatograph with a conductivity detector was invented as a dual column system for the rapid separation and determination of inorganic anions by Small *et al.*[1] Gjerde *et al.*[2] developed a single column method for a quantitative separation of several common anions and cations. Both apparatus have a separating column filled with an ion exchange resin of low exchange capacity and employed with very dilute solutions. Although many conductivity detectors for the determination of the amount of ions in a solution have been greatly improved in recent years, these conductivity detectors could not be used for the detection of the ions having the nearly same elution time such as Mn(II) and Fe(II).

By combining a radiation detector with the usual conductivity detector, we have been able to develop a successful system for the separation and detection of very low concentration of radioactive ions. The separated radioactive ions are easily detected by the radiation detector placed immediately after the conductivity detector. The aim of the present study is to develop a new ion chromatographic system that uses a NaI(Tl) detector and to apply it to the determination of the amount of Mn(II) ion in chalybeate water by means of the neutron irradiation.

The basic liquid chromatographic system (HLC-847) was connected to a radio-activation ion chromatograph with a single separation column containing a gel type resin and was used for the separation of divalent metallic ions in the aqueous solution. The radiation detector consisted of a 2"x2" NaI(Tl) detector with a polyethylene loop of 200 μl for the detection of radioactive nuclides. For the injection of sample solution, a sample loop of 200 μl was used.

The column was packed with a gel type cation exchange resin of particle size 5μ m. The dimensions of the column were 50 mm in length by 4.6 mm in diameter. The resin was sulfonated to give a low exchange capacity of the order of 0.3 milli-equivalents per gram.

The eluent was prepared with doubly distilled deionized water and passed through a degassing apparatus just before pump. The pump serves to force the eluent from a eluent tank to a fraction collector through the sample loop, column, and detector at a flow rate of 1.2 ml/min.

For a typical experiment, a small amount (0.3 ml) of the sample solution was irradiated with a thermal neutron flux of 2.75×10^{13} $n\cdot cm^{-2}\cdot sec^{-1}$ for 10 minutes at dry-ice temperature in the pneumatic tube facility of the Kyoto University Reactor (KUR).

The separation of several divalent cations in aqueous solution was achieved very easily within 20 minutes with the eluent of 2 mM ethylenediamine in 10 mM citric acid containing 10 % acetonitrile solution, and the sharpness of the eluted peaks is excellent.

The separation pattern obtained by the conductivity detector showed the total amount of Fe(II) and Mn(II) ions in the sample solution. On the other hand, the pattern obtained by NaI(Tl) radiation detector indicated only the amount of the radioactive nuclides formed by the irradiation of reactor neutrons. This pattern was independent of the eluent temperature and the pressure of the pump flowing the eluent, and the pattern was also not affected by the water dip that appears in the usual pattern observed with the conductivity detector. The elution time of Fe(II) ion was 16 minutes after the starting time of the separation using the eluent mentioned above. The elution time of Mn(II) was the nearly same elution time as Fe (II) ion.

It is difficult to determine the amount of Mn(II) ion in the sample solution containing large amount of Fe(II) ion by using the conductivity detector. However, it is quite expected that the detection limit of Mn(II) ion increases by a factor of 10^6 than that of Fe(II) ion by using the radio-activation ion chromatography. Because the calculated radioactivity per gram of the element from the radioactive ^{56}Mn formed by the neutron activation reaction is 10^6 times as much as that from the radioactive nuclides of Fe irradiated with the same condition as Mn.

It became clear that the trace concentration of Mn(II) ion in the chalybeate water could be determined very easily by the radio-activation ion chromatography. This technique might also provide a rapid and highly selective method for separating and determining the chemical species of carrier-free radioactive recoil atom formed in the nuclear reaction.

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S2-01

RAPID AND SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF PPB LEVEL PHOSPHATE BY A NOVEL METHOD USING A STOPPED-FLOW APPARATUS

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Although absorptiometric methods are in general appreciably less sensitive compared with emission (fluorescence and chemiluminescence, etc.) methods, the former is generally much less susceptible to interfering factors than the latter. It is significant, therefore, to enhance the sensitivity of absorptiometric methods.

Stopped-flow method is a widely used fast reaction technique. We have been successful to utilize this technique for fast and highly sensitive absorptiometric determinations of various substances (about 100 times as sensitive as those by the conventional absorptiometry). The term "stopped-flow time difference analysis" (abbreviated to SFTDA) is used for this novel method for the quantitative analysis, based on the magnitude of the absorbance change (ΔA) obtainable from the stopped-flow trace for the time course of the reaction involving a substance to be determined [1]. The reasons for the high sensitivity of this technique are as follows: (a) Since the cell and the solution are both immobile during the measurement, any possible error from the replacement and/or the movement of the solution can completely be eliminated. (b) A small absorbance change, even on a large background, (e.g., ΔA of 0.002 O.D. on 1.5 O.D. background) can easily be measured in a good precision. One of other advantages of this technique is that slower and/or faster interfering side reactions can readily be excluded to observe main reaction(s) to be examined.

HIGHLY SENSITIVE ABSORPTIOMETRIC METHODS FOR PHOSPHATE DETERMINATION BY USING "STOPPED-FLOW TIME DIFFERENCE ANALYSIS" (SFTDA) TECHNIQUE

For the rapid and sensitive absorptiometric determination of ppb/sub-ppb level phosphate, the SFTDA technique was successfully used in the following two ways: one (Method 1) is based on the conventional method using the colored complex formation of 12MPA (12-molybdophosphoric acid) with Malachite Green (abbreviated to "MG method") [2], and the other (Method 2) makes use of the combination of the conventional "molybdenum blue method" (using stannous chloride as the reducing reagent) with butanol-extraction [3]. The procedures and characteristics of the two methods are as follows:

(A) Method 1: To three volumes of phosphate solution to be determined, one volume of 0.2 mol L^{-1} ammonium molybdate in 4 mol L^{-1} H_2SO_4 is added to form 12MPA. After 15 min, this solution is mixed with an equal volume of Malachite Green solution (1.25×10^{-4} mol L^{-1} in 1 mol L^{-1} H_2SO_4) in a stopped-flow apparatus. The reaction curves are recorded at 650 nm for about 50 s. From the difference in absorbance changes ($\Delta A - \Delta A_0$) (ΔA_0 is the absorbance change due to the reagent blank) at a fixed time (30 - 50 s after the mixing), obtained from the progress curves, phosphate concentrations of ppb level can readily be determined. The calibration curve ($\Delta A - \Delta A_0$ vs. phosphate concentration) is linear from 0 to 1000 ppb. The detection limit is as low as 2 ppb. One of other advantages of this method is that the reactions of some anions interfering with the conventional "MG method" (such as AsO_4^{3-} etc.), can easily be differentiated from the main reaction of phosphate, since the reactions of these anions are much slower than that of phosphate.

(B) Method 2: To 500 ml of phosphate solution, 60 ml of 0.012 mol L^{-1} ammonium molybdate in 3.25 mol L^{-1} H_2SO_4 is added. After 15 min, the 12MPA thus produced is extracted with 20 ml of n-butanol. To 5 ml of this butanol-extract, 0.2 ml of 90 %(v/v) ethanol solution of 1 mol L^{-1} HCl is added. This solution is then mixed with an equal volume of stannous chloride solution (1.8×10^{-2} mol L^{-1} in n-butanol) in a stopped-flow apparatus. The reaction curves are recorded at 730 nm for 0.5 s, as shown in Fig. 1, from which ($\Delta A - \Delta A_0$) is obtained. The relative standard deviations in the determinations of 0.5, 1.0 and 2.0 ppb phosphate are 7, 4 and 3 %, respectively. Thus, Method 2 is about ten times more sensitive than Method 1. The calibration curve is linear from 0 to 25 ppb of phosphate concentration. In this case, the protection with N_2 gas is necessary, since stannous chloride is much more unstable against oxidation in butanol than in water.

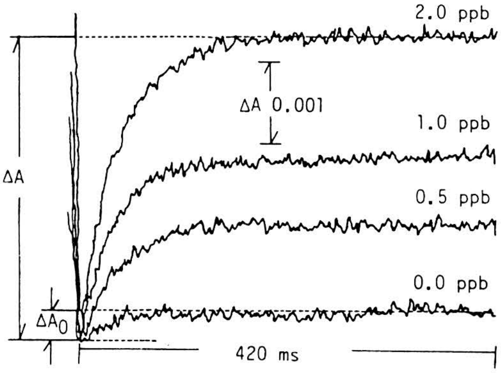

Fig. 1 Typical examples of progress curves in Method 2.

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S2-02

ANALYTICAL SOLUTION CHEMILUMINESCENCE IN ORGANIZED SURFACTANT MEDIA

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Solution chemiluminescence(CL) in organized surfactant media has been actively investigated in relation to the analytical use[1)2)]. The CL technique offers substantial advantages for sensitivity, linearity, instrumentation, and speed of analysis, but it is not yet utilized widely in practice in comparison with other spectral method. This is mainly due to the lack of selectivity and the pausity of CL reaction usable in analysis. In order to cope with those shortcomings and then extend CL analysis, our intensive efforts have been made to search new CL system. In the course of the investigations, we found that high selectivity and sensitivity were often yielded when CL reaction proceeds in the presence of surfactant molecular aggregates like micelles or bilayer vesicles which surfactant(amphiphile) molecules form spontaneously in aqueous solution. Such oriented surfactant molecular assemblies exhibit unique properties, e.g., solubilization, concentration and compartmentalization of reactants and/or analytes, alterations of microenviroment, chemical and photophysical pathways and rates, etc.[3)]. These properties are very attractive in the analytical use of CL because there is much possibility of enhancing quantium efficiency or energy transfer efficiency, because they permit the use of CL reagents and sensitizers insoluble in water, and because they serve to improve selectivity.

In this paper, we described about determinations of ultratraces of free cyanide and copper(II) by flow injection method with analytical solution CLs in organized surfactant media.

I. DETERMINATION OF COPPER(II) AT SUB-PICOGRAM LEVEL BY FLOW INJECTION METHOD USING MICELLAR ENHANCED CHEMILUMINESCENCE OF 1,10-PHENANTHROLINE

Micellar enhanced CL is used to determine copper(II) at sub-picogram level by using the 1,10-phenanthroline-hydrogen peroxide-sodium hydroxide-hexadecylethyldimethylammonium bromide micelle system. The CL mechanism is based on the following chemical reactions; the superoxide radical anion which is produced through the catalytic decomposition of hydrogen peroxide by the copper(II)-1,10-phenanthroline complex, reacts with 1,10-phenanthroline to form the excited 3,3'-diformyl-2,2'-dipyridyl via a 1,2-dioxetane derivative intermediate. The system is composed of three flow lines, in which optimum conditions are specified.

This method permits the determination of copper(II) much more selectively than any other CL method with a limit of determination of 8.0×10^{-14}g(20 µl sample injection) or 1.6×10^{-13}M(continuous sample flow at the sample feed speed 5.0 ml/min). The linear dynamic range is 4 orders of magnitude, the sampling rate is 180/h, and the reproducibility is less than 1.7 % in terms of coefficient of variation for 5×10^{-13}g copper(II) injection(n=10). Lead(II), the strongest enhancer after copper(II), provides signal 0.03 % of that for copper(II). The method is successfully applied to the determination of copper(II) in the tap water and rabit lens.

II. DETERMINATION OF ULTRATRACES OF FREE CYANIDE BY FLOW INJECTION METHOD WITH SURFACTANT BILAYER VESICLE-CATALYZED AND URANINE-SENSITIZED CHEMILUMINESCENCE

Flow injection analysis, with a new CL reaction, is used to determine trace amounts of free cyanide(CN^-) by means of the uranine-sodium hydroxide-didodecyldimethylammonium bromide(surfactant) system. The emission induced by CN^- is efficiently sensitized by uranine in organized surfactant aggregate solution. The method permits selective determination of CN^- with a detection limit of 1 pg for 20 µl sample injection. The linear range is 2.5 orders of magnitude, the sampling rate is 360/h, and the relative standard deviation is 2.0 % for 0.1 ng CN^- (n=10). Sulfide, the strongest enhancer after CN^-, provides a signal 0.1 % of that for CN^-. The present method is applicable to the determination of CN^- in river water and body fluids(blood, urine and sweat). The CL emission is produced by superoxide radical anion from dissolved oxygen and sensitized by uranine.

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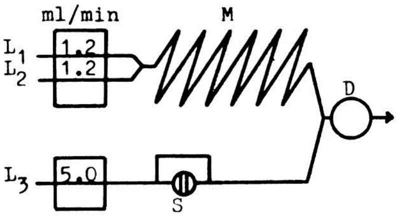
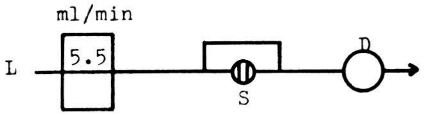


Flow system for I

L_1: 6.0×10^{-5}M 1,10-phenanthroline, 0.12M sodium hydroxide, 0.025M hexadecylethyldimethylammonium bromide & 2.8×10^{-9}M tetraethylenepentamine; L_2: 6.0 % hydrogen peroxide; L_3: Sample or water.
M: Mixing coil(1 mm i.d., 2 m long),
S: 20 µl sample injector, D: Detector.



Flow system for II

L: 1×10^{-4}M uranine & 7.5×10^{-4}M didodecyldimethylammonium bromide,
S: 20 µl sample injector($CN^-/5\times10^{-3}$M sodium hydroxide solution),
D: Detector.

S2-03

SPECIATION FOR TRACES OF LEAD, COPPER, ZINC AND CADMIUM IN INDICATOR FERN PLANTS, ATHYRIUM YOKOSCENSE

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Athyrium yokoscense (Fr. et Sav.) Christ is well known as a widely distributed fern growing on everywhere in Japan aside from alpine and subalpine forest zone. The dense population of the species is an anomalous vegetation always found in the vicinity of a metal mine. In ancient times, speculators utilized this species as an indicator plant in order to discover a meta mine, as was the case with famous Ikuno Silver Mine in Hyogo Prefecture.

During the course of the investigations of indicator plants correlating with heavy metals pollution (1-6), the authors have pointed out that the vegetation of the gregarious fern, Athyrium yokoscense, especially appears in the pollution areas of heavy metals like lead, copper, zinc and cadmium.

These pure communities of the fern were found in the areas of heavy metals pollution resulting from lead tiles of the ruins of Kanazawa Castle, now on the campus of Kanazawa University (1-6) and from mine drainage of the Kakehashi River from the Ogoya Copper Mine in Ishikawa Prefecture (2-5), and from smoke and waste water of the Mikka Ichi Zinc Smeltery from the Nippon Kogyo Co., Ltd. in Toyama Prefecture (3-5).

In the present investigation, the accumulation of heavy metals and tolerance of gregarious fern, Athyrium yokoscense, in the polluted areas have been examined by using histochemical techniques, especially by laying great emphasis on the distribution state of the ingredients in the tissues.

EXPERIMENTAL

A simultaneous analysis by x-ray fluorescence method was made of principal elements (K, Cl, Si, Ca, P, S, etc.) and traces of elements (Fe, Mn, Zn, Cu, Cd, Pb, Sr, etc.) in both nutritious organs of this fern species and its associated growing soils. A quantitative analysis by atomic absorption method was also made for heavy metals in both plants and soils. The root of Athyrium yokoscense in which heavy metals are accumulated in high concentrations was also cut with a microtome, and the small sections were stained with sodium rozizonate for lead, with rubeanic acid for copper, with dithizone for zinc, and with ferrous dipyridyl iodide for cadmium in order to ascertain the distribution of heavy metals in the tissues by means of microscopy. The concentrations of heavy metals on the surface of the transverse section were determined semi-quantitatively by bringing it into contact with ion test papers of Merckoquant Test Strips using specific color reactions. The distribution state of heavy metals in the root cell of the fern was also investigated by means of scanning-electron microscope combined with energy-dispersive x-ray analysis system. Amino acids in water extracts from the fern roots were also measured by using automatic amino-acid analysis.

RESULTS

1) A qualitative analysis by x-ray fluorescense method revealed that the ingredients like Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Pb, Cd, Rb and Sr were detected in plants and soils. In general, the underground parts (root and rhizome) contain lead, copper and zinc in high concentrations, while the above parts(petiol and leaf blade) contain cadmium in high concentrations. Lead, copper and zinc present in higher concentrations in the fern tissues were capable of being demonstrated histochemically.

It was found that the roots of Athyrium yokoscense accumulated a large amount of lead and copper over the superficial cell walls, while those of the species accumulated a large amount of zinc all over the cell including superficial and stele parts of the root cells. In the case of petiol and leaf blade of the fern, heavy metals were almost distributed over vascular bundle. Cadmium in the tissues could not be satisfactorily demonstrated by histochemical methods. The content of heavy metals in the section of the fern roots was detected more than 100 ppm for lead, 10 ppm for copper, and 100 ppm for zinc, respectively.

2) The accumulation of lead and its tolerance have some correlation with the concentration of sulfur in the plants and soils, while that of copper and zinc, and their tolerance have not such tendency. When Athyrium yokoscense grows, the concentrations of lead and sulfur in the root increase, while those of phosphorus, potassium, calcium, manganese and iron decrease. Asparagine and glutamic acid are present in much higher concentrations in copper accumulating fern-roots than in lead-accumulating fern-roots, while cystine in both fern roots was almost the same amounts. The distribution of lead and sulfur was almost the same pattern over the superficial cell walls. On the basis of these results, main chemical forms of heavy metals in the tissues were considered to be lead sulfate for lead, and to be metal complexes with some amino acid, pectic acid and cellulose for copper, zinc and cadmium.

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S2-04

DETERMINATION OF TRACE CONSTITUENTS AS GASEOUS METAL COMPOUNDS IN THE ATOMOSPHERE

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Air polluted materials are introduced into the atomosphere by the buring of fossil fuels. These materials are formed gaseous state, solid state(dust) and liquid state (mist and steam). Thus pollutant species are as follows; nitrogen oxides, sulfur oxides, some organic compounds and poisonous metal compounds in dust and/or adsorbed on surface od dust particles. The metal elements in the atomosphere has been investigated for mist, dust, rain water and snow as solid and liquid state substance. Studies of gaseous metal elements in the atomosphere have apparently not been published to date except about selenium and arsenic et cetra. Selenium and arsenic are existance in the atomosphere with gaseous substances such as methyl or ethyl compounds. The authors pointed out the fact that molybdenum was also existance in the air, from the resuls of the experiment on the particle size distribution of molybdenum in sea water and lake water with ultrafiltration method. The filtrate was always contaminated from nitrogen gas. Lead, copper, cobalt,cadmium, manganese and vanadium were also found in the air samples as a raw material of nitrogen gas. The air samples were collected with the apparatus as shown in Fig.1. Dusts in the air samples were eliminated by shifting with membrane filter (average pore size: 0.3 μm). And then mist substances in the sample were collected to a conical flask in a ice cooling NaCl solution. Dustless and drying air sample was liquefied at soak the test tube in a liquid nitrogen and cooling. Metal elements in the liquefied air sample were determined as follows. The metal compounds were adsorbed to concentrated nitric acid solution (The sample volume which pass through the nitric acid solution was measured), and concentrated to 5 ml with heating. The metal ions were measured with graphite furnace atomic absorption method. The sample contamination with metal ions from test tube which was used to the adsorption

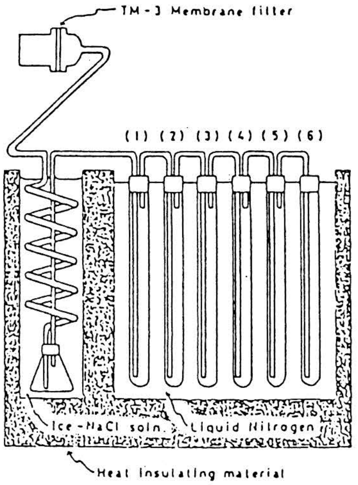

Fig. 1 Trapping device

process were investigated. The results are shown in Table 1. Concentration of metal ion in a sample was obtained from substraction the blank value from experimental value of the sample. The experimental results which were obtained in the way described above are shown in Table 2.

Table 1 Leaching contents of metal ions from test tube with nitric acid

Test tube	V	Mo	Co	Cu	Pd	Cd	Cr	Mn
Grass	N.D.	N.D.	N.D.	22.5	N.D.	N.D.	N.D.	N.D.
Quartz	N.D.	N.D.	N.D.	14.7 30.7 5.3	N.D.	N.D.	0.2 8.7 1.1	N.D.
Polypropylene	N.D.	N.D.	N.D.	9.5 11.2 22.3	N.D.	N.D.	N.D.	N.D.

(unit: ng/5ml)

Table 2 Gas state of vanadium, lead, copper, cobalt, molybdenum, chromium and total carbon content in the atmosphere

	Vanadium	Lead	Copper	Cobalt	Molybdenum	Chromium	TC
TOYO mambrane filter TM-3	N.D. (N.D.)	N.D. (N.D.)	0.00 (0.00)	N.D. (N.D.)	N.D. (N.D.)	N.D. (N.D.)	
Ice-Sodium chloride	0.00 (0.00)	351.65 (1.70)	670.46 (10.56)	57.68 (0.98)	35.22 (0.37)	N.D. (N.D.)	48.83 (4.07)
Liquid nitrogen (1)	N.D. (N.D.)	489.55 (2.36)	1020.26 (16.07)	62.44 (1.96)	75.52 (0.79)	776.84 (14.94)	237.60 (19.78)
Liquid nitrogen (2)	0.00 (0.00)	399.88 (1.93)	583.04 (9.38)	15.99 (0.27)	33.96 (0.35)	N.D. (N.D.)	87.88 (7.32)
Liquid nitrogen (3)	0.00 (0.00)	448.18 (2.16)	670.46 (10.56)	26.03 (0.44)	7.53 (0.08)	N.D. (N.D.)	61.85 (5.15)
Liquid nitrogen (4)	0.00 (0.00)	475.74 (2.30)	573.26 (9.03)	39.05 (0.66)	24.18 (0.25)	133.93 (2,58)	94.42 (7.86)
Liquid nitrogen (5)	10.77 (0.21)	455.06 (2.20)	767.66 (12.09)	19.23 (0.33)	63.43 (0.66)	N.D. (N.D.)	97.66 (8.13)
Liquid nitrogen (6)	N.D. (N.D.)	227.49 (1.10)	223.46 (3.52)	19.23 (0.33)	N.D. (N.D.)	N.D. (N.D.)	13.02 (1.08)

Sampling date: Fry. 10 May 1985 Sampling volume: 75.672 l ng/dm^3 ($\times 10^{-9}$ mol/dm^3)

S2-05

VISUAL DETERMINATION OF PHOSPHORUS IN ENVIRONMENTAL WATERS

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We have been developing simple methods for analysis of natural and environmental waters which can be widely used without any instrument. An effective and simple method for preconcentration of fluoride [1, 2] and phosphorus [3] and a portable device for the preconcentration [4] have been developed up to now.

In this work, we propose a direct visual method for determination of 10 to 250 ppb of phosphate-phosphorus which can be done only by addition of 1 ml of a reagent solution in a test-tube.

1. SPECTROPHOTOMETRIC STUDIES AND ESTABLISHED REFERENCE METHOD

The conventional spectrophotometric method as molybdenum blue is not sensitive enough to apply for the visual determination of phosphorus in environmental waters relating to eutrophication. Recently, Motomizu et al [5] proposed a sensitive spectrophotometric method for phosphorus (molar absorptivity = 7.8 x 10^4) which is based on the formation of a blue neutral color of malachite green (MG^+) by the ion association of MG^{2+} and phosphomolybdate, $H_2[PO_4(Mo_3)_{12}]^-$ in acid medium. However, this method was found that the color was not fully developed because of the shortage of the amount of malachite green. By increasing the amount of MG three times, a constant and maximum absorbance was obtained in 0.3 to 0.6M H_2SO_4. The molar absorptivity of the improved method was 1.12 x 10^5, and the method have a remarkable advantage over the original method [5] in large permissible amounts of foreign substances, as seen in Table 1.

Table 1. Effect of foreign ions

Ion	mg						
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	$SO_4{}^{2-}$	Si(IV)
Proposed method (3x10^{-4}M MG, 4.0 μgP)	300*	40	50	20*	450*	100	0.25
Motomizu's method (1x10^{-4}M MG, 3.7 μgP)	0.5*	1	0.5*	1*	-	-	0.015*

* Tolerance limit. Others are the largest quantities tested.

The established spectrophotometric method which have a role as reference method to the field visual method, is as follows.

To a water sample less than 20 ml (10 to 250 ppb) in a volumetric flask, add 1 ml of 7.5M H_2SO_4, 3 ml of molybdate-MG solution^{*1} and 0.5 ml of 1 % PVA. Dilute exactly to 25 ml with water, and measure the absorbance at 650 nm within 2 hours.

*1 Mix 50 ml of MG solution (2.78 g/l), 60 ml of ammonium molybdate tetrahydrate solution (120 g/l) and 9.4 ml of H_2SO_4. After allowing to stand for one night, filter the solution with membrane filter (0.45um).

2. VISUAL METHOD ESTABLISHED

Add 1 ml of a reagent solution^{*2} to 4 ml of water sample (10 to 250 ppb) in a test-tube. Compare the blue color immediately with that of a standard series of phosphorus^{*3}.

*2 Mix 56 ml of MG solution (0.41 g/l), 30 ml of ammonium molybdate tetrahydrate solution (120 g/l) and 13 ml of H_2SO_4. Filter as described in *1

*3 In preparation of the standard series, 0.1 ml of 1 % PVA is added. The colored solution can be used at least 2 days.

3. ANALYTICAL RESULTS

Table 2. Comparison of the analytical results

Sample	ppb P	
	Visual method	Reference method
Ohashi river	60	62.6
Spring, Mt. Daisen	20	18
Tap water:		
Matsue city	n.d.	n.d.
Shimane Univ.	200	194
Mt. Daisen	80	76.4

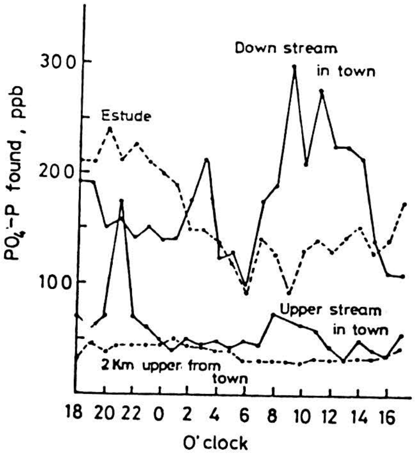

Fig.1 Change of phosphorus concentration in Tamayu river (June 5 to 6, 1986).

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S2-06

VISUAL DETERMINATION OF AMMONIA-NITROGEN AND FLUORIDE IN ENVIRONMENTAL WATERS

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A visual method for determination of NH_4^+-N in water samples has been developed, following the establishment of a highly sensitive visual method for determination of phosphate, relating to eutrophication. It is said that phenomena such as water bloom and/or red tide would appear in lake if concentrations of nitrogen and phosphorus exceed 200 ppb and 20 ppb respectively. The spectrophotometric method for NH_4^+-N using thymol [1] was not sensitive enough to determine less than 100 ppb of NH_4^+-N visually. Then, the extraction of the colored compound into an organic solvent was attempted to concentrate.

A visual method for determination of 0.1 to 0.5 ppm of fluoride has been developed by modification of the spectrophotometric method using lanthanum-alizalin complexone chelate (La•ALC) [2]. This method has been used to estimate the mixing rate of sea water containing 1.3 ppm of fluoride, in the analysis of brackish water of Lake Shinji.

1. SPECTROPHOTOMETRIC STUDIES

1) On determination of ammonia-nitrogen

The original spectrophotometric method includes formation of monochloramine at pH 10±0.3 and reaction of the monochloramine with thymol at pH 11.7±0.2. The addition of thymol must be done within 30 sec because of the instability of monochloramine. The blue color complex (λmax = 670 nm) was found to be extracted into xylene changing the color to red (λmax = 520 nm). For this reason, the increasing of the absorbance obtained was only two times, in spite of reducing the volume to one fifth. The extraction of the complex into iso-amyl alcohol gave blue color (λmax = 670 nm) in the presence of dispersed water, but was changed to red color (λmax = 520 nm) if the dispersed water was removed. The turbid blue color solution, however, can be used for the visual determination.

Recommended spectrophotometric method for nitrogen (NH_4^+-N > 50 ppb) is as follows:

To a water sample less than 25 ml in a separatory funnel, add 2 ml of buffer solution^{*1}, 0.2 ml of 0.3% sodium hypochlorite solution and 2.5 ml of thymol solution^{*2}. After allowing to stand for 1 hour, shake the solution with 10.0 ml of xylene. Measure the absorbance at 520 nm.

*1 Mix 60 ml of 1M $NaHCO_3$ and 50 ml of Na_2CO_3 and dilute to 1 l with water.

*2 Mix 50 ml of 5% thymol in acetone and 50 ml of 0.9M NaOH in ice bath.

2) On determination of fluoride

The simple method using La•ALC in which the fluoride complex is formed in aqueous solution [3], can not be be used for visual determination because of the presence of excess La•ALC (red color). For this reason, the blue La•ALC•F complex must be separated from La•ALC. The La•ALC•F complex formed in an aqueous solution is not extracted in organic solvents because of the interruption of the combined water. The extraction of the complex is performed with the addition of N,N-diethylaniline [2].

Recommended spectrophotometric method for fluoride (0.08 to 1.2 ppm F) is as follows:

To a water sample in a volumetric flask, add 5.0 ml of La•ALC solution (5.0 g of "Dotite alfusone" in 100 ml water) and 10 ml of acetone. Dilute exactly to 50 ml with water. After allowing to stand for 1 hour, measure the absorbance at 620 nm.

2. VISUAL METHOD ESTABLISHED

1) For determination of ammonia-nitrogen (NH_4^+-N > 20 ppb)

To 3.0 ml of water sample in a test-tube, add 1 ml of reagent A[*3] and 1 ml of reagent B[*4] successively. After standing for 1 hour, shake the solution with 1.0 ml of iso-amyl alcohol. Compare the blue color with that of a standard series of NH_4^+-N.

*3 To a solution containing 1.00 g of $NaHCO_3$ and 1.59 g of Na_2CO_3, add 20 ml of 0.3% NaClO solution and dilute to 1 l with water.

*4 Mix thymol solution (1.25 g in 50 ml of acetone) and 50 ml of NaOH (9 g/1).

2) For determination of fluoride (0.05 to 0.5ppm F^-; 3 to 40% sea water)

To 5.0 ml of water sample in a test-tube, add 3 ml of reagent C[*5] and 1 ml of reagent D[*6]. After standing for 15 minutes, shake the solution. Compare the blue color of the upper layer with that of a standard series of fluoride.

*5 Mix 160 ml of acetone, 10 ml of N, N-diethylaniline and 190 ml of iso-AmOH.

*6 Mix 30 ml of 5%"Dotite-alfusone", 30 ml of succinic acid solution (59 g/1) and 10 ml of NaOH solution (40 g/1).

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S2-07

SURFACE IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY: AND ITS APPLICATION TO TRACE ANALYSIS OF TERTIARY AMINES

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A new selective detector for gas Chromatography [1, 2] is discussed which uses an electrically heated Pt filament as an emitter surface. The operating mechanism of this detector is the positive surface ionization process in which the key parameters are the work function of the Pt emitter surface, the temperature of the Pt emitter surface, the ionization potential of the emitting chemical species, and composition of the gas environment in the immediate vicinity of the emitter surface. With the Pt emitter in an air environment, this detector provides extremely sensitive and specific response to organice compounds, which form their dissociative species at the low ionization potential.

The specific and sensitive detection for tertiary amines by the surface ionization detector (SID) was also presented.

1. SOME CONSIDERATIONS OF THE DETECTION MECHANISM

Surface ionization is interpreted convetionally by use of the Saha-Langmuir equation [3], which is based upon the assumption that thermal and charge equilibria are established between the species on the surface material and the surface material itself. This equation is expressed by

$$n_+/n_0 = g_+/g_0 \, \exp\left(\frac{\Phi - IP}{\kappa T}\right) \qquad (1)$$

where n_+/n_0 is the ratio of positive ions to neutral species, Φ is the work function of the surface at which ionization occurs at temperature T, κ is the Boltzmann constant, and IP is the ionization potential of the emitting chemical species, g_+/g_0 is the ratio of the statistical weights of the ions and the neutral species.

According to the rule established, in most cases the organics decompose into radicals on the hot surface, which have lower ionization potentials than the molecules and are ionized efficiently. For a given type of secondary species, S, formed on the surface, the resulting positive themionic emission currents (i) and their dependence on surface temperature (T) are described by the ionization efficiency, $\beta_s(T)$, and by $Y_s(T)$, the yield of chemical reactions on the surface, such that

$$i_s(T) = n\,Y_s(T)\,\beta_s(T) \qquad (2)$$

when a stationary beam of organic molecules, n, impinges from the gas phase on the surface. $\beta_s(T)$ is expressed as follows using the Saha-Langmuir equation, eq1, such that

$$\beta_s(T) = \frac{1}{1 + \frac{g_0}{g_+}\exp\left(\frac{IP - \Phi}{\kappa T}\right)} \qquad (3)$$

if the equilibrium thermal ionization can be assumed. The combination of eq 2 and 3 tells us that the emitter surface must have good pyrolytic properties ($Y_s(T)$ should be high) and the work function of the emitter, Φ, must be high. Also this equation indicates that the surface ionization process is specific, since it is strongly dependent on the IP of the species.

2. RESULTS

2.1 Sensitivity and Selectivity

As already mentioned, sensitivity of the detector is strongly dependent on the IP of the species as well as on the yield of the species generated through the chemical reaction on the surface. Presumably the relative sensitivity for different organics, which is easily determined by a comparison of the signal current, varies in a wide range from sample to sample. For a given organic compounds, the sensitivity of the detector can be also varied, depending on the operating conditions such as the emitter temperature. The sensitivity increases with the higher noise level and therefore the optimum has to be found for the detection limit. The sensitivity of the detector can be expressed as coulomb (C) per gram of sample. Under the optimum conditions for the detection limit, sensitivity was 1.58 C/g for tri-n-butyl amine (TBA) and 2.98×10^{-6} C/g for n-dodecane. Consequently selectivity of this detector, which is defined as the ratio of sensitivity, was 5.3×10^{5}.

2.2 Reproducibility

The reproducibility of the detector was determined from replicate analysis (20 times) of the standard sample at 260 pg of TBA when the coefficient of variance was 1.9%.

2.3 Linearity

The measurement of the linear range has been made with TBA as a test sample, showing that the straight portion of the calibration curve covers nealy 4 orders of magnitude for the TBA.

2.4 Performance comparison of the SID with thermonic ionization detector (TID)

The chromatograms in Figure 1 correspond to such a test sample comprised of n-butylamine, di-n-butylamine, tri-n-butylamine and n-dodecane in a solvent of acetone. The data illustrate clealy the substantial differences in response between SID and TID, and the very high specificity of SID for sensing the tertiary amines. This result demonstrates that the SID provides extremely high sensitivity, compared with well-established TID. The ionization signal of the tertiary amine in SID chromatogram is very large, indicating detectivity in pg and sub-pg range.

3. CONCLUSION

The principle of the detector described is consistent with a process of positive surface ionization on the hot surface. It is interesting contrast to the TID whose mechanism is negative surface ionization on low work function surface [4, 5]. This work reveals that the excellent performance for amine compounds, together with easy fabrication and operation, makes this detector promising for all areas of applications in gas chromatography.

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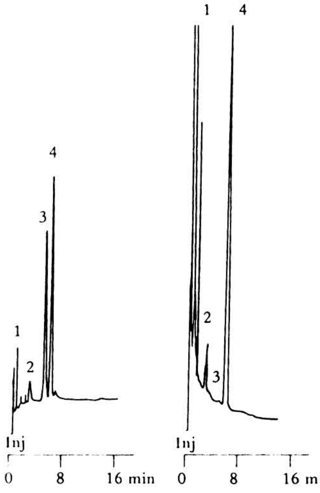

a) SID　　b) TID

1: n-butylamine	1.6ng	1: n-butylamine	25ng
2: di-n-butylamine	160pg	2: di-n-butylamine	2.5ng
3: tri-n-butylamine	16pg	3: tri-n-butylamine	250pg
4: n-dodecane	11.8μg	4: n-dodecane	185μg

Figure 1 Gas chromatogram of butylamine and n-dodecane by SID and TID

S2-08

SOLVENT EXTRACTION OF METAL IONS WITH 4-ACYL-5-PYRAZOLONE AND BIDENTATE PHOSPHINE OXIDE COMPOUND

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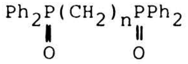
INTRODUCTION In the liquid-liquid extraction of β-diketonates, it is well known that the presence of a Lewis base such as trioctylphosphine oxide (TOPO) enhances the extraction owing to the adduct formation between the metal chelate and the Lewis base. The synergistic effects on the extraction with a monodentate neutral ligand have been widely investigated. The synergistic extraction with a bidentate ligand should be of interest, for it would be expected that peculiar adduct formation between the bidentate neutral ligand and the metal β-diketonate might result in more enhanced extraction and/or improved separation. Among the various kinds of neutral ligands, substituted phosphine oxide is one of the most powerful and versatile reagents. An attempt has been made to synthesize the bidentate phosphine oxide derivative and to apply this reagent to the synergistic extraction of alkaline earth, rare earth and some divalent transition metals. The results have been compared with those in the TOPO system.

EXPERIMENTAL

Bis(diphenylphosphino)alkane was synthesized according to the literature.[1] Bis(diphenylphosphinyl)alkane (Fig.) was synthesized by the oxidation of bis(diphenylphosphino)alkane with hydrogen peroxide. 4-Acyl-5-pyrazolones employed in the present work are 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (HPMTFP).



$$\underset{\underset{O}{\|}}{Ph_2P}(CH_2)_n\underset{\underset{O}{\|}}{PPh_2}$$

n=1 BDPPM
n=2 BDPPE

Fig. Bis(diphenylphosphinyl)alkanes

In the synergistic extraction of metal ions (M^{n+}) with a chelating reagent (HA) and a neutral ligand (L), the extraction constants, K_{ex} and $K_{ex,s}$, and the stability constant for the adduct formation reaction, β_s, are defined as follows: $K_{ex}= [MA_n]_o[H^+]^n[M^{n+}]^{-1}[HA]_o^{-n}$,

$K_{ex,s} = [MA_nL_s]_o[H^+]^n[M^{n+}]^{-1}[HA]_o^{-n}[L]_o^{-s}$, $\beta_s= [MA_nL_s]_o[MA_n]_o^{-1}[L]_o^{-s}$.

EXTRACTION OF ALKALINE EARTH METALS

The results for the extraction of alkaline earths are summarized in the table. In the BDPPM system, while the extraction of strontium and barium are much enhanced as compared with the TOPO system, the enhancement for magnesium and calcium is not so large. Although BDPPE is also a bidentate neutral ligand, its synergistic effects in the extraction of alkaline earths are very similar to those of TOPO. The number of the bidentate phosphine oxide compound which attaches to the metal chelate is found to be one for magnesium and two for calcium, strontium and barium. The reverse in the extraction order for magnesium and calcium in the BDPPM/HPMTFP system could be attributed to this difference in the number of BDPPM molecule in the extracted species.

EXTRACTION OF RARE EARTH METALS

The synergistic extraction of rare earth metals such as La, Pr, Eu, Ho and Yb into chloroform has been made with HPMTFP and BDPPM. The extracted species are MA_3L in the absence of sodium perchlorate and $MA_2L_2^+(ClO_4^-)$ in the presence of sodium perchlorate. The extraction constants of these systems do not increase monotonically with atomic number but have a maximum at Eu or Ho.

EXTRACTION OF SOME DIVALENT METALS

The phophine oxide compounds, BDPPM, BDPPE, and TOPO, have been also applied to the synergistic extraction of some divalent metals such as Co, Ni, Zn and Cd into benzene with HPMBP. The extracted species are $MA_2(TOPO)_2$ (M=Co, Ni and Cd), $MA_2(TOPO)$ (M=Zn) and MA_2L (L=BDPPM, BDPPE). The β_1 values for BDPPM are much larger than that for BDPPE and similar to β_2 for TOPO.

Table Extraction parameters for MA_2L_s

			Mg	Ca	Sr	Ba
BDPPM system						
	HPMBP	$pH_{1/2}$	3.84	4.26	4.93	5.36
		log $K_{ex,s}$	-3.08	-1.92	-3.26	-4.11
		s	1	2	2	2
	HPMTFP	$pH_{1/2}$	2.34	2.12	2.60	2.84
		log $K_{ex,s}$	-0.08	2.36	1.40	0.92
		s	1	2	2	2
BDPPE system						
	HPMBP	$pH_{1/2}$	4.34	4.86	5.96	6.72
		log $K_{ex,s}$	-3.78	-2.52	-4.72	-6.24
		s	1	2	2	2
	HPMTFP	$pH_{1/2}$	2.86	3.10	3.82	4.52
		log $K_{ex,s}$	-0.82	1.00	-0.44	-1.84
		s	1	2	2	2
TOPO system						
	HPMBP	$pH_{1/2}$	4.02	4.44	5.81	6.58
		log $K_{ex,s}$	-1.44	-2.27	-5.02	-4.56
		s	2	2	2	3
	HPMTFP	$pH_{1/2}$	2.37	2.56	3.62	4.32
		log $K_{ex,s}$	1.86	1.48	1.36	-0.04
		s	2	2	3	3

$pH_{1/2}$: $[HPMBP]_o=[HPMTFP]_o=5\times10^{-2}$ M, $[BDPPM]_o=[TOPO]_o=1\times10^{-2}$ M, $[BDPPE]_o=5\times10^{-3}$ M in benzene.
$NaClO_4$: none (L=BDPPM or BDPPE), 0.1 M (L=TOPO).

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S2-09

FLOW INJECTION ANALYSIS FOR THE ENVIRONMENTAL MEASUREMENT AND MONITORING

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The movement of an aqueous sample zone injected in a flowing reagent stream through a cylindrical tubing under laminar flow conditions makes a method of flow injection analysis (FIA), which is widely spread as a newly developed procedure in analytical automation. Figure 1 shows several flow analysis processes using two pumps. Among those processes, the FIA is optimum for both the environmental measurement and monitoring system. The present paper describes the high-pressure and high-temperature FIA system with HPLC micro-pumps for the environmental water analyses and their applications to continuous monitoring systems.

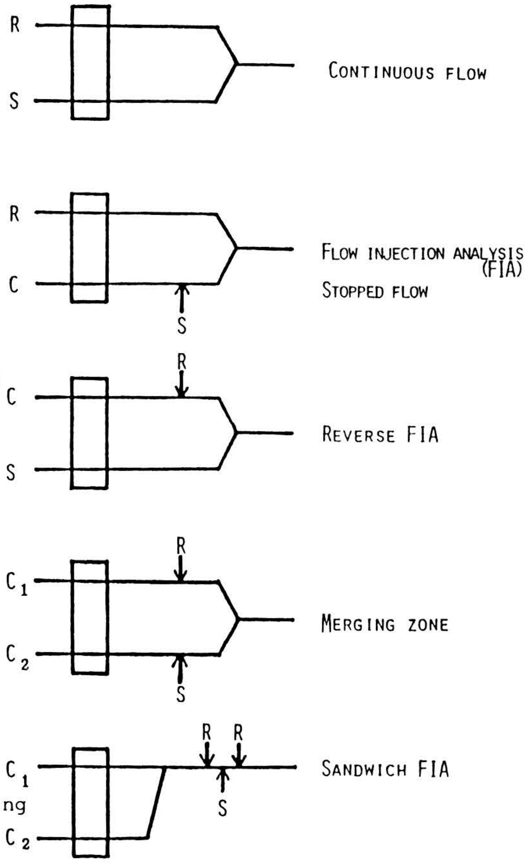

Fig. 1 Several flow analysis processes using two pumps

1. CHEMICAL OXYGEN DEMAND

To reduce the water pollution due to organic substances, total loads of chemical oxygen demand (COD) are regulated from 1981 in the Japanese water areas of closed character. Hence, the bacth COD analyzers have been developed and available in Japan. The authors have recently proposed the FIA system for the automatic measurement and continuous monitoring of COD with permanganate, dichromate, and cerium(IV) as oxidant. The system is constructed of commercially available parts for HPLC and PTFE tubings, such as a double-reciprocating micro-pump, an automatic sample injector, a thermostated bath, and a spectrophotometer with a flow cell.

With dichromate as oxidant, samples are injected into a water carrier stream which merges with an acidic dichromate oxidizing-reagent solution. After reaction in a PTFE reaction coil at 120 °C under at least 5 atm (by adding a bach-pressure coil just after a flow cell), absorbances are continuously measured at 445 nm. D-Glucose is satisfactory as a standard substance for COD. A sampling rate of 15 samples per hour can be achieved, and the detection limit and precision are 5 mg/l as COD and 0.4 %, respectively. The FIA system should be operated according to the following oxidation-reduction potentials.

Mn(VII)/Mn(II) system

$$MnO_4^{-} + 8\ H^{+} + 5\ e^{-} \rightleftharpoons Mn^{2+} + 4\ H_2O \qquad E^{o} = 1.51\ V \qquad (1)$$

$$E = 1.51 - 0.093\ pH + 0.012\ \log\ ([MnO_4^{-}]/[Mn^{2+}]) \qquad (2)$$

Cr(VI)/Cr(III) system

$$Cr_2O_7^{2-} + 14\ H^{+} + 6\ e^{-} \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O \quad E^{o} = 1.33\ V \qquad (3)$$

$$E = 1.33 - 0.135\ pH + 0.0097\ \log\ ([Cr_2O_7^{2-}]/[Cr^{3+}]^2) \qquad (4)$$

Ce(IV)/Ce(III) system

$$Ce^{4+} + e^{-} \rightleftharpoons Ce^{3+} \qquad E^{o} = 1.61\ V \qquad (5)$$

$$E = 1.61 + 0.058\ \log\ ([Ce^{4+}]/[Ce^{3+}]) \qquad (6)$$

2. TOTAL PHOSPHORUS AND TOTAL NITROGEN

Total phosphorus and total nitrogen are also important in water quality analysis. As shown in Fig. 2, samples are injected into an oxidant stream of potassium peroxodisulfate solution, and digested in the coil-1 by heating to 120 °C under about 8 atm. The sample is then merged with the reagent stream of acidic molybdate solution and heated at 75 °C to produce molybdophosphate blue. The absorbance of the blue complex is measured at 880 nm. The method can be applied to continuous monitoring of total phosphorus in environmental water samples. Total nitrogen is also measured with the FIA system having four stream lines automatically.

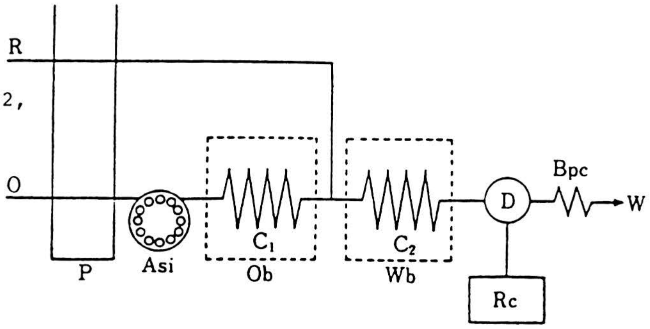

Fig. 2 Schematic diagram of the FIA apparatus for total phosphorus determination

3. MULTI-ELEMENTS ANALYSIS

For COD and total phosphorus, oxidation of roganic substances is carried out with acidic cerium(IV) sulfate in the first coil, and after COD measurement molybdate reagent is added into the stream of Fig. 2. The FIA systems are therefore joined to multi-elements analysis with satisfactory results.

S2-10

Simultaneous Extraction - Atomic Absorption Spectrometric Determination of Mg^{2+} and Zn^{2+}、Cd^{2+} in Lithium Salts or Lithium Metal

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It is well known that β- Diketone is very widely used for the solvent extraction of many metals.

Altogether Zn、Mg、Cd can be extracted quantitatively by O.I M dibenzolymethane solution (DBM) in benzene in the PH range of II. Extractability of Zn、Mg and Cd was Ioo、98.4 and 96.8% respectively. While lithium is not extracted at all. Thus very low concentration of trace elements is separated from the matrix before measured by a.a.s. With DBM solution the extraction and back-extraction equilibrium is usually reached within two minutes.

I p.p.m. of Zn、Mg、Cd ions can be determined in the presence of 0.5g of lithium metal and after dissolution is lithium chloride.

The relative standard deviation (n=2o) is I.5% by the recommended method. The mean recovery of Zn、Mg、Cd was 95-Io5%. This method was also applied to the determination of trace quantities of Zn、Mg、Cd in NaCL、KCL、LiCL、RbCL CsCL. Cl、No_3、SO_4 ions do not interfere and this method gives good resuLt.

Furthermore, In this course, Further purify analytical reagent LiCL.

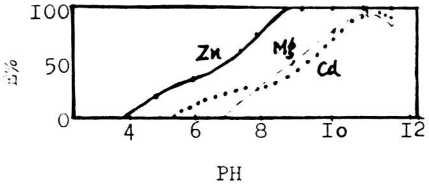

Fig. I. Extraction of Zn、Mg、Cd by O.I M DBM/benzene vs the PH value of the aqueous phase

Table I. Standard addition and recovery in the lithium salt sample

sample	weight g	result Zn%	found Zn μg	recovery Zn %	result Mg%	found Mg μg	recovery Mg%	result Cd%	found Cd μg	recovery %
LiCl	1.0	o.0009	19.o	95	o.0012	Io.5	1o5	o.oooI	2o.5	Io2.5
LiCl	I.o	o.ooII	I9.7	98.5	o.0009	1o.5	Io5	o.0001	2o.5	Io2.5
LiCl	1.o	o.ooo4	19.2	96	o.ooo5	9.8	98	o.ooo7	2o.5	Io2.5
Li metal	o.125	o.oo79	2o.8	Io4	o.0244	9.9	99	o.oooI	2o.3	Io1.5
$LiNO_3$	o.4	o.ooo2	I9.4	97	o.ooo5	Io.5	I05	o.oooI	2o.5	Io2.3
Li_2SO_4	I.o	o.ooo2	2o.I	Ioo.5	o.oooI	Io.5	Io5	o.oooI	2o.7	Io3.5
LiOH	I.o	o.ooo9	I9.0	95	o.ooo6	Io.5	Io5	0.oooI	2o.4	Io3
NaCl	4.o	o.oooI	I9.7	98.5	o.ooo2	Io.4	Io4	o.oooI	2o.4	Io2
KCL	4.o	o.oooI	I9.4	97	o.oooI	9.8	98	o.oooI	2o.5	Io2.5
CsCL	o.5	o.ooI3	2o.I	Ioo.2	o.ooI8	Io.5	Io5	o.oooI	2o.6	Io3
RbCL	o.5	o.ooI6	2o.3	IoI.5	o.ooo5	9.8	98	o.oooI	I9.9	99.5

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S2-11

CONTINUOUS DETERMINATION OF AMMONIA IN WATER BY A NEW MEMBRANE PRECONCENTRATION AND CONDUCTIVITY ELECTRODE SYSTEM

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INTRODUCTION

Ammonia in the environment has strongly relation with its biological system. It is one of the major eutrophic substances in the hydrosphere. Major quantities of ammonia are generated principally by bacterial breakdown of amino-acid in organic materials. Therefore, the concentration of ammonia in water changes frequently by the effect of the biological activities.

In the connection with such a property of ammonia mentioned above, it is required to measure the concentration of ammonia continuously. This paper presents a new techniques for continuous monitoring of ammonia in water by using a new membrane preconcentration and conductivity electrode system.

EXPERIMENTAL

The continuous ammonia determination system is shown in the flow chart in Figure 1. The sample solution is pumped by the peristaltic pump (P2) at 8 mL/min. and is continuously added the sodium hydroxide reagent by peristaltic pump (P3) at the sample and reagent volume ratio of 8:1. Well mixed alkaline sample is send to outer side of double tube system for separation and preconcentration of ammonia (Membrane Condense Separator). The inner tube of the membrane condense separator consists of micro-porus PTFE tubing (2mm i.d., 2.8mm o.d., 200mm length, maximum pore size 2μm). This inner tube is connected to three valves (V3, V4, V5) for changing the flow line and the peristaltic pump (P5) for sending the diluted sulpheric acid reagent (carrier solution). As figure 2 shows, molecular ammonia is liberated by mixing the sample with alkaline solution in the outer flow line of the double tube system, and it permuate through the inner micro-porus membrane into acidic carrier solution. In this process, as figure 3 shows, when the carrier solution in the micro-porus membrane is retained by changing the flow line, permuated molecular ammonia is condensed at the retained carrier solution in the micro-porus membrane tube (condensation mode in figure 2). Therefore, the conductivity decreases in proportion to its condensed time.

After enough preconcentration in carrier solution, the carrier solution in the membrane condense separator is introduced to the conductivity cell by changing the flow line (injection mode in figure 2). Then the conductivity cell **measures** the sample which is neutralized by ammonia.

The peak height is in proportion to the ammonia concentration. Figure 4 shows the example of the signal for various concentrations of ammonia of the signal for various concentrations of ammonia at the condense time of 300 sec. This method has high sensitivity compared with other methods such as the colorimetry or the ion selective electrode.

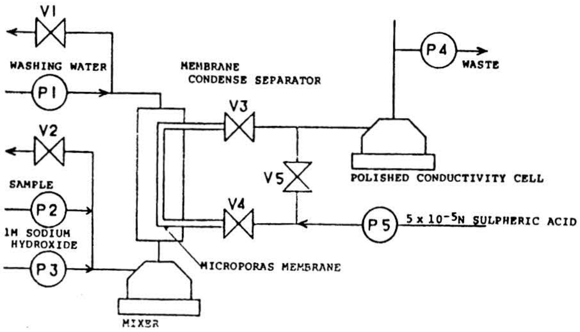

Fig. 1 Flow chart of the continuous ammonia analyser

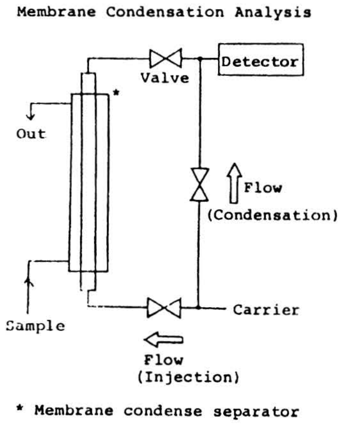

Fig. 2 Principle of the preconcentration system

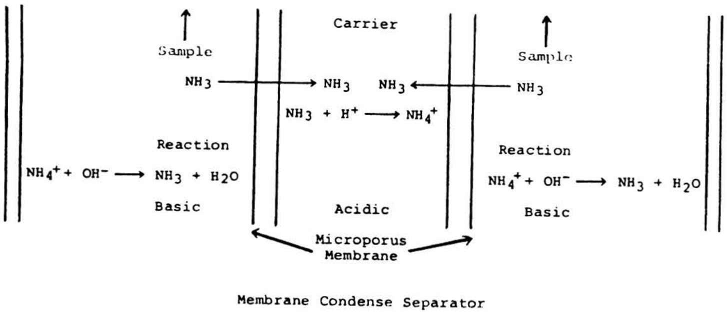

Fig. 3 The mechanism of the preconcentration of ammonia in the membrane condense separator

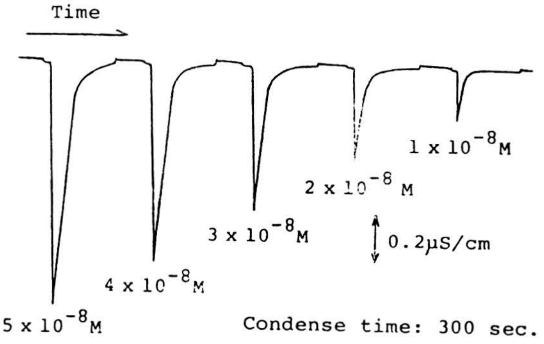

Fig. 4 Recording chart of the measurement for ammonia

S2-12

AC-1 MODEL SLIDE RULE FOR ANALYTICAL CHEMISTRY AND ENVISAGEMENT OF DESIGNING

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AC-1 model plate slide rule for analytical chemistry 25 cm in length is a new advanced special-purpose calculation stool to resolve general calculation problem in analytical chemistry and it won the third prize for great science-technologe achievement of Liao Ning Province.

Practice indicated that, it has good quality in high precision, many functions, and easily operating and has wide use value.

This slide rule has ten times as precision as general slide rules, has four significant figures.

It has been designed according to the principle of logarithm and achieved the goal of improving procision, conveniently setting up other special graduation of rule, and simplifying calculation operation by extending the C.D. rules to 1250 cm, then folding into five sections in order, and consisting of C-set and D-set.

This rule can be used not only in operation of multiplication, division, reciprocal, logarithm, involution and evolution etc, as general slide rule, but also in operation as following:

1) Calculation atom, molecular weight and rerlative problem.
2) Calculation the correct worth of gas volume.
3) Calculation the vapor pressure of water in aqueous solution.
4) Exchanging the indicatrix of concentration of six general acids and bases such as NaOH, HCl etc. (D_4^{20}, N, A%) and calculation (M, Cs)
5) Calculation the pH worth of solution.
6) General chemical constants.
7) General equivalent of acids and bases etc,

As this rule has some advantages such as the diversification of results calculated, rational distribution of the rule grade and compact structure, the calculation operations are simplified.

Some calculation examples showed that its speed of operation is as fast as pocket-size computer. Thus, by moving the vernier one time, the results, D_4^{20} =1.222, A=30.3 %, of 7.550 N H_2SO_4 solution can be given.

S3-01

EFFECTS OF HEAVY METALS POLLUTION ON ELEMENTAL CONCENTRATION IN HUMAN HAIR

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During the past two decades in Japan, some environments have been contaminated with the toxins so far as to cause the harmful somatic effects such as mercury poisoning(Minamata Disease), arsenic poisoning(Toroku Kogai) and cadmium poisoning(Itai-itai Disease). There still remains more than 2,000 officially designated tragic victims, and it is important to evaluate precisely the present situatuins of those living in these areas, as well as to study the effects of these elements to other elements on the metabolism in human body. We paid attention to the hair analysis because the hair is a reliable index of the living body and the hair sample is easy to collect and preserve.

MATERIALS AND METHOD

Hair samples were collected from those who live in Minamata(19 males and 25 females), Toroku(19&37) and Toyama(24&71:Itai-itai Disease) areas where it has been designated as the polluted areas. 342 samples were also collected from every corner of Japan. The latter sample constitute the normal sample.

Neutron activation technique was applied to detect the elemental concentration of the hair. Research Reactor of 5MW thermal power was used. Log-normal distribution model was applied to estimate the statistics for each three subgroups: males, females with permanent cold waving(pcw) and females without pcw. Those who are older than or equal to 20 years old were observed. Correlation coefficients were estimated for the sample groups in which the main 12 elements(Cl,Br,K,Al,Na,Hg,Mn,S,Cu,Zn,Mg,Ca) were all detected. Factor contribution and factor loading of the elements were also estimated for each factor by making use of the principal component analysis.

RESULTS AND DISCUSSION

We first conducted the principal component analysis for the normal Japanese whose details are shown elsewhere.(1) Its main conclusions are:
(a) The loadings of the 1st factor for Ca, Mg, Zn and Cu are large, and those of Cl and Br are large but in the opposite sign. This fact is consistent with the result of animal experiment that the concentrations of alkaline earth such as Ca or Mg are higher but those of halogens of Cl or Br are lower in hair of rats fed low Ca concentration diets than in hair of ordinary fed rats.
(b)The loadings of the 2nd factor for K or Na are large. This fact is also

consistent with the experimental results by HOUTMAN et al.⁽²⁾ that K is introduced from the blood in somewhat later stage of hair formation.

We then added the results from the polluted areas to the normal group. Factor loadings for 13 elements(main 12 elements plus Cd) in mormal and in (Normal+Toyama) group are shown in Fig.1 for the 1st and 2nd factors. Factor loading of Cd in normal group is large for the 2nd factor but small for the 1st factor,while in (Normal+Toyama) group the 1st factor changes to be large. It is concluded that while Cd is related to the 2nd factor in normal group, it tends to relate to the 1st factor significantly by the excess intake of Cd. It is also shown from Fig.1 that, in (Normal+Toyama) group, such elements as Br. Mn and Zn which have positive correlation to Cd, move in the same direction as Cd moves, whereas Cu, which does not aorrelate significantly to Cd, moves to the opposite direction of Cd. Br, which has large negative loading factor for the 1st factor in normal group, becomes to have large positive one in (Normal+Toyama) group.

Factor scores of each sample for the main 12 elements in (Normal+Minamata+Toroku+Toyama) group are shown in Fig.2 in which the females with pcw are excluded. Many samples in Toyama group have abnormal scores for the 1st score. Samples in Toroku show a tendency to have abnormal scores for the 2nd factor. Few samples in Minamata have abnormal scores for both 1st and 2nd factors. It is concluded from the above that the abnormal scores for the 1st in Toyama group are brought on by the effects of the Cd contamination. The abnormal scores for the 2nd factor in toroku group seem to be brought on by their food habits rather than by the As contamination, because As has a large loading for the 1st factor but a small loading for the 2nd factor.

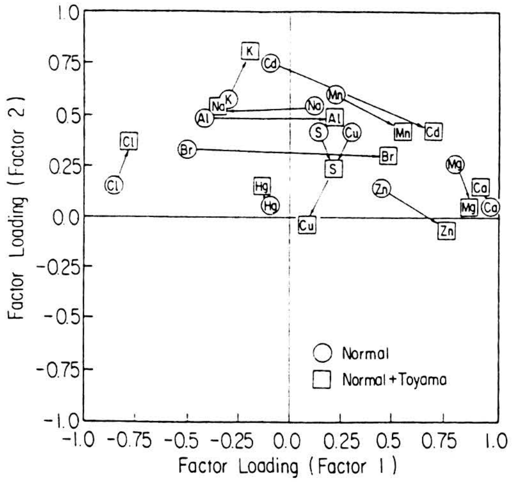

Fig.1 FACTOR LOADINGS FOR 13 ELEMENTS

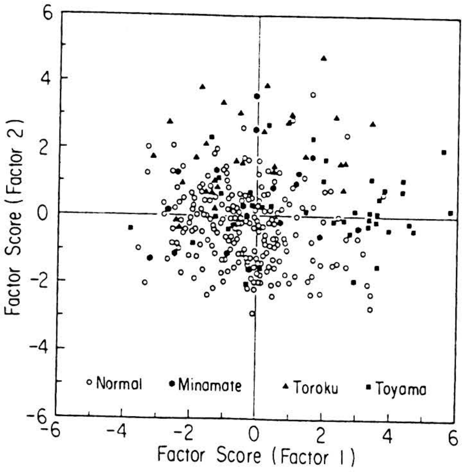

Fig.2 FACTOR SCORES FOR 12 ELEMENTS

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S3-02

CHEMILUMINESCENT METHODS FOR DETERMINATION OF HYPOBROMITE, BROMIDE, IODIDE, CYANIDE AND THIOCYANATE IONS IN ENVIRONMENTAL OBJECTS

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Highly sensitive methods are necessary for environmental analysis. One of the most sensitive is chemiluminescent (CL) method. We have used CL reactions of luminol oxydation to determine a number of anions.

CL oxidation of luminol (L) by hypobromite (bromine) in alkaline aqueous solutions and in the medium of organic solvents has been examined. Methods have been developed for determining hypobromite (bromine) with $1 \cdot 10^{-3}$ mg/dm^3 and 0.02 mg/dm^3 detection limits in aqueous solutions and in benzene-ethanol mixture respectively. The latter may be applied for determination of bromine in air. Solvent extraction-chemiluminescent method has been suggested to determine bromides in waters, based on their preliminary oxidation to bromine and determination of the latter in extract; detection limit for Br^- is 0.17 mg/dm^3.

The action of cyanide and thiocyanate ions in CL reactions $L\text{-}OBr^-$; $L\text{-}OCl^-$; $L\text{-}OI^-$ has been examined. Methods have been worked out for determining CN^- and SCN^- ions from inhibition action in the reaction $L\text{-}OBr^-$ with detection limits $5 \cdot 10^{-4}$ and $3 \cdot 10^{-4}$ mg/dm^3 respectively. The methods were applied for the analysis of electroplating plant sewage and air of production area. Properties of cyanogen halides (ClCN, BrCN and ICN) in CL reactions were investigated. It has been discovered that ClCN and BrCN do not oxidize luminol with light emission while ICN readily undergoes CL reaction with luminol. This is the basis for determination of microquantities of iodide: I^- is oxidized to I_2 by bromine, excess of bromine is linked by cyanide into non-active BrCN and formed here ICN is determined by means of the reaction with luminol.

Detection limit for I^- is $3 \cdot 10^{-3}$ mg/dm^3. Iodide has been determined in river and some ground waters by means of developed chemiluminescent method and for comparison with the help of catalytic cerium-arsenite one. Satisfactory agreement of results has been obtained. Indirect CL methods have been suggested for nitrites and chromates based on luminol oxidation with iodine. Developed methods are highly sensitive, quick, simple in performance and easily can be automatized.

S3-03

A NEW ANALYTICAL METHOD FOR THE CHEMICAL SPECIATION OF SELENIUM AND TELLURIUM IN SEA WATER

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Results of our recent studies on the chemical speciation of selenium in sea water clearly indicate that selenium is present in four different chemical forms, i.e., dissolved inorganic forms(IV and VI), dissolved organic form and particulate form. The coexistence of different chemical species in the ocean is a consequence of a dynamical equilibrium between organic production and oxidative decomposition[1,2]. The tellurium in the ocean is expected to behave similar with selenium. But, little is known on the distribution of tellurium, because of its low concentration and lack of appropriate procedures for sea water analysis. A new analytical method was developed for the separation of each chemical form(Inorg.IV, Inorg.VI and Org.) of selenium and tellurium in sea water by using XAD-2 resin and activated carbon, respectively.

1. ANALYTICAL METHOD

Immediately after collection of sea water sample, it was filtered through the membrane filter(HA, 0.45um) with minimum exposure to laboratory air and subjected to the analysis. Speciation procedures are as follows.

Total: Dissolved total Se and Te(Org. + Inorg.) were collected on activated carbon(5g) in the presence of reducing agent(hydrazine sulfate: 4g) in acid hot solution(HCl:4N). The elution of Se and Te adsorbed from activated carbon was done with hot nitric acid(4N).

Organic: Dissolved organic form was collected on the XAD-2 resin(30g) with a flow rate of 5 ml min^{-1} at the pH of natural sea water. The effluent was subjected to the analysis of inorganic forms. Organic form was eluted with MeOH(200 ml).

IV: Tetra-valent inorganic ion was separated on XAD-2 resin as DDTC complex in the presence of EDTA(10%:20ml) at pH4 to 5 and was eluted with a mixed solution of HNO_3 and $HClO_4$(10:1)(200 ml).

VI: Hexa-valent inorganic ion from the sample, which was passed through the XAD-2 resin column for tetra-valent ion, was separated by the same procedure as those of total.

Selenium in each fraction was determined by fluorometric method, after extraction DAN complex of selenium in cyclohexane. Tellurium was determined by graphite-furnace atomic absorption spectrometry coupled with H_2Te generation.

2. SOME EXAMINATIONS ON THE ANALYTICAL PROCEDURES

Total: 1. Activated carbon was heated at about 400°C with a electric furnace before use. At this condition, it is found that the blank values are the lowest less than 2ng for Se and 20pg for Te, and the recoveries are the highest as 95% for Se and 94% for Te.

2. The standard deviation of the results is within ±3%. Recoveries of inorganic species(5 to 100ng of Se and 40 to 200pg of Te) are 94 to 95% on an average through the whole procedures. Recoveries for organic form was examined by using organic species spiked sea water; natural organic concentrate on XAD-2 resin, albumine and selenomethionine. The average recovery was 97% except selenomethionine(less than 20%).

Org. : 3. Organic Se compounds with small molecular size(dimethylselenide and selenomethionine) were not adsorbed on XAD-2 resin. The detailed explanations of analytical procedures were described in another paper[3].

Inorg.:4. The adsorption of tetra-valent ion-DDTC complex on XAD-2 resin was done at pH 4 to 5. Under this condition, the formation of hexavalent ion-DDTC complex was not observed.

5. The concentration of both tetra- and hexa-valent ion was not changed within 15 hours at pH 4.5.

6. The standard deviation of the results is within ± 3%, an average recovery of tetra-valent ions(Se: 10 to 50ng, Te: 50 to 100pg) was 96%.

3. RESULTS OF SELENIUM AND TELLURIUM DETERMINED IN THE WESTERN NORTH PACIFIC

An example of vertical distributions of selenium and tellurium in the western North Pacific is shown in Fig.1. The total concentration dissolved of both selenium and tellurium showed fairly uniform values from the surface to the deep layer with about 140 ng l^{-1} for Se and 800 pg l^{-1} for Te. The concentrations of organic form of both elements are high in the surface and low in intermediate and deep waters. Tellurium dissolved in sea water is also present in three different chemical forms(IV,VI and Org.) like selenium.

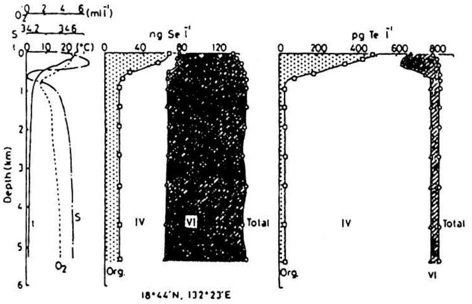

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Fig.1: The vertical distribution of Se and Te in the western North Pacific waters

S3-04

CHARACTERIZATION OF ENVIRONMENTAL SAMPLES BY X-RAY PHOTOELECTRON SPECTROSCOPY

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In the environment, solid components, especially particulate matters participate the chemical processes such as adsorption/desorption, dissolution and chemical transformation, mostly via their surfaces. With its capability of analyzing surface chemical composition of solids and of characterizing the chemical bonding state of elements, X-ray photoelectron spectroscopy (XPS) seems to be an attractive tool for analyzing environmental solid samples. However, its application to environmental samples has been mostly confined to the study of the surface chemical composition of aerosol and fly ash particles. We will describe some examples showing how XPS can characterize the surface elemental composition and bonding state of elements in the environmental and related samples.

1. POLLUTED SEDIMENT

Pollutants introduced into soil or sediment may be accumulated on the surface of soil or sediment particles. River sediment polluted by Cr (NBS SRM 1645) was analyzed by XPS. The surface concentration of Cr determined by XPS was about four times as large as its bulk value given by total analysis in the weight basis and its ratio to Si in the surface layers was 50 times as large as the bulk ratio (Fig. 1). It can be deduced that the Cr rich surface layers cover the Si rich particle core. The binding energy of Cr 2p photoelectron shows that Cr exists as Cr(III) and not as Cr(VI), probably as hydrous oxide or adsorbed on minerals. It could be also shown that Si-containing mineral in the surface layers was different from that in the bulk. A systematic study on the relation between the structure of silicate minerals and photoelectron binding energy of Si was necessary to reach such a conclusion.

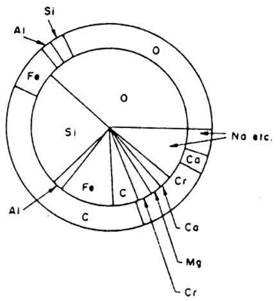

Fig. 1. Elemental composition of the River Sediment (NBS SRM 1645). The inner and outer circles represent the bulk and surface (determined by XPS) compositions, respectively.

2. ROCK POWDERS

The above result has prompted us to study how the surface composition of the weathered particles from rocks or, more simply, of powdered rocks can be different from the bulk composition. We have studied powdered rock reference materials issued from Japan Geological Survey by XPS. Most of samples showed characteristic surface compositions different from the bulk ones, while a glassy rock (obsidian) showed minimum difference of the XPS and total analysis as expected. Two samples of basaltic lavas from Japanese volcanos (Mt. Mihara and Mt. Fuji) have extraordinarily high surface concentration of Cu, more than 50 times as high as the bulk concentration (ca. 200ppm). Apparently, Cu is excluded from the silicate matrices to the boundaries of grains constituting the rock masses.

3. INCINERATION ASH

Ash produced by incineration or conbustion at high temperature may have very inhomogeneous distribution of elements. Volatile metals have been reported to be concentrated on the surface of coal fly ash particles. This is consistent with their higher average concentrations in the fraction of smaller particles. We examined fly ash and bottom ash from a waste incinerator by XPS. High surface concentrations of certain metal elements were found. Leaching of toxic elements from those particles is important in connection with the disposal of the ash. The relation between changes in the surface composition by leaching and the amounts of elements leached will be discussed.

4. CHARACTERIZATION OF HEAVY METALS ACCUMULATED IN MOSS

Certain mosses were found to accumulate heavy metals significantly from water. Liverwort Jungermannia vulcanicola collected from the upstream of Kashiranashigawa, Japan contained Hg as high as 1% in dry weight. XPS revealed that Hg was bound to S which could be distinguished from other S-species (sulfate and organic sulfide, see Fig. 2). For the liverwort collected from the downstream which contained negligible amount of Hg, sulfate-S prevailed over sulfide-S. An attempt has also been made to characterize Pb in the mosses of different origins.

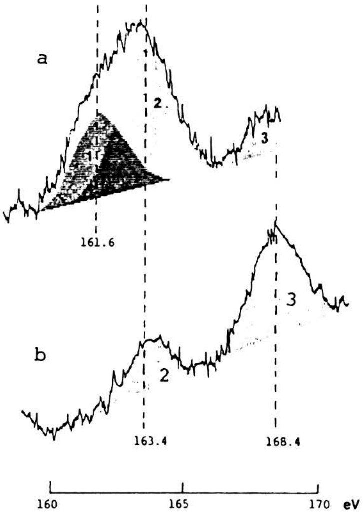

Fig. 2. S 2p spectra of the liverwort J. vulcanicola containing Hg (a) and negligible Hg (b). The peaks (1), (2) and (3) correspond to S bound to Hg, organic sulfide and sulfate respectively.

S3-05

SIMULTANEOUS DETERMINATION OF TUNGSTEN AND MOLYBDENUM IN SEAWATER

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INTRODUCTION

The concentrations of tungsten in coastal waters have been reported to be 220 - 650 pmol l^{-1}(ref. 1-4). However, the concentrations of tungsten and its distribution in the open ocean have not been reported on. This is due to lack of an adequate procedure for determining tungsten in seawater; that is, in addition to the fact that the concentration of tungsten in seawater is extremely low, by colorimetry molybdenum interferes with the determination of tungsten and by electrothermal atomic absorption spectrometry the nonvolatility of tungsten makes its determination impossible. Here, we report a new method to determine tungsten in seawater and the analytical results of tungsten in the north-west Pacific Ocean.

METHOD

In this study, an improved catalytic current polarography is used for the simultaneous determination of tungsten and molybdenum after a column concentration. The polarogram is measured in a potassium chlorate solution containing benzilic acid (2,2-diphenil-2-hydroxy acetic acid) and 2-methyl-8-quinolinol. Fig.1 shows polarograms of 1 ppm (10.4 umol l^{-1}) of molybdenum and 10 ppb (54.4 nmol l^{-1}) of tungsten. In the DC polarograph mode, the peaks of molybdenum and tungsten appear at -0.25 V and -0.85 V, respectively (vs. Ag/AgCl). This catalytic current polarography is highly sensitive, and the detection limits (S/N=2) for tungsten and molybdenum are 250 pmol l^{-1} and 10 nmol l^{-1}, respectively. The exact mechanism of this electrode reaction has up to now unknown. However, the catalytic current is probably produced by repeating the electrochemical reduction of metals from hexavalent to pentavalent and the chemical oxidation of them from pentavalent to hexavalent with chlorate alternately on the dropping mercury electrode[5].

Tungsten and molybdenum were concentrated using the Kelex-100 column in which XAD-4 resin loaded with Kelex-100 (7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-quinolinol) was packed. A 500 ml seawater sample adjusted to pH 5 with acetic acid-sodium acetate solution was pumped through the Kelex-100 column. Then both elements were eluted with 2M NH_4OH. The eluate was evaporated to dryness, and organic matter which might get mixed into the eluate were decomposed with HNO_3 and H_2O_2. The residue was dissolved with 10 ml of the supporting electrolyte solution and the polarogram was then recorded.

Recoveries from artificial seawater containing 10 ppb (104 nmol l^{-1}) of molybdenum and 10 ppt (54.4 pmol l^{-1}) of tungsten were 97% for molybdenum and 101% for tungsten. Relative standard deviations for seven replicate measurements were about 2% for both elements. Typical blanks were less than the detection limits for both elements.

ANALYTICAL RESULTS

This method was applied to the seawater samples collected in August 1985 in the north-west Pacific Ocean. Although the dissolved concentrations of tungsten show larger variations than those of molybdenum, the dissolved concentrations of tungsten are also almost uniform from the surface to the bottom as well as those of molybdenum. The average concentrations of tungsten through the water column are 53 - 60 pmol l^{-1}(normalized to a salinity of 35%), and the W:Mo ratios are about 1:1800.

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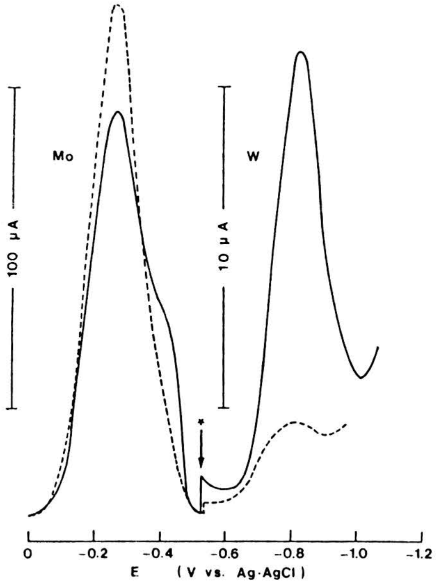

Fig.1 Polarograms of 1 ppm Mo and 10 ppb W in 0.5 M $KClO_3$ - 0.03 M H_2SO_4 - 3 x 10^{-4} M benzilic acid.
Broken line; without 2-methyl-8-quinolinol.
Solid line; with 2 x 10^{-4} M 2-methyl-8-quinolinol.
*; The current range is changed over.

S3-06

DETERMINATION OF MICRO AMOUNTS OF MERCURY IN SOIL AND BOTTOM SUBSTANCE BY HEAT DECOMPOSITION METHOD

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Flameless atomic absorption spectrometry is effective method for the determination of micro amounts of mercury. Atomization and determination of mercury in aqueous solution and in atmosphere is carried out easily. When solid samples are analyzed , mercury has been taken out from samples by wet decomposition method. But these procedurs are tedious and are needed to be skillful. As mercury gas is produced from solid sample by heat decomposition method and is collected on silver tips as amalgam , determination of micro amounts of mercury can be carried out easily.

EXPERIMENTAL SYSTEM

Schematic figure of mercury determination system is shown in figure 1. A ceramic boat on which solid sample was put was inserted into decomposition hearth. Mercury which had been erupted and atomized by heating was collected on silver tips as amalgam. The collected mercury was heated again and was driven to absorption cell and absorbance was measured there.

EXPERIMENTAL RESURT AND DISCUSSION

Composition of soil is very different on each sample ; they are mixture of inorganic compound containing silicate mainly and several organic compound. When the mercury standard sample was prepared using silica powder as diluent , the measured results were affected largely by temperature and fluctuation of value occurred due to absorption of mercury to silica powder. Now calcium fluoride as fusing inorganic agent and sucrose as organic compound are mixed , mercury(II) chloride solution is added to it and then mixed enough in agate mortar. When total weight of mixture is fixed as 300mg , mixing ratio of sucrose and calcium fluoride was changed at 2:1 to 1:4 to which mercury was included 100ng/300mg. In the ratio at 1:2 good reproducibility of measurement was obtained at and above 600 ℃. When sucrose was mixed in excess , carbon adhered on to every substance in passage though at higher temperatures.

Working curve for mercury determination in solid standard samples : mixture of calcium fluoride and sucrose at ratio 2:1 is shown in figure 2. Broken line shows working curve when mercury in aqueous solution was reduced and atomized by sulfuric acid - tin(II) chloride solution and was measured by the same condition as solid sample. When the quantity of mercury was less than

30ng , the measured values after heat decomposition method and after reduction method had good agreement and the despersion of measured values was small. But for the sample containing mercury more than 30ng the heat decomposition value was smaller than the reduction value. It is thought that formation of amalgam was carried out quantitatively in diluted mercury vapor but interaction between mercury molecules was occured in concentrated vapor so that formation of amalgam wasn´t carried out quantitatively.

When the determination of solid sample , as the sample is made into "diluted solution" by appropriate diluent such as this mixture of calcium fluoride and sucrose in the same manner as aqueous solution , determination of mercury is expected to be carried out quantitatively coinciding each other in defferent method e.g. heat decomposition method and wet one.

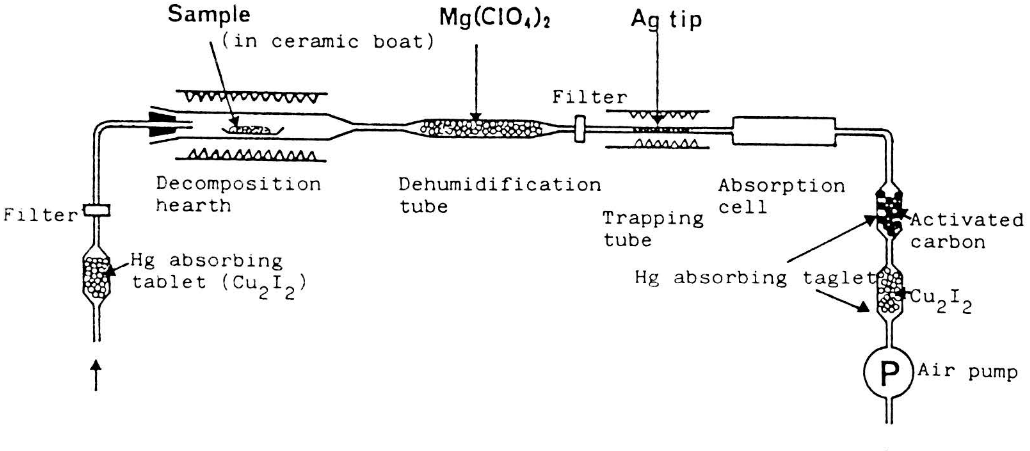

Fig.1 Schematic figure showing mercury measuring system.

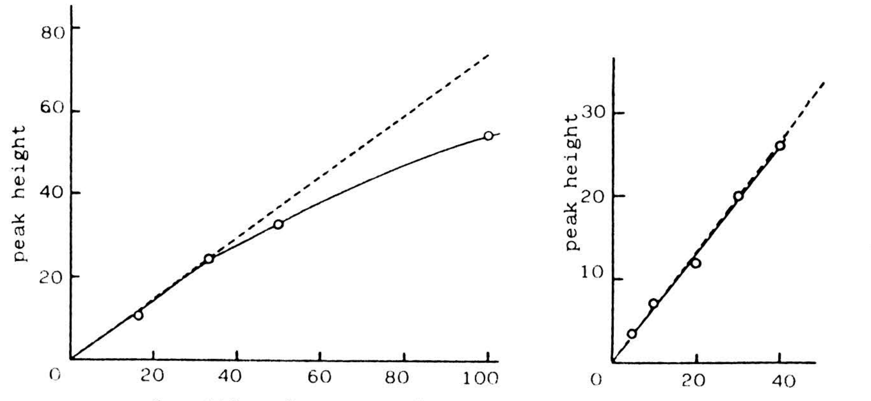

Fig.2 Working curves for mercury in solid standard sample (—) and in aqueous solution (---).
Flowing rate 0.8 l/min. Heating temperature 600 ℃.

S3-07

ION CHROMATOGRAPHY OF ANIONS OF WEAK ACIDS WITH CONDUCTOMETRIC DETECTION

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Ion chromatography (IC) with conductometric detection is a very useful tool for analysis of anions which are difficult to be measured by conventional methods[1,2]. However, there remain some problems to be solved, for example the determination of weak acids, improvement of sensitivity in nonsuppressed IC etc. We have investigated these problems in recent five years and found it possible to determine anions of weak acids, such as silicate, cyanide, sulfide, boric acid, and germanic acid etc. [3-6] We demonstrate the conductometric determination of these compounds after the ion-exchange or ion-exclusion chromatographic separation.

1. ION-EXCHANGE CHROMATOGRAPHY

At the beginning, IC was composed of a column packed with a low capacity anion-exchange resin, a conductivity detector and a suppressor column packed with H^+-form strongly acidic cation-exchange resin. However, with advances of a low-capacity anion-exchange resin and a sensitive conductivity detector, nonsuppressed IC, which did not include a suppressor column, was made possible by Gjerde and Fritz et al. We noticed this technique for measurement of anions of weak acids, and tried to use potassium hydroxide as an eleunt for this purpose and for the improvement of sensitivity of nonsuppressed IC.

This method permitted to determine both anions of strong acids and weak acids with high sensitivity; typical detection limits ranged from 10ppb to subppm level. Figure 1 shows an ion chromatogram of four weak acid, i.e. silicic acid, arsenite, cyanide, and sulfide, which were not detected by a conventional conductometric detection. Since potassium hydroxide is a weak eluent, it is difficult to rapidly elute polyvalent anions. However, many monovalent anions including inorganic and organic acids can be determined.

2. ION-EXCLUSION CHROMATOGRAPHY

Some weak acids were detectable by use of a potassium hydroxide solution as an eluent, but some were not in this way by a conductivity detector. Boric and germanic acids are typical examples of compounds, which are difficult to be detected, because their anions are weakly retained by an anion-exchange resin. Therefore, following method was considered for determining these compounds. Boric and germanic acids form complexes with polyols similar to molybdic or phosphoric acid, and in consequence of their complexation, their acidity increases. The reactivity of polyols with boric and germanic acids depends on configuration of the hydroxyl groups in the polyols. Polyols with adjacent hydroxyl groups in the cis configuration form strongly acidic complexes and those with adjacent hydroxyl groups in the trans configuration form weakly acidic complexes. Fructose, mannitol, and sorbitol are the examples of polyols resulting in strongly acidic borate complexes. These polyols were therefore employed in the eluents used for the determination of boric and germanic acids which were detected by a conductivity detector after ion-exclusion chromatographic separation.

As a result of the investigation, 0.1M fructose solution was found to be the best eluent. Figure 2 shows a typical chromatogram. Peak A is due to impurities such as chloride, and the peak D is caused by carbonate. In this method, the detection limits for B and Ge were 0.5ppb and 1.5ppb.

CONCLUSION

We have investigated problems of anion chromatography and solved some of these problems. Above all, the determination of weak acids is important because simultaneous detection of many compounds is one of the most valuable aspects of conductometric detection. These methods are expected to be useful in many fields of researches.

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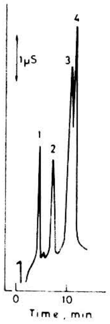

Figure 1. Ion chromatogram of four weak acids: 1, silicic acid (1 ppm); 2, arsenite (5 ppm); 3, sulfide (5 ppm); 4, cyanide (5 ppm).

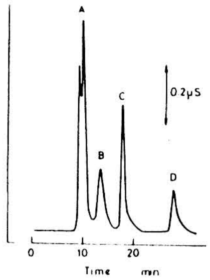

Figure 2. Ion chromatogram of boron and germanium. Eluent, 0.1 of fructose. Sample, 1 ppm of boron and germanium. Peaks; A strongly acidic impurities; B germanium; C boron; D carbonate.

S3-08

DISTRIBUTION OF MAGNESIUM IN MARINE SHELLS

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1. INTRODUCTION

A number of studies on trace elements in marine shells have been reported under the idea that these contents may indicate the physical and chemical environments in which the shell grew up. The trace elements has been thought to be supplied through their body fluids and related indirectly to those concentration in sea water. Accidentally we found that magnesium content in a turban shell was not uniform. Then, we have investigated the distribution of magnesium and strontium in a couple of shells by use of newly developed method for surface analysis of shell. The method is simple, and is based on measuring the ratio of trace element to calcium after dissolving thin layers of the surface in dilute acid.

2. ANALYTICAL METHOD OF MARINE SHELL

Various matters adhering to the outer surface of marine shells are scraped off. Square plates (ca. 15 x 20 mm) are cut off from the shells and washed with a ultrasonic wave washer. Then, the surface is coated with paraffin reserving a certain area (10 x 10 mm) after drying. Each plate is successively immersed in separate 3N HNO_3 for a desired period (some seconds to some minutes) to dissolve stepwise thin layers of paraffin-uncoated shell surface from the outer surface down to the inner surface. These solutions are treated with perchloric acid to decompose organic matters. Calcium is determined by EDTA titration and magnesium and strontium with AAS. A distance from outer surface toward inner side is estimated from the amount of calcium dissolved, using the density, 2.5, of calcium carbonate. The crystal form of calcium carbonate in marine shells is identified with X-ray diffraction method.

3. RESULTS AND DISCUSSION

The distributions of magnesium and strontium in a cross section from the outer surface down to the inner surface of a turban shell are shown in Fig. 1. A turban shell has a prismatic layer (calcite) in the outer side and a nacreous layer (aragonite) in the inner side. The interface between two layers, which is observed visually in the process of dissolution, exists at 0.8 mm depth from the outer surface. Magnesium content is higher in the outer surface layer and decreases gradually to a constant in the prismatic layer. The content further decrease to a constant in the nacreous layer. Strontium content is also high in the outer surface layer, and is higher in the nacreous layer than in the prismatic layer in contrast to the magnesium distribution.

Figure 2 indicates the distribution of magnesium near the outer surface (prismatic layer) of a turban shell. Since a turban shell grows from its apex toward its aperture, the point C nearest to the apex was most early formed in the three points tested. The content of magnesium which are enriched in the outer surface layer decreases (C > B > A). This suggests that the outer surface layer which is more early formed contains magnesium at higher level. However, magnesium contents in these three points are almost equal at low level at 0.4 mm depth from the outer surfaces.

Oyster shell forming only from a prismatic layer (calcite), also contains high in the outer surface layer and the content decreases to a constant toward the inner side.

The findings that magnesium content is higher in a prismatic layer (calcite) than in a nacreous layer (aragonite) and the trend of strontium content is opposite to that of magnesium content agree with the result on the incorporations of magnesium and strontium into calcium carbonate precipitated inorganically. This suggests that the crystal form of calcium carbonate (calcite and aragonite) in marine shells influences the incorporation of these metals into the crystal even through biomineralizations. Magnesium and strontium which are enriched in a outer surface layer may be incorporated inorganically from sea water, through inorganic mineralizations of calcium carbonate on the outer shell surface.

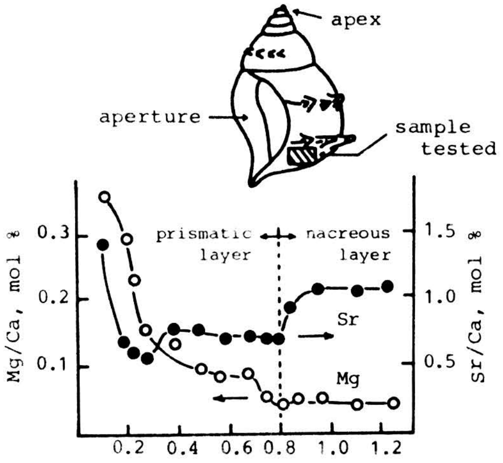

Fig. 1

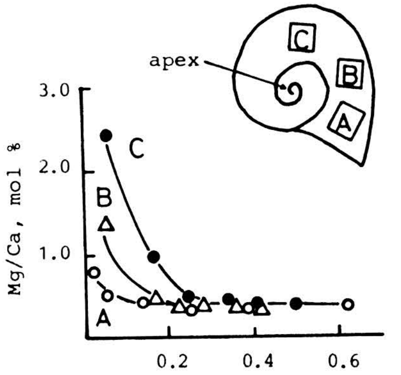

Fig. 2

S3-09

MORPHOLOGY AND ELECTRON PROBE X-RAY MICROANALYSIS OF SUBMICRON PARTICLES IN FRESH WATERS

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In environmental sciences, it has increasingly been recognized that submicron particles play an important role in fresh waters. Significant traces of heavy metals are physically or chemically adsorbed on these particles in water, their behavior in the environment and biological effects differing from those of the dissolved species. Electron microscopy is a powerful tool to morphologically characterize submicron particles. Furthermore, it has become posssible to analyze individual submicron particles for major elements by the analytical electron microscope (AEM), a high resolution electron microscope equipped with an energy dispersive X-ray analyzer. Nevertheless, the results of electron microscopical investigation and their interpretation depend greatly on preparation of specimens. The authors developed the centrifugation technique using a special specimen-grid holder inserted into a centrifuge tube for directly depositing particles on a carbon film mounted on a specimen grid for the AEM. This technique was found to be superior to other specimen preparation techniques for electron microscopy of submicron particles in fresh waters.

EXPERIMENTAL

A sample of pond water was filtered through a 1-μm pore Nuclepore filter beforehand to remove larger suspended particles.

Figure 1 shows the specimen-grid holder inserted into a 7-ml centrifuge tube. A 10-20 nm carbon film on a gold or copper specimen grid was treated by glow discharge to render hydrophilic. The grid was mounted on the specimen-grid holder and fixed by a Teflon frame. The holder was placed at the bottom of the centrifuge tube, into which 5 ml of water sample was carefully pipetted. Centrifugation was carried out in a swing-bucket rotor at 10000 r.p.m. for 18 min for quantitative sedimentation of particles

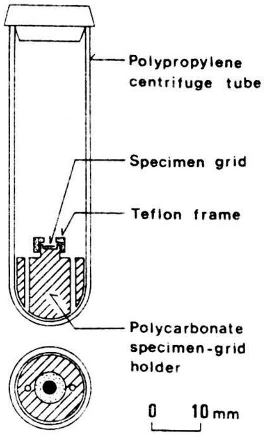

Fig.1 Specimen-grid holder in a centrifuge tube

having diameters larger than 0.1 μm and a density of 1.8 g cm^{-3}. After centrifugation, the water was slowly removed and the grid holder was drawn up by tweezers. The specimen grid was taken out and air-dried.

Other specimen preparation techniques evaluated were filtration (collecting particles on a 0.1-μm pore Nuclepore filter), direct drying (freeze-drying a ca. 3-mm diameter droplet of water on a specimen grid) and spray drying (air-drying ca. 10-um diameter droplets of water sprayed). In the latter two techniques, particles were preconcentrated by filtration to obtain enough population for observation with the electron microscope.

A scanning electron microscope (SEM)(operated at 15 kV) and an AEM (operated at 100 kV) equipped with an energy dispersive X-ray microanalyzer were used.

RESULTS AND DISCUSSION

Four specimen preparation techniques were evaluated by using submicron particles in a pond water as an example. The results are summarized in Table 1. Items 1 - 4 clearly show that filtration and centrifugation are superior to the other two techniques for preparing specimens for the SEM. The specimen prepared for the SEM by centrifugation gave slightly clearer images than that by filtration. Furthermore, it was suitable for the transmission electron microscope (TEM) and AEM. The TEM image of submicron particles in the pond water gave much more information than the SEM image because inner structures were clearly visible with high resolutions. X-ray microanalysis of submicron particles in the pond water suggested, for example, the existence of clay particles associated with a small, varying amount of hydrated iron(III) oxide.

Table 1. Comparison of specimen preparation techniques

Techniques Evaluation items	centrifugation	filtration	direct drying* (freeze-drying)	spray drying*
1.simplicity of operation	+	+	-	-
2.less contamination and loss	+	+	-	-
3.reproducibility	+	+	-	-
4.less agglomeration	+	+	-	-
5.size fractionation	±	+	-	-
6.applicability to TEM or AEM	+	-	+	+

\+ advantageous - disadvantageous

* after preconcentration by filtration

S3-10

APPLICATION OF A COMPLEX OF PHYSICO-CHEMICAL METHODS TO STUDY THE FORMS OF HEAVY METAL OCCURENCE IN NATURAL WATERS

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Problems in speciation of heavy metals (HM) in natural waters are connected with both methodical aspecta (absense of the comprehensive method allowing to conduct isolation, identification and quantitative determination different forms of HM directly in a water sample simultaneously) and specic features of natural waters (diversity of chemical composition, low level of concentrations of HM, readily varying equilibrium among the forms of HM coexisting in a solution). Due to this fact a combination of methods of resolution, isolation and concentration of different HM speciations with methods of quantitative determination of trace amounts of HM widely used. This approach was realized in the schemes of analysis suggested by Florence and Batley 1 , Nürnberg 3 , Lapin and Krasiukov 2 .

While choosing the methods of investigation of HM speciations in such complex heterogenious systems as natural waters it is desirable to fulfil the following requirements:

- methods of resolution and isolation applied in HM speciations should have a minimal influence on the distribution of HM among the forms of its occurence;
- multielement methods of high sensitivity and reproducibility should be used for the determination of HM concentrations;
- methods of analysis of HM speciations in natural waters should be combined with the methods providing information on their biological assimilability (conditional stability constants of complexation, molecular mass distribution etc.).

In this work the problem of combination of the methods of resolution and isolation (different types of liquid chromatography, dialysis, ultrafiltration) with the methods of HM detection (voltammetry, atomic emission and absorption spectroscopy and activation analysis) is discussed. In consideration of the specific features of the above methods the scheme of the analysis of the HM speciations in natural waters, developed on the basis of complex application of membrane filtration (MF), ion-exchange liquid chromatography (ILC), exculusion chromatography (EC) and induction-coupled plasma atomic-emission spectrometry (ICP AES) is suggested as optimal.

MF method is used for resolution of the basic physico-chemical speciations of HM. ILC method using cellulose sorbents allow to separate individual speciations of HM from water in relatively mild conditions without serious disturbance of the balance between co-existing forms with simultaneous concentration ($1 - 5 \cdot 10^2$) of the fractions of 10 individual speciations of HM at the stage isolation. EC at macropore glasses (MPS - GC) is efficient in resolution of the fraction to molecular mass and determination of conditional stability constants of complexation in them. Application of ICP AES method provides sensitivity necessary to measure HM concentrations in fractions and owing to multielemental character of determination to increase the number of HM and other elements studied.

The proposed scheme was applied to the analysis of river waters of the European part of the USSR. The information obtained proves that such metals as Mn, Zn and Pb migrate preferably (60-80 %) as inorganic complexes; 30-40 % of Fe are present as complexes with dissolved organic matter in water and 60-70 % migrate as different types of colloids. 60-90 % of HM, possesing distinct complex formation ability (Cu, Ni, Mo and Co) are bound with organic ligands with dominanting portion of humic substances.

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S3-11

ESTIMATION OF THORIUM SPECIES IN SEAWATER BY USING LIGAND EXCHANGE REACTION

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Thorium isotopes have been studied in the last decade to clarify the geochemical cycle of reactive trace metals in seawater. Because of the extremely low concentration, ^{232}Th concentration, which is a dominant species among the thorium isotopes, has yet been established for open ocean water. The previous observed and estimated ^{232}Th concentration in the open ocean water is less than 10^{-11}mol dm^{-3}[1,2]. However, this ^{232}Th concentration is still higher than the computed solubility of thorianite($Th(OH)_4$)in natural pH, which suggests the existence of complexes in addition to those formed with hydroxyl [3]. Then it is important to clarify the chemical species of thorium in the open ocean water. Unfortunately, it will be hardly possible directly to carry out the speciation of thorium in the seawater. We developed a new method to estimate the species of thorium in the seawater by using the complex formation reaction between spiked thorium and the organic reagent under the conditions of seawater.

Method:

The complex formation reaction between thorium and Xylenol Orenge (XO, H_6L) was carried out under the conditions of seawater. The Th standard solution was added to several Teflon bottles containing 500 ml seawater controlled by acetate buffer and dil. HCl solution. After the addition of known amounts of XO, the solution was mixed well, and was kept at room temperature of 25±1 °C for the periods of about 1 hr. Reaction equilibrium was reached 1 hr. After the equilibrium, separation of the Th-XO complexes from the reaction system was carried out adsorption on XAD-2 resin column. Under the experimental conditions, XO complexes were completely adsorbed on the resin whereas inorganic Th species remained in the effluent. The Th-XO complexes adsorbed on the resin were digested with conc. HNO_3 on a hot plate. After the removal of the resin by the filtration, the filtrate was evaporated to dryness. The residue was dissolved in 8 mol dm^{-3}HNO_3 solution, and Th was separated from others by means of an anion exchange resin. The Th fraction eluted by 9 HCl mol dm^{-3} was evaporated dryness, and was dissolved in 2 mol dm^{-3} HCl solution and ethyl alcohol. The Th fraction was electroplated on a silber disk. The radioactivity of Th was measured by an alpha-ray spectrometer.

Results and discussion:

When the Th-XO complex, M_iA_j, is formed under the conditions of seawater, the following equilibrium equation is given;

$$iM' \; + \; jA' \rightleftharpoons M_iA_j \;\; ; \; K_{app} = [M_iA_j][M']^{-i}[A']^{-j} \qquad (1)$$

where M and L show thorium and XO, respectively, and K_{app} is the apparent conditional stability constant of M_iA_j. The total Th concentration is given as follows;

$$C_{M,T} \; = \; [M'] + i\sum\sum[M_iA_j] \qquad (2)$$

When only the species of MA_j is present under the experimental conditions, the following equation is derived from eqns (1) and (2).

$$\log(R/(1-R)) = \log K_{app} + j\log C_L \quad ; \; R = C_{M,o}/C_{M,T} \qquad (3)$$

where $C_{M,o}$ and C_L show the Th-XO complex and total ligand concentrations, respectively. From eqn (3), the composition of the Th-XO complex and its apparent conditional stability constant can be determined from a linear relationship of log(R/(1-R)) vs. log C_L.

As shown in Fig. 1, the linear relationship with a slope of 2 between log(R/(1-R)) and log C_L was obtained under the experimental conditions. The result indicates the formation of the Th-XO complex with the composition of 1:2, which has been found by photometric investigation[4]. The conditional stability constant of $Th(H_2L)_2$, K^c_2, is given as follows;

$$K^c = K_{app}\,\alpha_M \;\; \alpha^2_{H2L(H)} \qquad (4)$$

where α_M and $\alpha_{H2L(H)}$ show the side recation coefficients of Th and H_2L under the conditions of the controlled seawater, respectively. In seawater, thorium forms known and unknown complexes with naural inorganic and organic ligands. Then, the side reaction coefficient of Th is given as follows;

$$\alpha_M = 1 + K_{ThOH}[OH] + \cdots + K_{ThSO_4}[SO_4] + \cdots + K_{ThX}[X] + \cdots + K_{ThY}[Y] + \cdots$$

X: halide, Y: unknown ligand

If the contribution of the Th complexes with unknown ligands is negligible, the side reaction coefficients can be calculated as summarized in Table 1. The logarithmic conditional stability constant of $Th(H_2L)_2$ is calculated to be 20.2 ± 0.5 which is in agreement with the value(19.31) determined by photometric method[4]. This result suggests that the dominant species of Th in the seawater are hydroxo complexes and no significant complexation with unknown natural ligands is present under the conditions of seawater.

Fig. 1

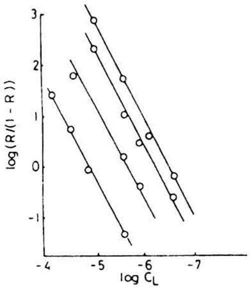

Table 1.

pH	log K_{app}	log $\alpha^2_{H2L(H)}$	log α_M	log K^c
2.20	9.80	11.10	0.12	20.78
2.60	11.34	8.97	0.13	20.44
3.05	12.40	7.19	0.15	19.74
3.40	19.94	6.72	0.22	19.89
			average	20.2

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S3-12

DETERMINATION OF CADMIUM AND COPPER-SPECIES IN PLANT TISSUE

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The analysis of cadmium, copper and other trace elements in food, including plants, has been elucidated over the past 25 years. Concerning the bioavailability, however, not only the total content, but also the species of a certain trace element is of special interest /1,2/. The uptake of trace elements in the food-chain is dependant on several conditions, such as oxidation state and complex form. Speciation is therefore required for both, toxic and essential elements.

In this paper a separation procedure is introduced that allows qualitative and quantitative determinations of cadmium and copper-species in native plants. The procedure that was developed for the determination of cadmium and copper-species in lettuce, Lactuca sativa /3/, is a combination of Ultra Turrax homogenisation in Tris-buffer and following ultracentrifugation and gelfiltration of the cytosol. The metals were analysed by off-line ET- AAS. The solid fragments of the cell, containing 50 % of the total cadmium and 20 % of the total copper respectively were not further specificated.

From the cytoplasma, a high molucular weight metal binding- protein (> 75000 dalton) containing 55 % of the cytoplasmic cadmium and 20 % of the cytoplasmic copper and a low molecular weight metal binding-protein (3200 dalton) containing 45 % of the cytoplasmic cadmium and 70 % of the cytoplasmic copper were isolated. Besides, there are two copper binding-proteins of about 57000 and 25000 dalton, containing only few copper. There is a broad variation in the metal balance from plant to plant.

Ion exchange chromatography of the low molecular weight protein fraction yielded one single metal binding-protein, containing both cadmium and copper. This strong anionic protein is rather heatstable. The low UV absorption at 280 nm indicates a low content of aromatic amino acids, while the high UV absorption at 254 nm indicates a high cystein content. Therefore, it is proposed that the cadmium and copper binding-protein belongs to the metallothionein class.

Using the procedure mentioned above, quantitative assertions about the distribution of the metal species in one plant, as well as comparisons of metal species in different plants are possible.

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Speciation of cadmium and copper in native lettuce (Lactuca sativa)
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S3-13

DETERMINATION OF SELENIUM AND TELLURIUM IN ENVIRONMENTAL SAMPLES

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A method has been developed to determine total Se and Te in coal with graphite furnace atomic absorption spectrometry(GFAAS), in which a coprecipitation technique with As(III) as a carrier was used to separate Se and Te from matrix after mineralization of the sample. Applying this method to environmental samples such as coal, coal fly ash, vehicle exhaust and pond sediment, we obtained some results for Se and Te in them. On the other hand, S and Al of the same samples were determined by X-ray fluorescence spectrometry to make clear their distributions and behavior in the environment.

INTRODUCTION

Many researchers have investigated the distribution of S and Se because of the necessity of urgent control of rapid deteriorations of the environment. Te,another member of chalcogen elements had not attracted much attentions of people. Recently, a new interest in the analysis of Te of environmental samples arose from a discovery that the enrichment factors of Te in airborne particulate samples were very high.

In our preliminary test carried out using GFAAS to determine Se and Te in coal, we found it necessary to separate Se and Te from matrix before measurement because of severe depressing effects due to major metal ions such as iron and aluminium and perchloric acid remaining after mineralization of the sample. So we have reported a method for determining simultaneously total Se and Te in coal in 7th Clean Air Congress held in Sydney on 25th August this year.

This paper describes the method used and results for Se and Te of some environmetal samples obtained by GFAAS combined with a coprecipitation technique using As(III) as a carrier. The ratios of Se/S, Te/S, Te/Se and the enrichment factors of Se and Te are calculated using S and Al values obtained by X-ray fluorescence spectrometry.

EXPERIMENTAL

All samples(< 60 mesh) were dried in a vacuum desiccator at room temperature for 24 hours before use. To determine Se and Te, each sample of 0.3g to

2.0g was taken in a Teflon beaker and digested on a hot plate, first with HNO_3 and HF and then with HNO_3 and $HClO_4$. Add 5mg of As(III) and 25ml of 35% HCl to the digest. Then heat 90-100°C for 30min. Add 10ml of 34% H_2PO_3 and heat until the precipitate is formed. Stand the sample solution containing the precipitate over night, and filter it. Wash the precipitate with water, dissolve it with hot HNO_3(1+1), and then evaporate to 1-2ml. Make the volume of the solution up to 10ml with 0.5M HNO_3. Standard solutions for the calibration curve were also prepared in the same manner as described above. Measure absorbances of Se and Te with an atomic absorption spectrometer(Hitachi Model 180-70).

For determination of S and Al by X-ray fluorescence spectrometry, samples were ground to such a particle size that the whole sample passed a 149μm sieve. Dry the sample in a vacume desicator. Weigh 0.1g of sample and 0.9g of boric acid and mix them thoroughly. Take 0.6g of the mixture in an aluminium ring and press it with a pressure of 10ton for 10min. The instrument was a RIGAKU System 3080 of X-ray fluorescence spectrometer used with a rhodium-target X-ray tube at 50kV(40mA) and PET-crystal for Al and Ge-crystal for S. A gas flow propotional counter was used and the goniometer angles were 110.95°(2θ) for the S Kα line and 145° for the Al Kα. The counting time was 40 sec.

RESULTS

Seven sorts of coal samples and each one sample of coal fly ash, vehicle exhaust, soil and pond sediment have been analyzed for S, Se, Te and Al using the procedure described above. In the coal samples analyzed, Se and Te concentrations were in the range of 0.20 to 1.38ppm with an average value of 0.51 ppm and in the range of 0.023 to 0.075ppm with an average value of 0.058ppm respectivery. And Te/Se ratios were in the range of 0.034 to 0.28 with an average value of 0.098, which is half of 0.20 calculated by Taylor number. And Se/S ratio of coal samples ranged from 0.24 to 1.76×10^{-4} and Te/S ratio ranged from 0.20 to 1.13×10^{-5} . These results mean that there are certain constancies in ratios of the chalcogen elements in coal. On the other hand, the crustal enrichment factors calculated as

$$\text{EF crust} = \frac{(X/Al)\text{aerosol}}{(X/Al)\text{crust}}$$

where X are the concentrations of Se and Te, ranged from 24 to 149 with an average value of 76 for Se and from 23 to 88 with an average value of 43 for Te. From these results, it was found that Se and Te was enriched several tens times in coal as compared with those in crust.

Because we have only a few data for the other samples, experiments to obtain more data are in progress.

S3-14

DISTRIBUTION AND CHEMICAL FORM OF ARSENIC COMPOUNDS IN NATURAL WATER

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INTRODUCTION

Arsenic compounds exist in natural water in a variety of chemical forms such as arsenic(III), arsenic(V), monomethylarsonic acid(MMAA), and dimethylarsinic acid(DMAA). Therefore, it is important to investigate the chemical form and behavior of arsenic compounds in natural water in order to understand the cycle of arsenic in the environment.

In this study, a method was investigated for the selective determination of arsenic compounds{As(III),As(V),MMAA,and DMAA} by using hydride generation atomic absorption spectrometry, and the concentration of arsenic compounds in natural water at trace levels were measured at various sites in Japan.

ANALYTICAL METHOD

Hydride generation method was used. As(III), As(V), MMAA, and DMAA in a sample solution were reduced to arsine, monomethylarsine(MMA), and dimethylarsine(DMA), respectively, by an addition of $NaBH_4$ after adjusting pH of the sample solution with HCl. The arsines generated from the sample solution were collected in U glass tube packed with glass beads which was cooled with liquid nitrogen, the separation of arsines was accomplished by the sequential vaporization due to their different boiling point (AsH_3 -55°C, MMA 2°C, DMA 37°C). Arsines vaporized from the trap were carried to a quartz furnace by helium carrier gas and were analyzed by atomic absorption spectrometry. The reduction of arsenic compounds depended on pH of the solution. As(III) was reduced at pH 4, while As(V) was not reduced above this pH. Therefore, As(III) was determined at pH 4 by an addition of 5% of potassium biphthalate buffer, and total inorganic arsenic{As(III)+As(V)} was determined at pH 0.5 by an addition of HCl.

The good separation of MMA and DMA was obtained by using 15% OV-3 on Chromosorb W AWDMCS 60/80 mesh as a packing material due to collection for arsines. The elimination of interferences due to foreign ions was examined, and the use of ethylenediaminetetraacetic acid(EDTA) and tartaric acid was very effective for the MMAA and DMAA analysis. The detection limits by this method were 1 ppt for As(III), 1.5 ppt for As(V), 3 ppt for MMAA, and 6 ppt for DMAA with a 200 ml sample solution. The coefficient variation for replicate determinations was within a few percent for each arsenic compounds analysis. Therefore, this method is suitable for the determination of arsenic compounds at trace levels in natural water.

SAMPLING OF NATURAL WATER

The samples were collected at various sites in Japan from 1983 to 1985. Rain water were collected at Hiyoshi, Yokohama near Keihin industrial area. All samples were filtrated with Millipore membrane filter (Type HA poresize 0.45 μm)

RESULTS AND DISCUSSION

The analytical results of concentration of arsenic compounds and the concentration ratios of inorganic and organic for total arsenic are shown in Table 1. The average concentration at 29 sampling sites in Tonegawa was 1.57 (0.18~5.88)ppb for As(V), 0.61(0.16~3.31)ppb for As(III), 21(8~77)ppt for MMAA, and 40(11~140)ppt for DMAA. It was found that more than 97% of arsenic in the river water was inorganic arsenic {As(III)+As(V)} and a few organic arsenic existed as MMAA and DMAA. However, high concentrations of organic arsenic were observed at Tamagawa, Ushikunuma, and Kasumigaura, so that organic arsenic occupied more than 9% of total arsenic. The increase of organic arsenic observed in these sites might be due to the methylation of inorganic arsenic by the eutrophication.

Table 1 Analytical results of inorganic arsenic and organic arsenic in natural water and concentration ratio of [inorganic As]/[total As] and [organic As]/[total As]

Sample	Concentration (ppb)		Ratio (%)	
	in.As[1]	org.As[2]	in.As[1]	org.As[2]
River water				
Tamagawa	1.38	0.24	85	15
Arakawa	1.78	0.10	95	5
Edogawa	1.46	0.07	95	5
Av.(n=3)	1.54	0.14	92	8
Tonegawa Av.(n=29)	2.18	0.06	97	3
Lake water				
Motosuko	0.23	0.007	97	3
Yamanakako	0.22	0.003	98	2
Tazawako	0.31	0.003	99	1
Av.(n=3)	0.23	0.005	98	2
Ushikunuma	1.28	0.27	83	17
Kasumigaura	2.21	0.21	91	9
Av.(n=2)	1.74	0.24	87	13
Sea water				
Hachijoujima	1.94	0.06	97	3
Chichijima	1.66	0.06	97	3
Av.(n=2)	1.80	0.06	97	3
Tokyowan Av.(N=14)	1.31	0.07	95	5
Rain water				
Yokohama Av.(n=4)	0.48	0.004	99	1

[1] in.As : inorganic arsenic {As(III)+As(V)}

[2] org.As : organic arsenic {monomethylarsonic acid + dimethylarsinic acid}

S3-15 SPECIATION OF METAL ION IN SOLUTION BY FLOW-COULOMETRY
—DETERMINATION OF PLUTONIUM AND URANIUM IONS BY FRACTIONATING THEIR OXIDATION STATES—

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Analytical method for the speciation of ions in the solution (we define the determination of ions by fractionating their oxidation states as "speciation") has to satisfy the following requirements. First, oxidation states of the objective ion, i_{obj}, should not be changed by such procedure as the addition of reagent. The second requirement is that the method is applicable to the rapid and continuous detection, since the oxidation state of i_{obj} frequently changes momently. Potentiometry using ion-selective electrode, ISE, and the spectrophotometry fill these requirements. Highly sensitive and selective ISE, however, cannot be prepared for all of ions of interest. In particular, ISE for transition-metal ion or multivalent ion which is feasible to the practical use is limited. Spectrophotometry can be applied only to i_{obj} which gives a sharp absorption peak with a large molar extinction coefficient. In addition, the coexistence of a large amount of other ions often disturbs the determination of i_{obj} in these methods. Hence, one of important problems in the speciation is how to eliminate the interference from other ions without disturbing the oxidation state of i_{obj}.

By flow-coulometry using column electrode[1] an electrolysis can be performed quantitatively and rapidly. Employing twin-column electrode, one can eliminate the effect of other ions by the complete pre-electrolysis at the first column electrode, E_1, and can determine i_{obj} coulometrically at the second column electrode, E_2.

This paper deals with flow-coulometry using twin-column electrode for the speciation of Pu(III), Pu(IV), Pu(VI), U(IV), and U(VI) in nitric acid solution of their mixture, which has been a long-pending subject required not only for the fundamental solution chemistry but also for nuclear technology.

COLUMN ELECTRODE (Fig. 1)

A working electrode, W, is a bundle of glassy carbon fibers (11.5 μm in diameter, Tokai Carbon Co., GC-20) packed in a porous Vycor glass cylinder, D, (Corning Co.) as an electrolytic diaphragm. Sample solution, S, was introduced into the column electrode and was electrolyzed by the aid of a platinum counter electrode, C, and saturated KCl-Ag/AgCl (SSE) reference electrode, R. For multi-step flow-coulometry an appropriate number of column electrodes were connected in series using a neoprene seal.

REDUCTION AND OXIDATION OF PLUTONIUM AND URANIUM AT COLUMN ELECTRODE (Fig. 2)

Current-potential (I-E) curves for 10^{-3} M plutonium and uranium ions of various oxidation states in 1 M HNO_3 + 0.5 M Na_2SO_4 were recorded introducing the solution to the electrode at 1.5 ml/min and scanning the working electrode potential at 0.1 mV/s. When electrolysis is attained quantitatively, the current, I (ampere), flowing at the electrode can be expressed by I = nFfC, where n, F, f, and C are the number of electrons involved in the reaction, Faraday constant, flow-rate of the solution(l/s), and concentration of the depolarizer(M), respectively.

SPECIATION OF Pu(III), Pu(IV), Pu(VI), U(IV), AND U(VI) IN A SOLUTION OF THEIR MIXTURE

The I-E curves in Fig. 2 suggest that Pu(IV) and Pu(VI) are quantitatively reduced to Pu(III) at +0.20 V where neither oxidation of U(IV) nor reduction of U(VI) takes place. Hence, the current at E_1 of +0.20 V is due to the reduction of Pu(IV) and Pu(VI). Using twin-column electrode with E_1 of +0.20 V and E_2 of -0.05 V, the concentration of U(VI) can be determined from the current at E_2, since Pu(IV) and Pu(VI) have already been completely reduced to Pu(III) at E_1. Using E_1 of +0.20 V and E_2 of +0.45 V, the current due to oxidation of U(IV) to (VI) can be measured at E_2, and using E_1 of +0.20 V and E_2 of +0.80 V, the current due to oxidations of both U(IV) and Pu(III) can be measured at E_2. The difference between currents at E_2 of +0.45 V and +0.80 V corresponds to the oxidation of Pu(III) to (IV), where Pu(III) is sum of that in the original solution and that generated from Pu(IV) and Pu(VI) at E_1. When the sample solution is introduced to E_1 of +0.80 V, the oxidation current due to both Pu(III) and U(IV) in the original solution is detected at this electrode. From the currents flowing at each column electrode of various potentials, the concentrations of ions can be determined on the basis of the equation mentioned above. Proposed method is feasible to 10^{-5} to 5 x 10^{-2} M plutonium and uranium ions.

REFERENCE[1] T. Fujinaga and S. Kihara, "CRC Critical Reviews in Analytical Chemistry", Vol. 6, CRC Press Inc., 1977, p223.

Fig.1

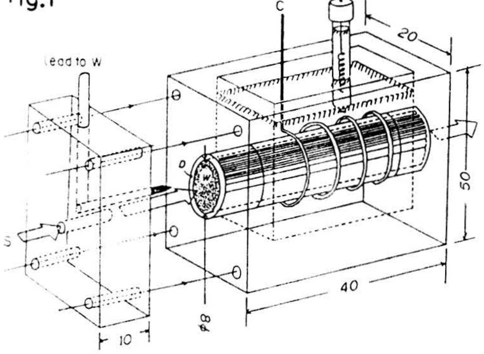
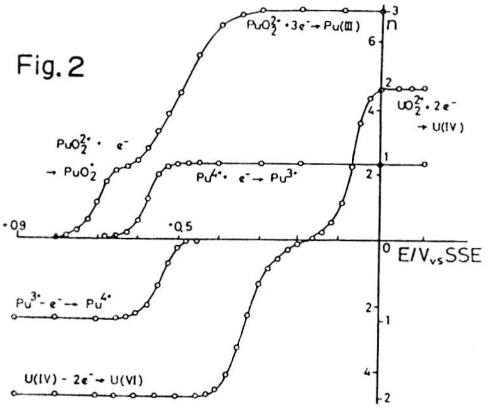


Fig. 2



S3-16

DETERMINATION OF NITRATE NITROGEN IN WATER BY STANDARD ADDITION METHOD

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For determination of nitrate nitrogen in water, UV-spectrophotometry have been recommended by "Standard Methods for the Determination of Water and Waste Water"(15 edition, America). It is only useful to sample of water containing a little organic material. For general water sample, the pretreatment is necessary before testing, otherwise interference is found.

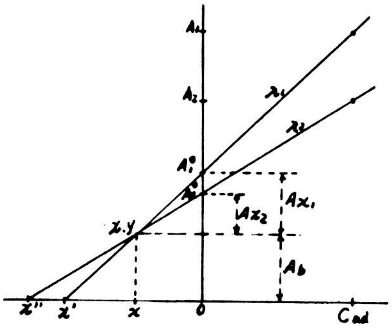
This paper deals with a new method for determination of small amount nitrate nitrogen in water by standard addition method and UV-spectrophotometry. It is simple, rapid and accurate. The separation is not required when the water turbidity and colour are less than 30 degree. The results obtained are identical with those of phenoldisulfonic acid method and aren't affected by nitrite. This method is suitable for testing of drinking water.

1. PRINCIPLE

Suppose the absorption peak of nitrate is λ_1 , the absorbance of solution at this wavelength is A_1°. The absorbance of solution adding a nitrate standard solution of concentration C_{ad} is A_1, then painting the oblique line A_1° and A_1'. They intercept on the abscissa X' when they are extended, as indicated in Figure. The function equation of the straight line is:

$$Y_1 = A_1^\circ + K_1 X$$

in accordance with extrapolation, X' is the nitrate concentration in solution. As a result of the background interference is present, so the true value of X'



Figure, Diagram showing the method and principle is X. For this reason

$$A_1^{\circ}=A_x+A_b$$

where A_x is nitrate found absorbance; A_b is background interference absorbance. If wavelength change into λ_2 when determining, the value is A_2° and A_2, its function equation is:

$$Y_2=A_2^{\circ}+K_2X$$

where K value relate to λ range. When absorption peak wavelength is made some change($\Delta\lambda$ =5-10nm), the change of A_x value is very large, but the change of background interference absorbance(A_b) is very small. Then, two oblique lines across to the X,Y, and correspond to X value. The true value of X is obtanined by means of solving equation, this is found value of nitrate nitrogen. Since $K_1=(A_1-A_1^{\circ})/C_{ad}$; $K_2=(A_2-A_2^{\circ})/C_{ad}$, and inserting K_1 and K_2 in above two equation, then a equation group obtanined is :

$$\begin{cases} Y_1=A_1^{\circ}+\left[(A_1-A_1^{\circ})/C_{ad}\right].X \\ Y_2=A_2^{\circ}+\left[(A_2-A_2^{\circ})/C_{ad}\right].X \end{cases}$$

so:

$$X=(A_2^{\circ}-A_1^{\circ})\ C_{ad}/A_1-A_1^{\circ}+A_2^{\circ}-A_2)$$

$\because A_2^{\circ}<A_1^{\circ}$, X is minus. We take X to be positive number in order to easy to calculate, above equation is change into:

$$X=(A_1^{\circ}-A_2^{\circ})\ C_{ad}/(A_1-A_1^{\circ}+A_2^{\circ}-A_2)$$

where X represents nitrate nitrogen concentration(ppm) in water; A_1° and A_2° are water absorbance at 210nm and 220nm respectively; A_1 and A_2 are absorbance of water adding standard solution at 210nm and 220nm respectively; C_{ad} is nitrate concentration(ppm) of water after adding standard solution.

2. METHOD

We may directly determine nitrate nitrogen when turbidity and colour of water under 30 degree. Aluminum hydroxide suspension is added for settling before determination if its turbidity and colour are large.

Pipet 10ml water sample into 50ml volumetric flask and dilute to volume S_1, again pipet 10ml water aample and 2ml standard solution(1ml=0.01mg NO_3^--N) into another 50ml flask, dilute to volume S_2. The thickness of quartz cell is 1cm. Frist adjusting zero point with deionized water, then S_1 and S_2 absorbances are determined at 210nm and 220nm respectively. From $A_1A_1^{\circ}$ (λ_1=210nm) and $A_2A_2^{\circ}$(λ_2=220nm) values, using above equation one can calculate the content of nitrate nitrogen. For this instance the C_{ad} is 0.02mg/10ml(2ppm).

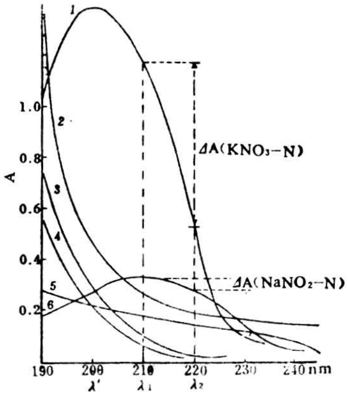
If the content of nitrate nitrogen is larger than 5ppm, the water sample may change to 2-5ml. If it is less than 0.5ppm, the water sample used for determination may change to 20-40ml. Generally speaking, the absorbance value (A_1) between 0.3-0.8 is appropriate.

(Continued)

3. RESULTS AND DISCUSSION

(1) THE WAVELENGTH SELECTION

Prepare nitrate nitrogen standard solution(2ppm) and some interference ion solution, regulate the instrument zero point with water and draw absorption spectra(Figure 2). It is seen from Figure 2 that the nitrate absorption peak is at 200 nm and that at this wavelength, greater part of the absorption peaks of interference substances come to go up, too. In order to avoid background interference and keep sensitivity of the nitrate, λ_1 and λ_2 are chose at 210 nm and 220 nm, respectively. Difference value between λ_1 and λ_2 is 10 nm, and the absorbance difference value for nitrate(KNO_3-N) is ΔA. Under these condition, the change of background interference A_b value is only a few(see Fig. 1). In the Figure 2, the nitrite absorbance stands for background interference. When the nitrite concentration is 1 ppm, the absorbance change of the background interference is $\Delta A(NaNO_2\text{-}N)$. This value is very small when it compare with $\Delta A (KNO_3\text{-}N)$. In the general way, in the common drink water, nitrite concentration is less than 0.1 mg/l, therefore background interference absorption may be neglected. If λ_1 and λ_2 wavelength difference increased to double, the error (A_b) also increase proportionally. But the absorption of nitrate is not increased correspondingly. Therefore, it is proper to keep the difference value between λ_1 and λ_2 within 10 nm. The waste water of industry and daily life contain a lot of interference substances, so this method do not use directly. In order to examine the nitrite effect upon this method, we use two samples of water, one containing nitrate is lower, and another containing nitrate is higher, then according to



1: KNO_3-N(2ppm); 2: $K_2Cr_2O_7$(8ppm);
3: Na_2CO_3(50ppm); 4: $NaHCO_3$(200ppm);
5: $FeCl_3$(12ppm); 6: $NaNO_2$-N(1ppm).

Figure 2. The wavelength selection

this method add nitrite 0, 0.05, 0.10, 0.25, 0.50 ppm to each sample respectively. The results are as follows: for one sample, the nitrogen mean value is 5.826 ppm, S D 0.079, RSD 1.35%; for another sample, mean value is 0.583 ppm, S D 0.036, RSD 6.2%. It suggests that when the nitrite concentration is under 0.5 ppm, its content do not effect on determination.

(2) ACCURACY AND RECOVERY

Use 5 natural water samples which contain the nitrate nitrogen 0.745-12.5 ppm range, determine respectively 5 times for each sample according to above procedure, RSD obtained is 1.2-2.9%.

Take 18 natural water samples which contain the nitrate found value 1.48-12.14 ppm range, then add standard nitrate solution 1.0, 2.0, 5.0, ppm, respectively, mean Rec obtained are 102%, 98.6%, 98.5%.

(3) COMPARISON THE NEW METHOD WITH PHENOLDISULFONIC ACID METHOD

Sampling 20 natural water, examine nitrate nitrogen content with two methods at the same time. The results obtained are basically identical, $T=1.86 < t_{0.05(20)}$, $P > 0.05$.

S3-17

SIMULTANEOUS DETERMINATION OF TRACE ELEMENTS IN NATURAL WATER BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY FOLLOWING PRECONCENTRATION BY SOLVENT EXTRACTION

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Simultaneous determination of trace elements in natural water was investigated with inductively coupled plasma emission spectrometry. The sample was preconcentrated with dithiocarbamate or dithizone extraction. In order to get as high enrichment factor as possible, initial volume ratio between natural water sample and extracted solvent was set to 250. Lake waters (Lake Biwa, Japan) were analyzed by this method.

ITRODUCTION

On evaluation of aquatic environment, the knowledge about concentrations and chemical states of trace elements in the environment is indispensable. If simultaneous determination of trace elements is possible, both absolute and relative changes in concentrations among the elements can be obtained and it will be not only convenient but also very useful for studies in geochemistry or environmental chemistry. Inductively coupled plasma emission spectrometry (ICPES) is able to analyze many elements simultaneously and adequate to this object. However, the concentrations of many elements in aquatic environment are generally very low, and thus preconcentration procedures are necessary. In this investigation, the prenoncentration method which had high enrichment factor and applicapability to many elements was studied by solvent extraction method. Dithiocarbamate and dithizone were used for chelating agent which can form complexes to many elements.

EXPERIMENTAL

A Japan Jarrell-Ash model 96-953 ICP emission spectrometer was used. A representative analytical procedure adopted for the determination of trace elements in lake water is as follows. The lake water sample which was filtered through 0.4 μm Nucleopore filters was acidified to pH 1.0 by the addition of hydrochloric acid. A 1 l sample was placed in a 1 l TEFLON separatory funnnel and 10 ml of 2 % (w/v) ammonium tetramethylenedithiocarbamate (ATMDC) solution was added. The pH was adjusted to a desired value (4.3 or 6.9) with aqueous ammonia and 10 ml of 1 M buffer solution (NH_3 + CH_3COOH) was added. After the addition of 4 ml of 2-ethylhexyl acetate containing 5 % (w/v) dibenzylammonium dibenzyldithiocarbamate (DBADBDC), the mixture was shaken for 1 h. The organic phase was analyzed directly by ICPES.

RESULTS AND DISCUSSION

The organic solvent was selected from the points of low solubility in water and plasma stability in introducing the solvent. 2-Ethylhexyl acetate was used in dithiocarbamate extraction, and the loss by dissolution in water in the above procedure was about 2 %. The effect of pH on the extraction of seven ions (Cd^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, VO_2^{+}, Cu^{2+}) was studied with various dithiocarbamate. There were pH regions in which the extraction efficiencies were independent of pH for Cd, Ni, Fe, and Cu, but the efficiencies of Mn, Cr and V were generally poor. Therefore, the extractions with combination of two dithiocarbamates were investigated, and the combination of ATMDC and DBADBDC was the most efficient extractant. Fig. 1 shows the effect of pH on the extraction of the seven ions and the other elements with the combination. These results indicate that thirteen elements (As(III), Se(IV), Mo(VI), Zn(II), Cd(II), Ni(II), Co(II), Sn(II), Fe(II, III), Cr(VI), Pb(II), V(V), and Cu(II)) are simultaneously extracted at pH 4.1-4.6, and Mn(II) and Cr(III) are extracted at pH 6.9-7.0. Extraction efficiencies, detection limits and analytical blanks are listed in Table 1. The extraction efficiencies for all the elements except for Mn and Cr were >96 %. Lake waters were analyzed by this method, and the results are shown in Fig. 2. In addition, the extraction with dithizone will be expressed.

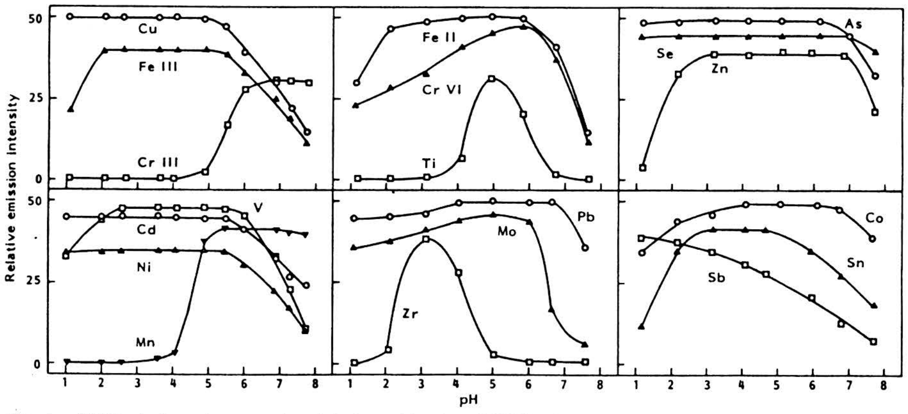

Fig. 1 Effect of pH on the extraction with thr combination of ATMDC and DBADBDC. Each element concentration: 10 μg/l.

Table 1 Characteristics of the analytical procedure.

Element	Extraction efficiency (%)	Detection limit (ng/l)	Analytical blank (ng/l)
As	99	620	<620
Se	99	810	<810
Mo	99	73	<73
Zn	98	63	66
Cd	96	9	11
Ni	99	46	<46
Co	99	13	<13
Sn	96	93	<93
Mn	91	7	8
Fe II	98	9	18
Fe III	99	5	18
Cr III	43	22	<22
Cr VI	89	12	15
Pb	98	260	<260
V	98	5	<5
Cu	99	2	9

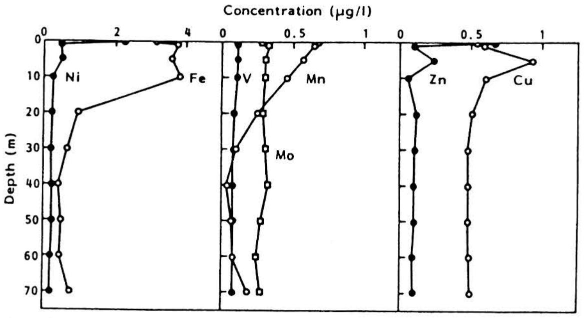

Fig. 2 Vertical distributions of trace elements in the Lake Biwa.

S3-18

CHARACTERIZATION OF ARSENIC IN SEA WATER BY HYDRIDE GENERATION-ATOMIC ABSORPTION SPECTROPHOTOMETRY

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In the previous study, we described a differential determination of inorganic species of As and Sb according to their oxidation states by hydride generation-atomic absorption spectrophotometry, which was confirmed quite preferable for the trace analyses in sea water with high sensitivity[1]. In the present study, a simple and precise method is described for the determination of total amount of arsenic including inorganic As(III), As(V) and organic species such as mono methyl arsenic acid and dimethyl arsenic acid.

The apparatus for HG-AAS were described in the previous paper[1]. As(III) was determined at pH 6. Total amounts of inorganic species(As(III) + As(V)) were determined at 2M hydrochloric acid. Then the total amounts of inorganic and organic species were determined at 2M acidity after persulfate digestion. Concentrations of each species were estimated from the difference of the three determinations. Sea water samples were immediately frozen just after sampling and stored below -20 °C in 20 l polyethylene bottles. The digestions and measurements were done within three months. Sub ppb level of arsenic species in sea water could be determined with a sample volume of 100 ml. Digestion with persulfate solution(5%) was done in alkaline medium, where recoveries of each arsenic species were satisfactory with the relative stnadards deviations of 1.3-2.1 %. The digestion process was complete by heating the solution for 30 min. at 80 to 85°C on hot plate.

Average values of concentrations of arsenic species are shown in Tables 1 and 2. As(III) and organic species of arsenic were distributed in upper waters, less than hundred meters in depth, and the concentrations of As(V) were found lower in upper waters than in deep waters as reported by Andreae.[2] However, the total were nearly constant from surface to deep seawater[6]. The concentration and distributions of arsenic species did not show regional dependences between the northwestern Noth Pacific Ocean and Japan sea[6]. The values of inorganic species in shallow water are comparable with those reported by Sugahara et al.[3] and Gohda[4] for the sea water, nearly the same district.

Then, the similar investigations for the characterization of arsenic species were carried out for Seto inland sea waters as well as Tokyo bay sea waters. The results are shown in Fig. 1. It is interesting to note that the organic species has been converted into inorganic species as the salinities of the sea waters increased. However, the total amounts of arsenic species were kept constant with the value of 1.5 ppb for both sea waters of Seto Inland and Tokyo bay.

The flow injection analysis has been currently developed mainly in the field of conventional spectrophotometry with color reactions. We have recently introduced the flow injections technique to the hydride generation-atomic absorption spectrophotometry for the determinations ofAs, Sb, Bi, Se, and Te.[5] Here, the hydride atomic Absorptions spectrophotometry combined with the flow injection analysis has been applied successfully to the determinations of inorganic arsenic species. When 0.5 ml of sea water sample is injected, the analyses can be carried out automatcally and continuously on the boat just after the sampling of seawater. More than thirty samples coud be analyzed with good precision within an hour. An example of the results has been shown in Fig. 2, which shows the vertical distribution of inorganic arsenic species in the sea water in the Pacific Ocean, near Hawaiian Island.

Table I Average values of concentrations of arsenic species

Depth/m	Number of samples	Found/μg l⁻¹ As(III)	As(V)	As(org)	Total
<200	17	0.17±0.08	1.66±0.14	0.08±0.05	1.92±0.08
>2000	7	(0.03±0.05)	2.09±0.14	(0.01±0.01)	2.10±0.13

Table 2 Arsenic species in surface sea water[a]

Station	Found/μg l⁻¹ As(III)	As(V)	As(org)	Total
1	0.25	1.55	0.17	1.92
4	0.17	1.60	0.15	1.92
5	0.21	1.50	0.20	1.91
6	0.21	1.50	0.13	1.84
7	0.15	1.70	0.10	1.95

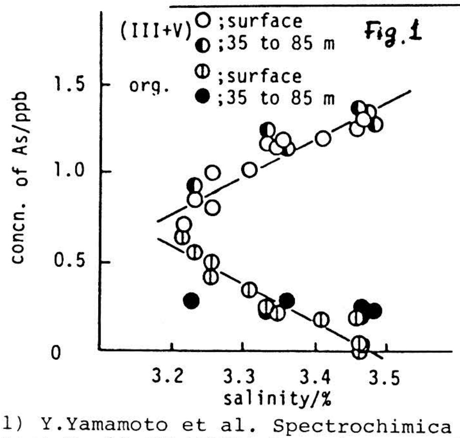
Fig.1

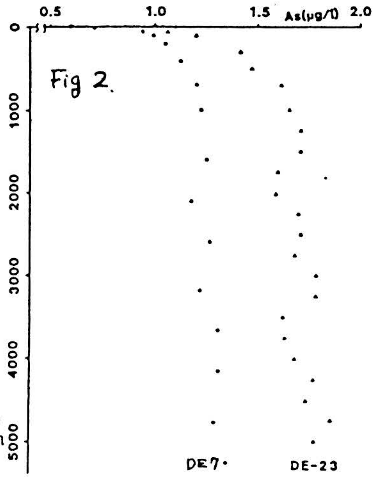
Fig 2.

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S3-19 CHARACTERIZATION OF ARSENIC IN MARINE LIFE BY HPLC WITH ICP/AES DETECTION

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By using inductively coupled plasma atomic emission spectrometry (ICPAES) as an element specific detector of high performance liquid chromatography (HPLC), it is possible to characterize chemical species of metals and metalloids with high sensitivity. The method is applied to the analysis of water-soluble arsenic compounds in marine life. Arsenic appears in various forms as shown in Fig. 1. Analytical standards of these are either synthesized or isolated and purified from natural samples. These compounds are separated with gel-permeation chromatography(Asahi-pak GS220), anion exchange chrcmatography(Nucleosil SB) and cation exchange chromatography (Nucleosil SA) and detected with ICP argon plasma emission spectrometry at the wavelwngth of 193.8 nm. Detection limit of these arsenic compounds ranged 20-50 ng as arsenic.

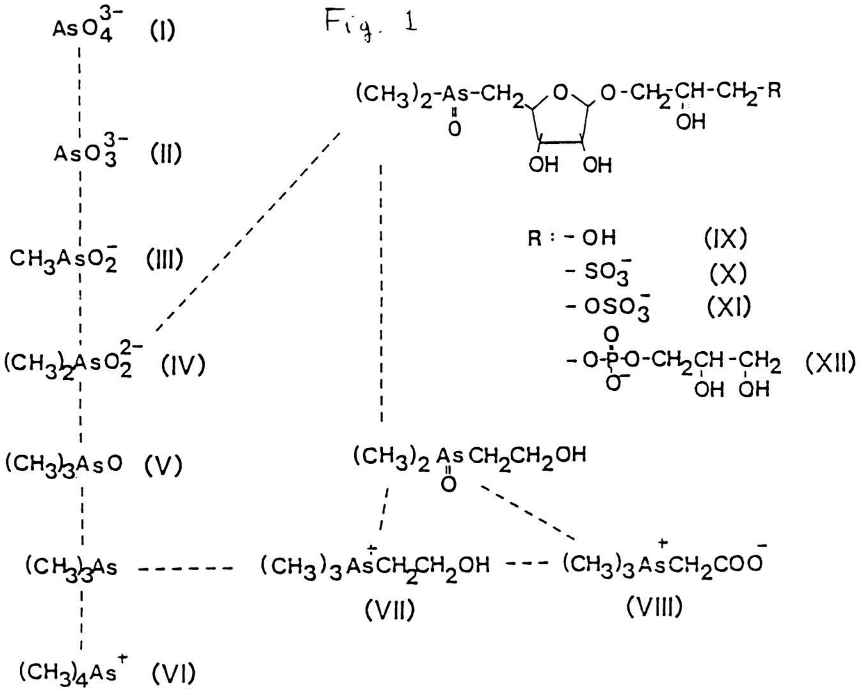
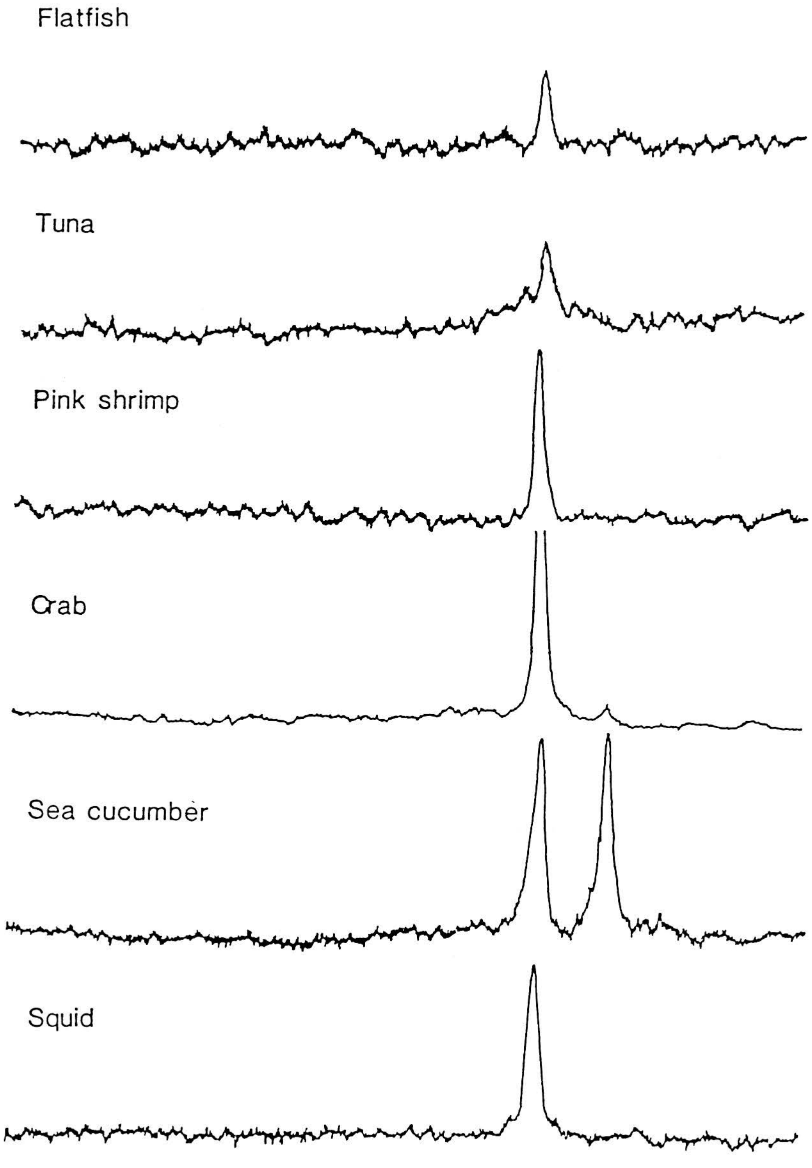


Fig. 1

Typical chromatogram is shown in Fig. 2. Major component of arsenic in marine animal was arsenobetaine. In shellfish arsenosugar and tetramethyl arsonium ion was identified. Marine algae contained arsenosugars.

Fig. 2



S3-20

DETERMINATION OF SMALL AMOUNT OF SILICON CARBIDE IN SOIL BY GRAVIMETRIC AND X-RAY DIFFRACTION METHODS

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Characterization and determination of pollutants in soils have been done usually by elemental analysis using various kinds of methods. However, the elemental analysis does not always give direct and enough information for resolution of the environmental problem, because the behavior or toxicity of any element depends on its chemical, physical and often crystallographic states. The authors have studied so far about the application of x-ray diffraction method (XRD) to the analysis of environmental samples such as airborne particulates [1-3] and soil [4] — the studies have given very useful informations.

Silicon carbide (SiC), which is not a natural product, is used in various fields of industries and sometimes found in soils around the works. In the previous paper [4] was described a method in which a large soil sample of 5 to 10 g was subjected to heavy liquid separation and chemical treatments to isolate SiC and polymorphic SiC was gravimetrically determined after examination by XRD. However, the method described above is a little laborious and time-consuming.

The present paper has been described simple x-ray diffractometric and gravimetric methods for 'the determination of small amount of SiC in soil samples using about 1-g sample.

Procedures are outlined as follows : The sample of about 1 g was ignited and treated with hydrochloric and hydrofluoric acids to remove organic matter, silicate and other soluble substances. [Procedure 1] After adding 1 mg of silicon powder as internal standard, all of the residue and silicon were transfered onto a membrane filter and followed by XRD analysis. [Procedure 2] The residue from the mineral acid treatments also was subjected to a heavy liquid separation to isolated SiC, which is gravimetrically determined using a ultramicro balance.

Results and discussion : One mg of SiC was successfully transfered onto the menebrane filter using a 0.05 % dextrin solution. Orientation effect of SiC on XRD was neglected when particle size of less than 400 mesh was used. Linear calibration curves of SiC were constructed of intensity ratios of SiC vs. Si using their strong diffraction lines. Appropriate combination of the intensity ratio made free from interference of foreign substances contained. A comparison will be done between XRD and gravimetric methods.

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S3-21

CHARACTERIZATION OF MOLYBDENUM IN NATURAL WATER

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Molybdenum is one of the bio-essential elements for many organisms and of interest from both environmental and biochemical viewpoints. Since the molybdenum content in natural waters is very low, a suitable concentrating technique and sensitive analytical method have been desired. The present work describes a simple and sensitive procedure for the determination of molybdenum by graphite furnace atomic absorption spectrometry with 8-quinolinol - DIBK extraction. The proposed method was applied to the determination of molybdenum in natural waters. It was found that the method might be used for the state analysis of molybdenum in natural water.

1. DETERMINATION OF MOLYBDENUM IN NATURAL WATERS

Immediately after sampling, the water sample was filtered through a membrane filter (pore size, 0.45 μm). The filtered water was divided into two aliquots: one will be for the "oxidized" aliquot, the other for the "untreated" aliquot. In the case of lake water, to 150 cm^3 of the "oxidized" aliquot, 5 cm^3 of concentrated nitric acid was added and the mixture was boiled for 3 h on a hot plate. After cooling, the mixture was neutralized with ammonium hydroxide solution. Three cm^3 of 0.1M EDTA solution, 3 cm^3 of 8-quinolinol solution and 3 cm^3 of 10% ammonium acetate solution were added to each of the "oxidized" and "untreated" sample aliquots, respectively, and the pH was adjusted to 3.5. The resulting solution was transferred to 200 cm^3 separatory funnel, and shaken with 2 cm^3 of DIBK for 6 min. DIBK phase was separated into test tube and dehydrated by centrifugation. The molybdenum absorbance was measured at the wavelength 313.3 nm by using 20 mm^3 of organic phase.

The total content of molybdenum was calculated by the analysis of "oxidized" aliquot and the difference of the measured values between "oxidized" and "untreated" aliquots was taken as the so-called "unextractable molybdenum".

2. INSTRUMENTAL CONDITIONS FOR GFAA MEASURMENT OF MOLYBDENUM

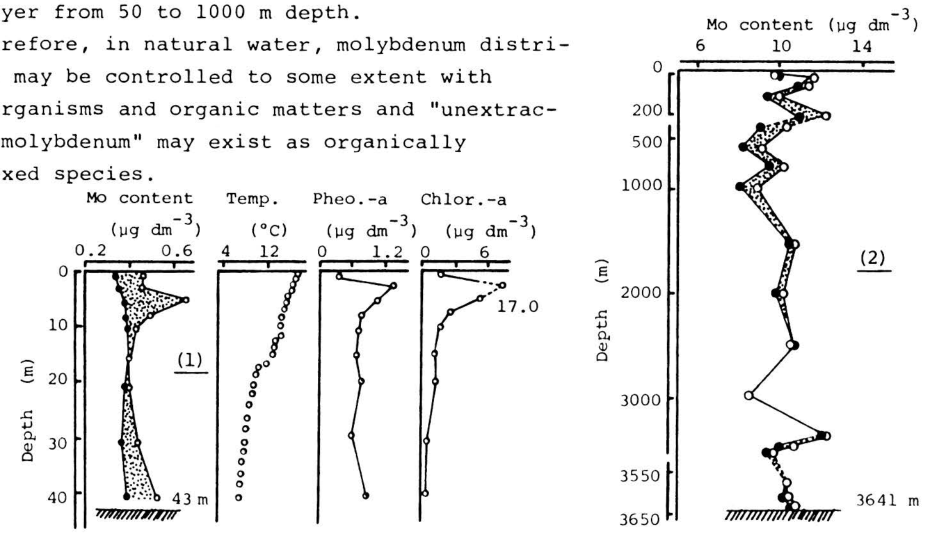
In the graphite furnace atomic absorption spectrometry, it is known that the molybdenum absorbance is significantly influenced by the heating conditions, since molybdenum forms a thermally stable interstitial carbide with graphite. Effects of heating temperature and time on molybdenum absorbance at charring and atomizing stages were investigated.

A constant absorbance for molybdenum-8-quinolinolate - DIBK extract was obtained over charring temperature from 400 to 600 °C, it was not influenced over the charring time range of 15 to 40 s at 500 °C. At the atomizing stage, the molybdenum absorbance increased with the increase of the temperature and time. When 20 mm^3 of sample solution was injected into the pyrolytic graphite furnace, the optimum conditions obtained at heating stages were as follows: drying for 30 s programmed from 150 to 200 °C, charring at 500 °C for 30 s, atomizing at 2800 °C for 15 s and cleaning at 2900 °C for 10 s.

3. OCCURRENCE AND CONTENT OF MOLYBDENUM IN NATURAL WATERS

Molybdenum seems to exist as two kind of chemical species in natural waters: one is easily extracted as molybdenum-8-quinolinolate complex with DIBK (extractable molybdenum); the other is unextractable as it is, unless the solution is oxidized with nitric acid before the extraction (unextractable molybdenum). Therefore, the recommended procedure was applied for the determination of molybdenum to reveal the vertical distribution of its occurrence in lake and sea waters. The results are shown in Figure. In Lake Biwa, the "extractable molybdenum" contents are in the range of 0.31 to 0.39 $\mu g\ dm^{-3}$, and it seems to be almost without change with depth. On the other hand, total molybdenum content varies significantly in upper and bottom layers. The vertical distribution patterns of the "unextractable molybdenum" content are similar to that of chlorophyll-a and pheophitin-a. In the Japan Sea, total molybdenum content are in range of 8.5 to 12.4 $\mu g\ dm^{-3}$, and the significant amounts of the "unextractable molybdenum" were also observed in the layer from 50 to 1000 m depth.

Therefore, in natural water, molybdenum distribution may be controlled to some extent with microorganisms and organic matters and "unextractable molybdenum" may exist as organically complexed species.



Vertical profiles of molybdenum, chlorophyll-a, pheophitin-a and water temperature in water samples. (1) Lake Biwa (May 24, 1984), (2) Japan Sea (Hakuho Maru Cruise KH-84-3, stn. AN-11)

—○— total Mo —●— extractable Mo ▨ unextractable Mo

S3-22

EVOLUTION OF VOLATILE SELENIUM COMPOUNDS FROM SOILS AND SEDIMENTS

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INTRODUCTION

Selenium is highly susceptible to biomethylation. Inorganic selenium compounds may be converted to volatile metabolites by microorganisms in soil and sediment. This reaction may be an important step in their transformation and transport in the environment. The release of volatile selenium compounds from soils and sediments is greatly influenced by the soil physicochemical characteristics including availability of selenium, carbon supply, temperature and water content as well as microbiological parameters. This investigation was carried out to ascertain the quantity that could be released to the atmosphere from sediments and to determine some of the factors affecting it.

EXPERIMENTAL

Ten grams of air-dried sediment was placed in a 250-ml flask fitted with a ground glass stopper having two glass tubes for air inlet and outlet. Five ml of sodium selenite solution containing 1000 μg/ml of Se(IV) was added to the sediment. The sediment samples were incubated at 20 C for a definite period. A stream of high-purity air was passed through the sample flask at the flow rate of 30 ml/min to sweep the volatile selenium metabolites present in the headspace into a 30-ml concentrated nitric acid trap. A hydride generation atomic absorption spectrometry was employed for the determination of selemium in the trap.

RESULTS AND DISCUSSION

No volatilization occurred from the autoclaved sediment samples spiked with sodium selenite and incubated them for 10 days. In the absence of soil moisture, no volatile selenium metabolites was detected in sediment.

These results indicated the essential role of microorganisms in the volatilization process.

As the microbiological nature of the process, the volatilization of selenium is temperature dependent. As can be seen from Fig. 1, active volatilization ended within 10-20 days after addition of sodium selenite. The quantities of selenium volatilized at 20°C during 40-day incubation periods summed to 7.5 % of selenium added initially. Total quantity of selenium volatilized at 20°C was more than two times that at 37°C and more than thirty times that at 65°C.

Selenium volatilization could be dependent upon the populations of the various microorganisms in the sediment. The sediment under the anaerobic condition exhibited a decrease in the production of volatile selenium. In this case, reddish deposits appeared on the surface of sediment, indicating that some selenite had been reduced to elemental selenium. Bacteria seem to play an important role in the reduction of selenite. No reddish deposits was observed in the autoclaved sediments. The sediment amended with streptomycin also produced no reddish deposits and released about 25 times more selenium metabolites than the original sediment. Fungi (and/or bacteria) seem to be responsible for the volatilization of selenium. A biologically active sediment grown about with fungi exhibited an increase in the production of volatile selenium.

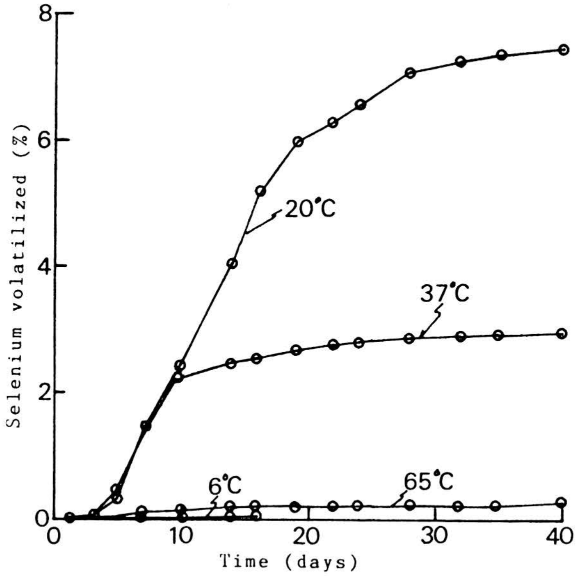

Fig. 1 Volatilization of selenium from sediments incubated at 6 C, 20 C, 37 C and 65 C.

The rate of volatilization of selenium from sediments incorporated with nutients such as ammonium sulfate, potassium dihydrogen phosphate, urea, oxalic acid, tartaric acid, glutamic acid and glucose was also evaluated in detail.

S3-23

SPECIATION OF MONOVALENT ANIONS IN WATER BY THE POLAROGRAPHY AT THE AQUEOUS/ORGANIC SOLUTIONS INTERFACE

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Since most of such anions as halides and their oxo-acid anions, NO_3^-, NO_2^-, BF_4^- and SCN^- are not easily reduced or oxidized in solutions, the ordinary redox voltammetry cannot be applied and the electrochemical determination of them had been limited to the potentiometry with the ion selective electrode, ISE. The potentiometry, however, is not appropriate for the precise determination because the potential in the method depends merely on the logarithm of the concentration of the objective ion.

As the results of the review of the voltammetry for the ion transfer at the interfaces of two immiscible electrolyte solutions (VITIES), which had been recently developed, we concieved that the precise determination of ions mentioned above is possible by the voltammetry based on the limiting currents, I_{LC}, which were proportional to the concentration of the ions. Not only the precise determination but also the speciation of ions is expected for the VITIES, because the half-wave potentials, $\Delta V_{1/2}$s, in VITIES depend on the ionic radii and charges.

In the present work, polarographic behavior for the ion transfer of monovalent anions, including halides, oxo-acid anions and derivatives of carboxylate or sulphonate anions at the water(W)/1,2-dichloroethane(DCE), W/nitrobenzene(NB) or W/chloroform($CHCl_3$) interface is investigated by the current-scan polarography with the electrolyte dropping electrode.

EXPERIMENTAL

The current-scan polarogrms were recorded following the method described previously [1].

RESULTS AND DISCUSSION

The half-wave potentials of the polarograms, $\Delta V_{1/2}$s, for halides, their oxo-acid anions, other oxo-acid anions, carboxylate anions and sulphonate anions from W to DCE were summarized in Table 1. The polarograms were reversible for most of the anions in Table 1 and, therefore, it was concluded that the transfer process of these anions are controlled by the diffusion of anions in the aqueous and/or organic solutions.

For inorganic anions, it was found that there exists a linear relation between $\Delta V_{1/2}$s and the reciprocal of the thermochemical radii (not the Stokes' radii), irrespective of the kind of organic solvent [2].

For *n*-alkane-carboxylate and -sulphonate anions, with the lengthening of alkyl chain by one methylene group, $\Delta V_{1/2}$ shifts about 37 mV more positive. By the substitution of carboxyl group for sulphone group, $\Delta V_{1/2}$s shift about

70 to 80 mV more positive. The $\Delta V_{1/2}$s for meta-nitro, -iodo and -methoxy benzoate anions are nearly equal to those for para-substituted benzoate anions, respectively. When these substituents are at ortho position, $\Delta V_{1/2}$s are less positive than those for respective substituents at meta- and para-positions. However, the $\Delta V_{1/2}$ for ortho-hydroxybenzoate anion is more positive than that for meta- or para-hydroxybenzoate anion.

The polarograms for the ion transfer for such monovalent anions as Cl^-, OH^-, IO_3^-, HCO_3^- and $CH_3(CH_2)_nCOO^-$($n \leqq 4$) and such divalent anions as MoO_4^{2-} and WO_4^{2-} from W to DCE merged with the final descent of the residual current when the concentration of the depolarizer was less than 10^{-3} M.

The limiting currents, I_{LC}, were proportional to the concentration of anions in W in the range $2.5 \times 10^{-5} - 10^{-3}$ for anions superscripted by *, $5 \times 10^{-5} - 10^{-3}$ for **, $10^{-4} - 10^{-3}$ M for ***.

In conclusion, since the $\Delta V_{1/2}$ depends on the character of the ion and the I_{LC} is proportional to the concentration of the ion as mentioned above, the polarography for the ion transfer at the interfaces of two immiscible electrolyte solutions is feasible for the speciation of monovalent ion in aqueous solutions.

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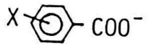
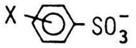
Table 1 The half-wave potentials, $\Delta V_{1/2}$s, of polarograms for the anion transfer

Anions	$\Delta V_{1/2}$				
	(V vs TPhE$^{1)}$)	X	$\Delta V_{1/2}$	X	$\Delta V_{1/2}$
IO_4^-	-0.12^{*}	H	-0.35^{***}	H	-0.28^{**}
ClO_4^-	-0.12^{*}	*p*-CH_3	-0.33^{***}	*p*-CH_3	-0.25_5^{**}
ReO_4^-	-0.11^{*}	*o*-NO_2	-0.31^{***}	*m*-NO_2	-0.19^{**}
BF_4^-	-0.15^{*}	*m*-NO_2	-0.27_5^{**}	*p*-NO_2	-0.19^{**}
I^-	-0.21^{**}	*p*-NO_2	-0.27^{**}	*p*-Cl	-0.20_5^{**}
Br^-	-0.33^{***}	*p*-Cl	-0.28^{**}	$CH_3(CH_2)_nCOO^-$	
ClO_3^-	-0.29^{**}	*p*-Br	-0.28^{**}		
BrO_3^-	-0.35^{***}	*o*-I	-0.30_5^{***}	n	$\Delta V_{1/2}$
NO_3^-	-0.29^{**}	*m*-I	-0.23_5^{**}	5	-0.33^{***}
ClO_2^-	-0.37^{***}	*p*-I	-0.23_5^{**}	6	-0.29^{**}
NO_2^-	-0.37^{***}	*o*-OH	-0.23_5^{**}	7	-0.25_5^{**}
CN^-	-0.38^{***}	*m*-OH	<-0.38	8	-0.22^{**}
$HCrO_4^-$	-0.28^{**}	*p*-OH	<-0.38	$CH_3(CH_2)_nSO_3^-$	
		o-OCH_3	-0.36^{**}		
		m-OCH_3	-0.33_5^{**}	n	$\Delta V_{1/2}$
		p-OCH_3	-0.33_5^{**}	5	-0.25^{**}
				6	-0.21^{**}
				7	-0.17_5^{*}
				8	-0.13_5^{*}

S4-01

THE LONG PATH NON-DISPERSIVE INFRARED ANALYZER FOR POLLUTANT GASES IN AMBIENT AIR

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A uniquely designed long optical non-dispersive infrared (NDIR) gas analyzer allows for direct measurement of the trace amount pollutant gases in ambient air with dramatically reduced several interference factors

1. Introduction

Many atmospheric trace gases absorb radiation to attenete light in the infrared effectively enough to measure their abundences urban dirty air with a reasonable optical path length. At background mixing ratios, however, this technique, a cuvett type NDIR, is not sensitive enough for trace gases. The auther have developed an optical system for long open path,material correlation measurement mechanism, operation and data handring system. This report is on the long path, 300 m, NDIR gas analyzer for direct measurement to the pollutant gases in ambient air which was desugned and constructed.

2. Optical system

Fig.1 shows a schematic lay out of the optical system of the NDIR. Double beams from an ir souce, one of which is stable reference beam by through an absorption sapphire cell contaning of a pure measurement gas at pressur 101.3 KPa, and another beam of measurement arrangement utilizing the optical null method with the changing transmittance disk filter are used. A both beams are alternately radiate to an ambient air after a parallel collimate by passing through an off-axis reflectin telescope. The Ne-He laser beam was use for seting and ajustment of reflectors. The retroreflector used in this system is cube corner. A ray of light incident on a corner is returned in the direction from which it came, regardless of the initial angle of incidence.

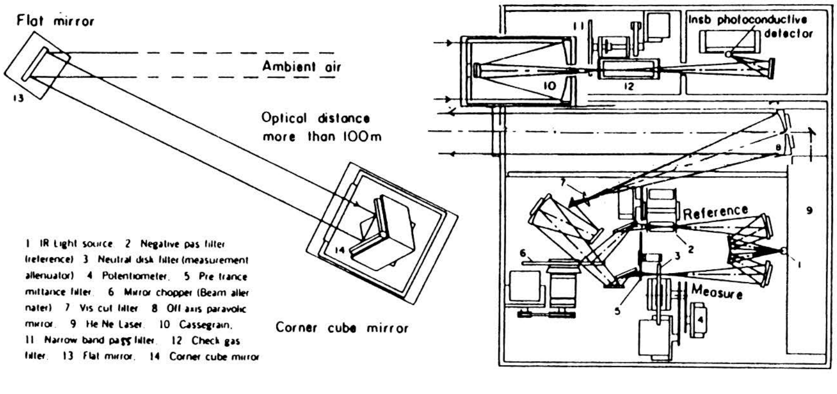

Fig. 1 Optical layout

The ray of good parallel collimate which can be observed enough energy on the detector in this optics practical up to about 400 m optical path in the ambient air. The receiver, consist of the large apparture, O 250 mm, cassegrain telescope, a narrow band pass filter and a heigh sensitive InSb detector with electric coolin element..

3. Measurement mechanism

In this NDIR analyzer, one of the features is mechanism of changing the absorption gas cell and narrow band pass filter even durin the rotation with contrered by the parsonal computor. Each wheel can hold 4 kinds of the above cell and filter. Since this analyzer can be obtaindfor 4 speies of gas in one cycle measurement time. The principle of measurement operation is based on the correlation of measurement gas in the atmospher and in the cell own absoption characteristics. Fig.2 shows a schematic representation of the beam which was traveled long path in the ambient air.

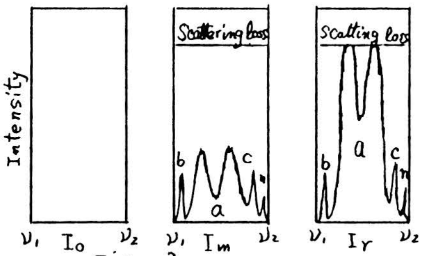

Fig. 2

The narrow band widgh is ν_1 to ν_2. I_m is

$I_m=I_0-\mu(A_aC_a+A_bC_b+A_cC_c+ --- A_nC_n)-S-M$

Where I_m is measurement beam, is optical path length, I_0 is ideal beam which was traveled μ m in the nothing absorption and scattering ambient air, a is absorption coefficient, C is concentration, a is the measurement gas, b,c -- n are interference gases, S is scattering coefficient to floating particules, and M is factor of optical materials.

The reference beam is I_r $I_r=I_0-\mu(A_aC_a+A_bC_b+A_cC_c+ --- A_nC_n)-A_{gc}-S-M$

Where A_{gc} is the absorbance of gas filed cell. A differece between I_m and I_r is $I_m - I_r = \mu(A_aC_a) - A_a(C_a + l\ C_{gc})$ Where l is optical path length of cell and C_{gc} is concentration of measurement gas in the cell at pressur 101.3 KPa. The gas cell is corresponding to 333 ppmv on the path length 300 m. This value is very large concentration than the trace gas values,and then the absorbance of gas cell can be use the reference standard that is not change by C_a. This NDIR is obtaind the relative data to I_r. It's make a calibration curve by using the gas cell of 1.00m path length with mirror system and a known 100 ppmv level's standard gases. The optical null measurement method can be eliminate the secular change of M.

4. Data handling system

The refractive index inhomogeneities in the ambient air spread the beam as it travels and cause intensity fluctuation at the reciver. The measurement data from potentio meter of disk filter is continually changing with feedback mechanism to energy balance between I_r and I_m. The data is only sampling when the both beam energys became equal, and add up in the seting time by the computor. The value of C_a is obtain from compare to the calibration data and the time averaged data after the correction of air density by temperature and pressuer.

The paformance of this NDIR gas analyzer will be describe and the results of recent test will be show at the symposium.

The auther would like to thank Fumio Asakawa for constructed this instrument.

S4-03 POLAROGRAPHIC STUDY OF ION TRANSFER ACROSS TWO IMMISCIBLE SOLUTIONS INTERFACE IN THE PRESENCE OF NON-IONIC DETERGENT

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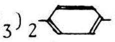
Voltammetry of ion transfer across the interface between two immiscible solutions has been recognized not only to be powerful for understanding the dynamic feature of the ion transfer reaction fundamentally but also to be very promising for the analytical application. One of the attractive application of this new method is the determination of such ions as alkali metal, alkalline-earth metal, heavy halide, and oxyacid ions and various organic ions to which ordinary redox voltammetry is not applicable. Another is the detection of a neutral organic substance, Y, based on the transfer of an ion, M^{n+}, in the presence of Y which forms ionic complex $(M{\cdot}Y)^{n+}$. Investigations in detail of various systems are required for wide application of the ion-transfer voltammetry to the field of analytical chemistry.

This paper deals with the ion transfer reaction in the presence of non-ionic detergents as an example of Y, which was studied by current-scan polarography using aqueous electrolyte dropping electrode, AEDE [1]. Such non-ionic and amphiphilic ethers as poly(oxyethylene)octylphenyl ethers, $(CH_3)_3CCH_2C(CH_3)_2$--$C(CH_2CH_2O)_xH$; Triton X-100(x=9.5), -305(x=30), or -405(x=40), have been known to form complexes with alkali and alkalline-earth metal ions, and have been used as an extractant and as an ionophore in the liquid membrane of the ion-selective electrode for these metal ions. Because Triton X-series detergents have an identical hydrophobic portion and different length of oxyethylene chain in the molecule, a systematic investigation can be carried out.

CURRENT-SCAN POLAROGRAPHY

The current-scan polarograms were recorded with use of a polarographic cell with four electrodes configuration which was identical with that described previously[1]. The aqueous electrolyte solution, w, was forced upward dropwise into the organic solution, o, through a Teflon capillary. The flow-rate of w was controlled by changing the height, h, of the w-level in the reservoir. The organic phase was 1,2-dichloroethane, DCE, containing tetraphenylarsonium dipicrylaminate, $TPhAs^+DPA^-$, as a supporting electrolyte. To obtain polarogram the current I was supplied and was scanned at 0.5 μA/s, and the potential difference at the w/o interface was detected.

TRANSFER OF METAL ION FROM w TO o IN THE PRESENCE OF Triton X

Polarogram 1 in Fig. 1 were obtained when w was 0.5 M KCl and o contained 5 x 10^{-4} M Triton X-100. Polarogram 2 is background curve recorded in the absence of Triton X. The anodic wave is observed in polarogram 1. Similar anodic wave appeared, when Triton X was added to w instead of o. The limiting current, i_l, of this wave was proportional to the square root of h indicating that the ion transfer reaction is controlled by the diffusion of one of species involved.

As shown in Fig. 2 the i_l of the anodic wave is proportional to the concentration of Triton X, C_T, over the range of 1 x 10^{-4} to 1 x 10^{-3} M, when Triton X is originally present in o (plot 1). If Triton X-100 is added to w, the i_l vs C_T plot displays two lines with different slopes (plot 2). The C_T corresponding to the intersection of two lines is 4 x 10^{-4} M. This concentration is very close to the critical micelle formation concentration of Triton X-100 in the aqueous solution.

The half-wave potential $\Delta V_{1/2}$ of the anodic wave shifts to negative with the increase of the concentration of potassium ion in w, $C_{K^+,w}$, and a relation between $\Delta V_{1/2}$ and log $C_{K^+,w}$ was found to be linear with a slope of -52 mV. The $\Delta V_{1/2}$ was not affected by C_T.

Consulting with results of the measurement of the drop time of AEDE under the polarographic condition,the reaction mechanism is proposed as follows. Triton X molecule diffusing from bulk solution phase adsorbs at w/o interface orienting its oxyethylene chain to w phase. The Triton X at the interface complexes with metal ion in w by forming ion-dipolar bond based on negative charge located at oxygen atom in the oxyethylene chain. The hydrophobic and cationic complex transfers into o, which gives anodic wave in the polarogram.

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Fig. 1

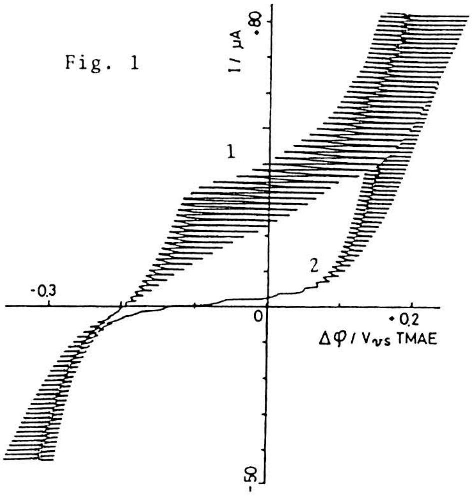
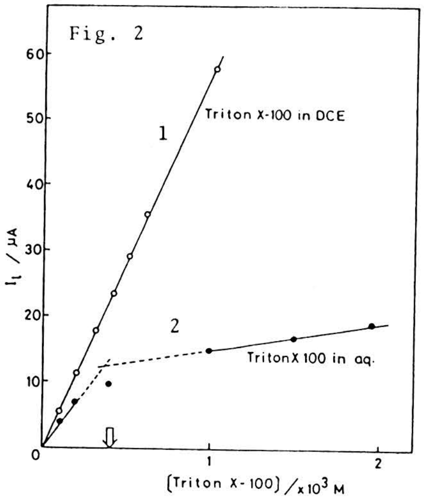


Fig. 2



S4-04

CHEMICAL SENSING BY ELECTRICAL OSCILLATION

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INTRODUCTION

Chemical sensors that can detect various molecular species at low concentrations would be useful. The electrodes developed so far, such as, pH electrodes, measure the activities of test ions in soultion as D.C. voltage differences genarated when electrodes are immersed in solutions of these ions. In taste and olfaction, in contrast, electrical impulses in the nerve are generated at sensory organs by various chemical stimuli, that is, chemical information on chemical structure and concentration is converted into frequencies of nerve impulses. Thus to mimic the molecular mechanism of recognition in sensory organs, an excitable artificial sensing system must be developed. In the present paper, we will show the posibilities of developing a new type of chemical sensor capable of distinguishing various chemical substances on the basis of information on the frequency and the shape of impulses.

CHEMICAL SENSING BY AN EXCITABLE LIQUID-MEMBRANE

It was found that a simple liquid membrane showed characteristic responces to inorganic ions, alcohols and sugars in a similar manner to biological chemoreceptive membrane (1-5). The liquid membrane consisted of an oil layer between two aqueous layers: that on left containing a cationic surfactant. This system showed sustained rhythmic oscillations of electrical potential of 200-400 mV with an interval in the order of 1 min. The frequency, amplitude and shape of impulses changed markedly with the addition of various chemical species to the aqueous phase. When optical active detergants were used, the frequencies of the oscillation were found to be different between chiral amino acids or sugars presernt in the aqueous phase (6).

NOVEL EXCITABLE LIQUID-MEMBRANE WITH ANIONIC SURFACTANT

It was found for the first time that oscillation occurred at an oil-water interface in the presence of anionic detergants (7). It will be demonstrated that the frequency, amplitude and shape of the electrical oscillation refect the chemical structure and concentration of added chemical species sensitively.

ELECTRICAL OSCILLATION INDUCED BY AMINE VAPOR

Studies were made on the electrical potential across a liquid membrane consisting of an oil layer, oleic acid, between aqueous solutions of NaCl and KCl. When the oil phase was exposed to amine vapor, the system showed periodic changes of electrical potential of 10-20 mV (8). It is suggested that this system can serve as a model of biological olfactory transduction.

ARTIFICIAL MEMBRANE MIMICKING NERVOUS MEMBRANE

It was found that spontaneous firing can occur for the membrane made of various lipid molecules having the oleyl moiety, monoolein, triolein and Span-80 (9-11). It is demonstrated that an Na^+/K^+ concentration gradient can cause excitation in a Langmuir-Blodgett film of dioleyllecithin (12,13). It is shown that the excitable artificial membranes developed by the present authors exhibit unique electronic properties; negative resistance, switzing and memory effect.

ELECTRICAL OSCILLATOR AS A NOVEL CHEMICAL SENSOR

Electrical oscillations across two platinum electrodes connected to an external circuit and immersed in a test soultion were measured (14,15). It is demonstrated that the frequency of oscillation reflects the concentration of the chemical species in the test soultion.

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S4-05

UPHILL TRANSPORT MEMBRANE ELECTRODES

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The mode of mass transfer often encountered in analytical chemistry is diffusion in which ions and molecules are transported in general following their concentration gradient. On the contrary, their exists a different type of mass transfer called uphill and active transports in which chemical species are transported against their concentration gradients. The latter mode of mass transfer appears to be attractive in view of analytical applications.

In biological systems, the transport of metabolites or nutrients through cell membranes occurs in many cases against their concentration gradient, i.e., by the so-called active transport. Rosenberg defined the active transport as a transfer of chemical matter from a lower to higher chemical potential(in case of charged components, electrochemical potential). We can achieve active transport and uphill transport by using artificial lipophilic liquid membrane systems. For driving uphill ion transport by artificial liquid membrane systems, we need to supply "energy" from outside, which is consumed with movement of ions against their concentration gradients.

In the present paper , a new mebrane electrode, what we call "Uphill Transport Membrane Electrode", will be described. The electrode can boost selectively virtual concentration of specific analytes by uphill transport against their concentration gradient across a built-in liquid membrane into its inner filling solution whose volume is purposely made very small. Cd(II), UO_2^{2+} and Cu(II) ion uphill transport membrane electrodes constructed here as illustrative examples utilize three different types of input energies, i.e., complexation, concentration gradient of other ions, and redox, respectively, for uphill transport of each analyte. Voltammetric detections were demonstrated for Cd(II) and UO_2^{2+} ion uphill transport

electrodes and a potentiometric detection for a Cu(II) ion uphill transport membrane electrode is also described as well as some other examples in terms of fundamental behaviors and a possible use for a new type of electrochemical sensors.

S4-06

STUDIES ON THE SUCCESSION STANDARD ADDITION METHOD WITH EQUIPOTENTIAL CHANGE IN ION-SELECTIVE ELECTRODE ANALYSIS

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The succession standard addition method with equipotential change is a new technique in ion-selective electrode analysis. It is similar to the potentiometric titration with preset end-point determined by a standard addition, and to the method of double standard addition. It is not necessary to determine the slope of the electrode response.

The calculating formulas of the method are introduced.

1. In the cells with liquid junction

Reference electrode // sample solution / ion-selective electrode

$$C_x = \frac{C_s V_1^2 (V_1 + V_2 + V_x)}{V_x \left[V_x (V_2 - V_1) - V_1^2 \right]} \qquad (1)$$

Where C_x and C_s are the concentrations of the determinand in the sample and standard, respectively. V_x is the volume of the sample solution; V_1 is the volume of standard solution firstly added; V_2 is the volume of standard solution added next V_1 while the difference between the potentials before and after the addition of V_1 is equal to that of V_2. It should be notice that several assumptions are made in the derivation of the equation (1).

(1) The change in the liquid junction potential of the reference electrode is negligible.

(2) The degree of complexation and the activity coefficient of the determinand remains constant.

(3) The concentration of the determinand and the final concentration should be within the linear response of the electrode.

2. In the cells without liquid junction

A ion-selective electrode / sample solution / B ion-selective electrode

Two kinds of A and B electrodes with same slopes are used as indicator and reference electrode. Both A and B concentrations can be determined continously by this method, only if their concentrations before and after the addition of the standards are within their own limit of linear response of the electrodes respectively. The calculating formula is

$$C_A = \frac{C_s V_1^2}{V_x (V_2 - V_1)} \qquad (2)$$

Where C_A and C_s are the concentrations of the determinand A in the sample and standard, respectively.

The dependence of relative error on the volumes of addition for the method can be derived from Eq.(2).

$$RE = \frac{dC_A}{C_A} = -\frac{dV_2}{V_2 - V_1} \qquad (3)$$

The difference of V_2 and V_1 shouldn't be too small in order to minimize the error of the method. As a general rule, the accuracy of the method is less than that of the volumetric analysis because of ($V_2 - V_1$)$<V_2$, whereas the **relative error** of the volumetric analysis, RE is equal to dV/V generally.

The examples of sulfide, sodium/potassium, chloride/fluoride in some water show that these methods are simple and rapid. The precision is higher than that of the equal volume method of double standard addition. The accuracy is improving with the increasing of the concentration of determinand in the sample solution. The results are given in Table 1 and 2.

Table 1. Determination of the sulfide in the cells with liquid junction

Taken/mol·l^{-1}	Found/mol·l^{-1} EVDA*	Found/mol·l^{-1} Proposed method	Recovery
1.0×10^{-6}	$(1.34 \pm 0.09) \times 10^{-6}$ **	$(1.43 \pm 0.02) \times 10^{-6}$ **	94 ± 12
2.0×10^{-6}	$(2.18 \pm 0.19) \times 10^{-6}$ **	$(2.37 \pm 0.09) \times 10^{-6}$ **	
5.0×10^{-6}	$(5.22 \pm 0.26) \times 10^{-6}$ ***	$(5.28 \pm 0.17) \times 10^{-6}$ ***	99 ± 7
1.0×10^{-5}	$(1.02 \pm 0.05) \times 10^{-5}$ ***	$(1.02 \pm 0.03) \times 10^{-5}$ ***	

* The equal volume method of double standard addition .

** Result of five determinations.

*** Result of nine determinations.

Table 2. Determination of potassium/sodium, chloride/fluoride in the cells without liquid junction (g/l)

Sample	Sodium			Potassium			Chloride		
	PM*	EVDA	AAS	PM*	EVDA	GM**	PM*	EVDA	MM***
Sea water	10.15♁ ± 0.16	9.98♁ ± 0.18	10.0	0.354♁ ± 0.002	0.353♁ ± 0.003	0.368	17.73♁♁ ± 0.06	17.70♁♁ ± 0.11	18.14
Lake brine	5.15	4.98	5.06	0.144	0.144	0.145	6.07	6.03	5.98
Bittern 1	30.3	29.5	29.0	22.8	22.8	23.1	245.0	245.0	242.6
Bittern 2	78.0	77.8	78.3	12.4	12.4	12.4	202.4	202.9	202.1

* Proposed method.

** Gravimetry using sodium tetraphenylborate.

*** Mercurimetry.

♁ Result of eight determinations.

♁♁ Result of nine determinations.

S4-07

NONCYCLIC POLYETHERS CONTAINING SULFINYL GROUPS; A NOVEL TYPE OF NEUTRAL CARRIER FOR ION-SELECTIVE ELECTRODES.

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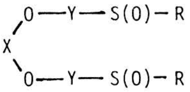
Liquid membrane type ion-selective electrodes based on neutral carriers are in focused for its excellent selectivity.

Some macrocyclic and noncyclic polyether-amides have been synthesized as neutral carriers for calcium ion-selective electrodes. Recently we have reported that noncyclic polyether-sulfoxides also exhibit calcium ion-selectivity.[1)] In this study we wish to report the preparation and the properties of the sulfur-containing neutral carriers derived from substituted catechols and diols to investigate the influence of the structure of the polyethers on the selectivity.

The general structure of the sulfur-containing neutral carrier in this study is shown bellow.

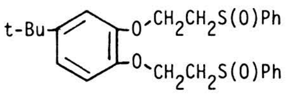


Ion-sensing PVC membrane was prepared from o-nitrophenyl octyl ether (NPOE), PVC, potassium tetrakis(4-chlorophenyl)borate (KTCPB), and the neutral carriers. The membrane was mounted on an ORION model 92 electrode body for electromotive force (EMF) measurement. Test solutions were prepared from analytical grade chlorides of alkali and alkaline earth metals and deionized water. The EMF response of the test solutions at 25 °c was measured with ORION model 701A digital ionalyzer. The potentiometric selectivity coefficient log $k^{pot}{}_{i,j}$ of the ion i over the ion j was determined by the separate solution method using the Nicolsky-Eisenman's equation (eq. 1), where R : gas constant, a' : ion activities, T : absolute temperature, Z : charge of the ion, F : Faraday constant.

$$E = E_i^0 + \frac{2.3RT}{Z_i F} \log \left[a_i' + \sum_{i=j} k_{ij}^{pot} (a_j')^{Zi/Zj} \right] \qquad \text{eq. 1}$$

The structures of the carriers are depicted in Fig. 1. The selectivity coefficients for Ca^{2+} are listed in Table 1.

Fig. 1 Noncyclic neutral carriers for ion-selective electrodes.



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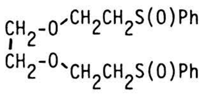

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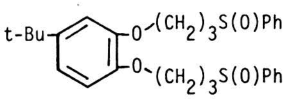

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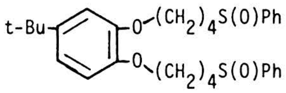

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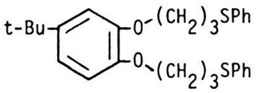

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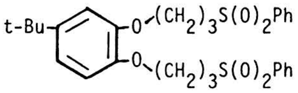

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Table 1 Selectivity coefficients of ion-selective electrodes based on neutral carriers 1-6.

	$\log k^{pot}_{CaM}$				
carrier	Mg^{2+}	Li^{+}	Na^{+}	K^{+}	H^{+}
1	-1.8	-1.3	-1.5	-1.4	-0.4
2	-1.2	-0.1	1.2	3.0	1.7
3	-2.1	-2.0	-3.0	-2.5	-1.3
4	-1.6	-2.2	-2.1	-0.5	0.4
5	-0.8	0.1	1.9	5.0	2.9
6	-0.7	-1.6	0.1	3.0	0.8

1,2-Bis(phenylsulfinylethoxy)-4-t-butylbenzene 1 showed Ca^{2+}-selectivity over other ions, whereas 1,2-bis(phenylsulfinylethoxy)ethane 2 showed no Ca^{2+}-selectivity. The rigid o-phenylene structure seems important for the appearance of the Ca^{2+}-selectivity.

The structure of the subunit Y also affect the potentiometric ion-selectivity. Carriers, 1, 3, and 4, with ethylene, trimethylene, and tetramethylene as subunit Y, respectively, showed Ca^{2+}-selectivity. 1,2-Bis(phenylsulfinylpropoxy)-4-t-butylbenzene 3 showed the best selectivity among them.

The oxidation number of sulfur atom is fatal for the appearance of the ion-selectivity. Carrier 3 showed an appreciable Ca^{2+}-selectivity, while carriers with sulfenyl groups 5, or sulfonyl groups 6 did not show any Ca^{2+}-selectivity. Thus, only the noncyclic polyethers containing sulfinyl groups showed Ca^{2+}-selectivity.

Other structural dependence on ion-selectivity such as the terminal group R, and the substituent of the o-phenylene subunit will be also presented.

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S4-08

A NOVEL AMPEROMETRIC AMMONIA SENSOR

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The polarizable interface between two immiscible electrolyte solutions (oil/water interface) functions as an ion-selective electrode (ISE) surface for both amperometric (or voltammetric) and potentiometric analyses of ions[1,2]. In other words, there are two kinds of ISEs; one is the amperometric (or voltammetric) ISE and the other is the potentiometric ISE. The former gives the current response proportional to the concentration of ion, whereas the latter the potential response linear to the logarithm of ion activity (concentration). The presence of an ionophore, which selectively binds an ion to form the hydrophobic complex in the oil phase, renders the oil/water interface ion-selective for the ion[2].

Ammonium ISEs: In this study, it is shown that the nitrobenzene(NB)/water(W) or poly(vinyl chloride)-nitrobenzene gel(PVC-NB gel)/water(W) interface, when dibenzo-18-crown-6 (DB18C6) is present in the NB or PVC-NB gel phase, works quite satisfactorily as an ISE surface for voltammetric analysis of NH_4^+ ion. The NH_4^+-ion transfer facilitated by DB18C6 at the NB/W or PVC-NB gel/W interface was investigated by means of cyclic voltammetry and potential-step chronoamperometry. The electrochemical cell studied was:

		I	II	III			
Ag	AgCl	0.1 mol dm^{-3} TBACl (W)	0.1 mol dm^{-3} TBATPB 0.02-0.10 mol dm-3 DB18C6 (NB or PVC-NB gel)	0.05 mol dm^{-3} $MgCl_2$ 0.25-1.0 mmol dm-3 NH_4Cl pH 7.3 or 9.7 (W)	AgCl	Ag,	(A)

where TBACl and TBATPB are tetrabutylammonium chloride and tetrabutylammonium tetraphenylborate, respectively. The aqueous solution (phase III) is buffered at pH 7.3 or 9.7, respectively, by dissolving 0.05 mol dm^{-3} L-histidine or 0.05 mol dm^{-3} L-lysine in the aqueous solution. In potential-step chronoamperometry, well-defined reversible polarographic waves of the NH_4^+-ion transfer at the NB/W interface were obtained in the presence of 0.05 mol dm^{-3} DB18C6, at $E_{1/2}$ = 298 mV and 328 mV at pH 7.3 and 9.7, respectively. The limiting currents were proportional to the bulk concentration of NH_4Cl in the aqueous solution. Well-defined cyclic voltammograms were also obtained for both the NB/W and PVC-NB gel/W interfaces. The peak currents were proportional to the bulk concentration of NH_4Cl. These results indicate that the interfaces work quite satisfactorily as the ISE surface for voltammetric analysis of NH_4^+ ion.

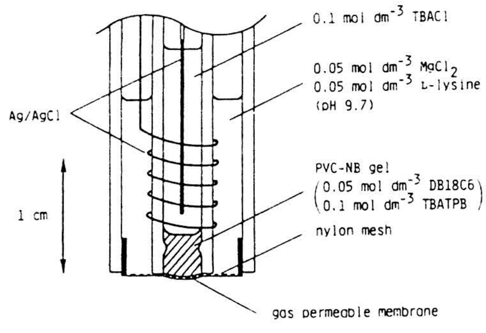

Fig. 1. Amperometric ammonia sensor

Ammonia Sensor: In order to construct an amperometric ammonia sensor for practical use, the NH_4^+-ion selective PVC-NB gel electrode containing 0.05 mol dm^{-3} DB18C6 was covered with a gas permeable Teflon membrane (Fig. 1). This sensor was used in the base solution (Na_2CO_3-H_3BO_3-KCl buffer, usually, pH 10.8), and an aliquot of NH_4Cl solution was injected into the base solution, which was stirred at adequate speed to obtain the current response independent of the stirring rate. The current response was proportional to the concentration of NH_4^+ ion in the sample solution, in the range between 2 and 2000 μmol dm^{-3} (Fig. 2). The current response changed with the pH of the base solution according to a S-shaped curve, indicating that the current depends on the fugacity (pressure) of NH_3 gas in equilibrium with NH_4^+ ion; $NH_4^+ \rightleftarrows NH_3 + H^+$ ($pK_a = 9.2$). The presence of inorganic ions (such as Na^+, K^+, *etc.*) and some organic ions (such as acetylcholine, choline, *etc.*) did not interfere with the analysis of ammonia with this sensor.

Urea Sensor: Urease was immobilized on the gas permeable membrane using glutaraldehyde and albumin. This urea sensor gave the current response proportional to the urea concentration between 1 and 2000 μmol dm^{-3} (Fig. 3).

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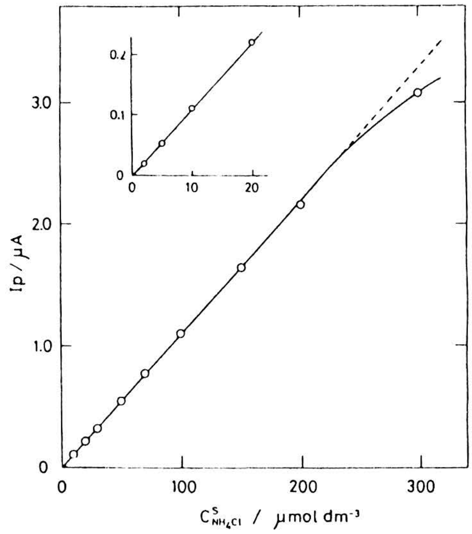

Fig. 2. Calibration curve of ammonia sensor
Electrode potential: 370 mV, pH: 10.8

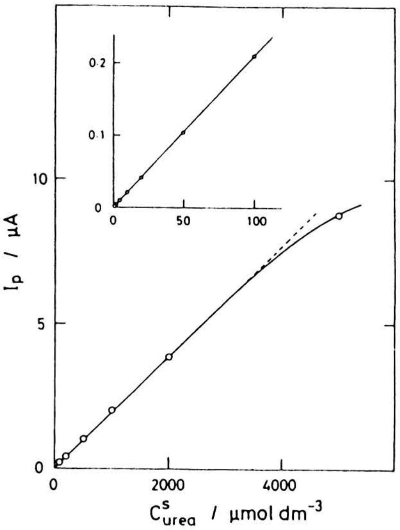

Fig. 3. Calibration curve of urea sensor
Electrode potential: 370 mV, pH: 9.0

S4-09

DETERMINATION OF HYDROGEN PEROXIDE BY ELECTROCHEMILUMINESCENCE

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In general, the electrochemiluminescence means that both cation and anion radicals electrolytically produced on electrode surface undergo annihilation, and that the reaction product emits light. Radicals are, usually, unstable in aqueous solution, so that this process is difficult to apply to the reaction in an aqueous medium. In this report we treated a different process, that is, the electrolytically oxidized substance reacts with other chemicals in the aqueous solution, and produced an excited state which emits light.

EXPERIMENTAL

Cyclic voltammetry(CV)

A model 312 potentiostat (Fuso) with a model HB 104 potential scanner (Hokuto) was used. The working electrode was a platinum disc electrode (2.1 mmϕ). The auxiliary electrode was a Pt wire and was referred to SCE. Temperature was controlled at 25± 0.1°C.

Emission

A model BLR-102 luminescence reader (Aloka) and a spectrophotofluorometer, RF-510 (Shimadzu) were used. The flow-cell is shown in Fig. 1.

RESULTS AND DISCUSSION

Luminol is known to emit light with some oxidants in basic solution. In this reaction an excited state of aminophthalic acid is formed. Here, instead of the chemical oxidation, luminol was electrolytically oxidized in a solution with lower pH, and light was emitted by the oxidized luminol which reacted with hydrogen peroxide.

CV of luminol and hydrogen peroxide

The reversibility and the oxidation, re-reduction potentials on Pt electrode were investigated by CV.

Luminol was oxidized to diazaquinone at the anodic peak potential of $E_p^a = 0.54 - 0.05(pH - 7.4)$ V vs. SCE. The electrode process was fairly irreversible, so that the re-reduction peak could not be observed.

Hydrogen peroxide was more easily oxidized than luminol. The anodic and cathodic peak potentials were $E_p^a = 0.45_6 - 0.06(pH - 7.4)$ V, $E_p^c = 0.10_6$

- 0.08(pH - 7.4) V.

Emission on the platinum electrode

At the potentials where the oxidation of luminol did not occur, no luminescence was observed. In the neutral solution, strong luminescence was observed at the applied potentials more than 0.6 V.

At the lower pH than 5.0, no luminescence was observed. At the pH higher than 6.0, the luminescence became stronger. At the pH higher than 9.0, the luminescence occurred even in the absence of oxygen or hydrogen peroxide.

In several seconds, after the application of the oxidation potential the luminescence showed maximum. And it also took time to disappear after the potential was off (Fig. 2). The half decay time was about 10 sec. From the result of CV, hydrogen peroxide was also oxidized to super oxide at the applied potential to oxidize luminol. The chemical reaction of super oxide with luminol oxide might occur at a distance from the electrode, and gave delay of light emission.

Luminescence spectrum by this electrolytic oxidation was obtained in the neutral solution; the maximum wavelength was 432 nm.

This method was applied to the trace determination of hydrogen peroxide using a flow injection method. The carrier solution contained 25.9 mM luminol in neutral solution, and the applied potential was 0.7 V. A straight calibration curve was obtained. The investigation to find the suitable conditions is now in progess.

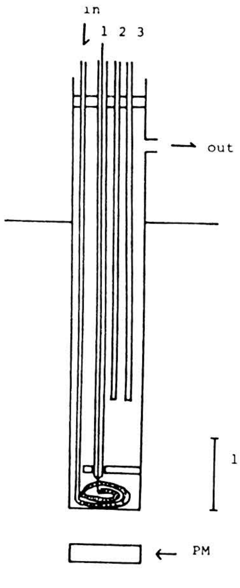

Fig. 1 Flow-cell
1. working electrode: Pt wire in polyethylene tube, 2. auxiliary electrode, and 3. reference electrode

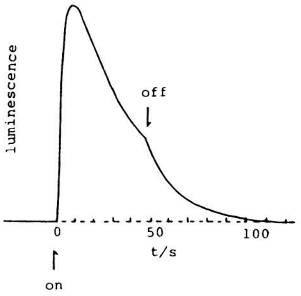

Fig. 2 Effect of applied potential (0.7 V) 3.53 mM luminol and 6.6 x 10^{-5}M hydrogen peroxide in pH 7.4 solution

S4-10

DETERMINATION OF CYANOCOBALAMIN BASED ON ITS COBALT CONTENT USING TETRATHIOCYANATOCOBALTAE(II) SELECTIVE COATED-WIRE ELECTRODE.

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A coated-wire electrode selective to tetrathiocyanatocobaltate(II) based on its salt of Brilliant Green has been developed and applied to cyabocobalamin (Vitamin B_{12}) assay via its cobalt content.

A dry silver electrode after treatment with concentrated hydrochloric acid and hydrophobizing with carbon tetrachloride was coated with electroactive mixture. The coating mixture was prepared from 2.5 percent of the electroactive salt, 24.5 percent of polyvinyl(-chloride) and 73 percent of 1-chloronaphthalene (plasticizer) in a minimum volume of tetrahydrofuran. The electrode responded rapidly to 10^{-5} - 5.0×10^{-2}M cobalt(II) containing sixty-fold or more molar excess of thiocyanate in acetic acid-acetate buffer (pH 4.7-5.8), with a negative slope of 28±1 mV per decade change of concentration. The life-time of the electrode has been extended to more than six months when tightly stored in a dropper bottle saturated with 1-chloronaphthalene.

One of its applications studied was the determination of cyanocobalamin, 25-500mg of the vitamin was boiled off with 15-20ml of aqua regia and the residue was filtered and washed with 25ml acetic acid-acetate buffer, diluted to 50-100ml volumetric flask with distilled water. A portion of the sample was exposed to UV radiation (254 nm) to photoreduce tervalent covalent to cobalt(II). Direct and standard addition methods with the coated-wire electrode relative to a calomel reference electrode were employed to determine as low as 50ppm of the vitamin with a maximum error of 5 percent.

S4-11

ION-SELECTIVE ELECTRODES BASED ON THIA-CROWN LIGAND AS NEUTRAL CARRIER

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Macrocyclic polythiaethers (thiacrown ethers) have been the focus of much research since recognition of their properties as selective complexes agents. They are typically uncharged compounds with an internal sulfur-donor-rich cavity capable of soft cation encapsulation with selectivity toward cation being primarily a function of the number of sulfur donors and ring size. Applications of thiacrown ether have been quite diverse, including characterization of some new mixed-valence complexes, the extraction of trace class b metals, and utilization in ion-selective membrane electrode. Increasing attention has been focussed on sensor as tools for biological application as well as for environmental analysis and separation of the ions. Their ion-selectivities often depend on thiacrown ether's cavity size. It is presumed that the thiacrown ethers, when they were dissolved in organic solvent or incorporated into membranes, can be behave as ionophores selective for particular metal ion. We wish to report the development of sensors which are coated with thiacrown-PVC on a spectroscopic graphite rod, a platinum wire and PVC membrane kit, and which are highly selective for the mercury(II),copper(II),and thallium(I) ions. The use of sensor in the potentiometric titration of mercury(II) solution was also examined.

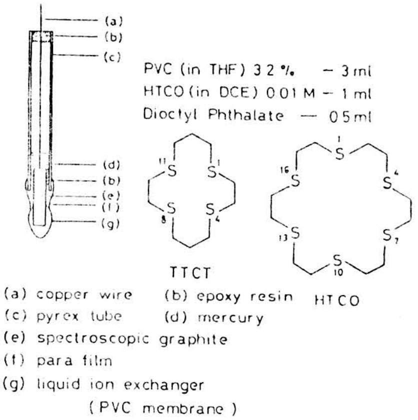

Fig.1 Schematic diagram of HTCO-CGMSE.

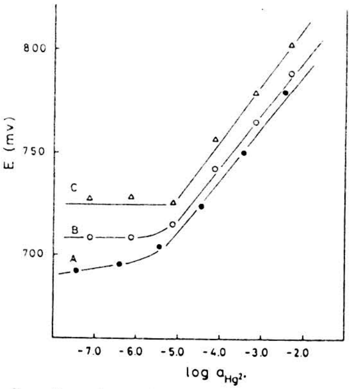

Fig. 2 Dependence of HTCO-CGMSE potential on Hg(II) activity in solution containing interfering ions with concentration of 10^{-3} M. A: Hg(II) B: Hg(II)• Cd(II) C: Hg(II)• Co(II)

1. CONSTRUCTION OF ELECTRODES.

The mercury(II) electrode coated with HTCO (1,4,7,10,13,16-hexathiacyclo-octadecane) or TTCT (1,4,8,11-tetrathiacyclotetradecane)-PVC on spectroscopic graphite rod(HTCO- or TTCT-CGMSE) was prepared as follows. Solid ,cylindrical segment (1 cm long,0.5 cm diameter) was cut from a plate of highly-ordered spectroscopic graphite rod. The cylindrical segment was prepared so that the basal planes of graphite might be perpendicular to the axis of the cylinder. Prior to use, the surface of the rod cleaned by polishing a 600 mesh carborundum and deer skin,and rinsed with acetone and allowed to dry. It was sealed to the ends of glass tubing. Electrical contact was made to the rear face of rod using several drops of mercury. A schematic illustration of finished electrode is presented Fig.1. Coated wire ion-selective electrodes (Tl^+ and Cu^{2+}) were prepared as reported[1]. Tip membrane electrode using DKK kit was prepared as reported in making of Thomas PVC electrode.

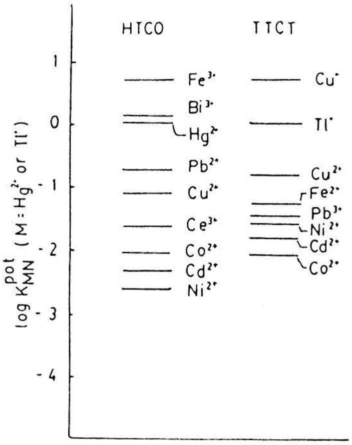

Fig.3 Selective coefficients, log K_{MN}^{pot} .

2. HTCO-CGMSE AND CW (Tl^+ and Cu^{2+})-SELECTIVE ELECTRODE

A typical calibration curve is shown in Fig.2. The electrode exhibited the Nernstian behavior over the activity range of 10^{-2} to 10^{-5}, the slope was 26 mV/decade, and the detection limit near $10^{-6.3}$. The electrode was much more sensitive and reproducible for the mercury(II) ion than response of TTCT-CGMSE (slope: 14 mV/decade). HTCO was found to be a useful sensor material for mercury(II) ion. Comparison of all data obtained so for on the extraction and complex formation of mercury(II) by thiacrown ethers shows that the HTCO with mercury(II) forms complex of higher stability. The stability indicates that macrocyclic hole of HTCO is just large enough to fit the mercury(II) inside the hole. This fact reflects to rapid response and good potential stability. Extraporation of the rectilinear portion of this curve gave intersection at 920 mV vs. Ag/AgCl. CW Tl^+ and Cu^{2+}- selective electrodes containing TTCT responsed in a pseud- Nernstian (10^{-2} to 10^{-5}, slope: 46 mV/decade) and in a Nernstian (10^{-2} to 10^{-6},slope: 27 mV /decade) ways, respectivly.

3. THE EFFECT OF AN INTERFERING CATIONS

Fig.3 shows logarithmic selective coefficients for carrier HTCO and TTCT. The interferig ions for HTCO-CGMSE in the order of decreasing interference are: $Fe^{3+} > Bi^{3+} > Pb^{2+} > Cu^{2+} > Ce^{3+} > Co^{2+} > Cd^{2+} > Ni^{2+}$.

4. COMPLEXIMETRIC TITRATION

Fig.4 shows titration curve of Hg(II) titrated with EDTA used HTCO-CGMSE as indicator Electrode. This electrode was successful for use in the titration.

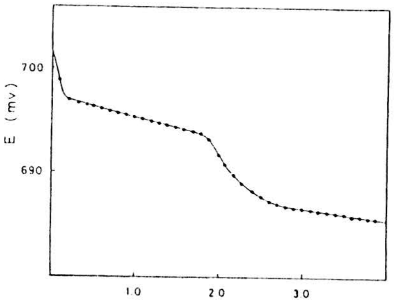

Fig.4 Titration curve of a 20 cm^3 containing 0.001 M total mercury(II) nitrate at pH 3.40(acetate buffer) with a 0.01 M EDTA solution.

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S4-12

CADMIUM-113 NMR SPECTROSCOPY AS A TOOL FOR STATE ANALYSIS OF CADMIUM(II) IN SOLUTION

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The chemistry of d^{10} metal ions (Cd^{2+}, Zn^{2+}, Cu^{+}, etc.) has become of interest in recent years because of their important characteristics of possesssing properties of both transition and nontransition elements. One of the major problems in the cadmium chemistry is the lack of the state analysis technique. ^{113}Cd NMR technique has recently been attempted to provides a powerful tool for the state analysis of Cd(II) compound in solution. However attempts at deteiled correlation of the solution ^{113}Cd NMR spectra with Cd(II) compound structures are hampared by the first chemical exchange of the compounds. We attempted to reduce the chemical exchange of labile Cd(II) compounds and to determine simultaneously the seven species in the equilibrium state by employing cooling of nonaqueous solution with temperatures down to -90 °C.[1]

SIMULTANEOUS DETERMINATION OF SEVEN Cd(II) COMPLEXES IN THE EQUILIBRIUM STATE. The Cd(II) complexes with monodentates such as imidazole (im) do not have a large stability constant. In solution, some species coexist at equilibrium. Reduction of the chemical exchange in Cd(II) complexes with im by cooling is illustrated in Fig. 1, for which an ethanol solution of 0.5 M $Cd(ClO_4)_2$ and 1.5 M im was examined by ^{113}Cd NMR from 23 °C to -90 °C. At 23 °C, a single resonance (Fig. 1 a) was observed, indicating rapid chemical exchange. As the temperature was lowered, the resonance broadened(Fig. 1 b) and then resolved into two distinct resonances (Fig. 1c and d). The stepwise formation of the im complexes progresses from solvated Cd(II) ion with an increase in the concentration of im. This progression is illustrated in Fig. 2. On the basis of the stability constants and Scheme I, ^{113}Cd chemical shifts can be assigned as follows: A, Cd^{2+}; B, $Cd(im)^{2+}$; C, $Cd(im)_2{}^{2+}$;

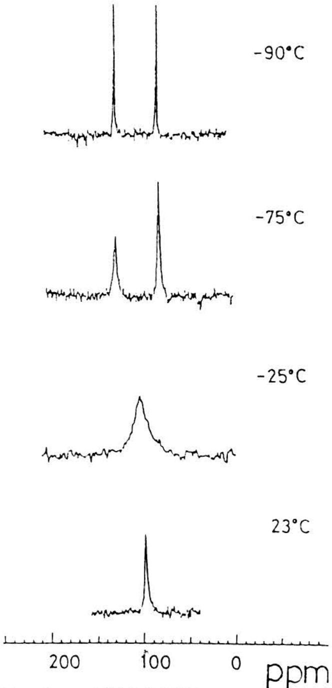

Fig. 1 ^{113}Cd NMR spectra of an ethanol solution of 0.5 M $Cd(ClO_4)_2$ and 1.5 M imidazole The ref. was 0.5 M $Cd(ClO_4)_2$

D, $Cd(im)_3{}^{2+}$: E, $Cd(im)_4{}^{2+}$; F, $Cd(im)_5{}^{2+}$; G, $Cd(im)_6{}^{2+}$. The chemical shift of $Cd(im)_6{}^{2+}$ is in good agreement with the solid ^{113}Cd NMR chemical shift.

Scheme I

$$Cd^{2+} + 6im \rightleftharpoons Cd(im)^{2+} + 5im \rightleftharpoons Cd(im)_2{}^{2+} + 4im \rightleftharpoons Cd(im)_3{}^{2+} + 3im$$

$$Cd(im)_3{}^{2+} + 3im \rightleftharpoons Cd(im)_4{}^{2+} + 2im \rightleftharpoons Cd(im)_5{}^{2+} + im \rightleftharpoons Cd(im)_6{}^{2+}$$

The percentages of $Cd(im)_n{}^{2+}$ (n=0~6) were calculated from the peak area (Fig. 3). This is the first case in which the seven species in the equilibrium state were successfully determined.

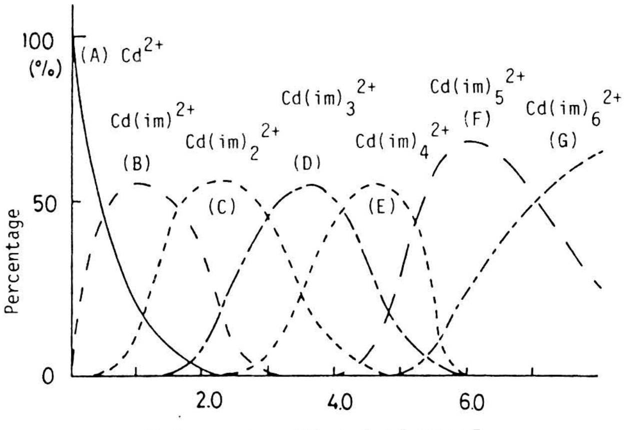

Fig. 3 The precentage of mole fractions of Cd(II) species present at [im] / [Cd^{2+}] mole ratio of 0-6.

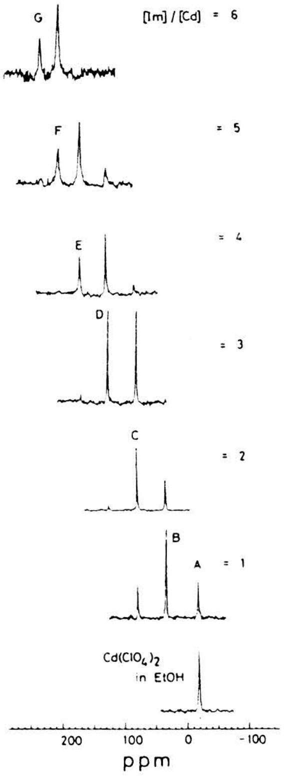

Fig. 2 ^{113}Cd NMR spectra of ethanol solutions at -90 °C. All solutions contain 0.5 M $Cd(ClO_4)_2$. The mole ratio of imidazole to $Cd(ClO_4)_2$ was varied from 0 to 6. The ref. was 0.1 M $Cd(ClO_4)_2$.

COMPARISION OF SOLUTION ^{113}Cd NMR SPECRTA WITH THE SOLID NMR SPECTRA. One of the most important advantages of ^{113}Cd NMR technique is its applicability to both solutions and solids. Comparision of ^{113}Cd chemical shifts between the solution and the solid NMR is especially noteworthy in connection with the effects of solvent, packing, and counteranion upon the structure of the Cd(II) complexes. Plot of the solution ^{113}Cd chemical shifts of Cd(II) complexes with 1,10-phenanthroline and the derivatives against those of the solid give a good linear correlation with the slope equal to 1. The good linear correlation clearly demonstrates that the structures of these Cd(II) complexes in solution are substantially the same as those in the solid state when ligand dynamics are unimportant in the solution.

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S4-13 NEW BOD SENSOR UTILIZING A FUNCTIONAL POLYMER WHICH CAPTURES MICROORGANISMS ALIVE

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The biochemical oxygen demand (BOD) is one of the most important and widely used index of organic pollution. The conventional method of BOD determination requires a five-day incubation. Recently, however, Suzuki et al. (1) proposed a method for rapid estimation of BOD using a microbial electrode, which consisted of immobilized living whole cells of yeast and an oxygen electrode. In this case, the living cells were immobilized by entrapment inside polymer matrices. On the other hand, a recent publication from this laboratory (2) described a novel and remarkable ability of cross-linked poly(N-benzyl-4-vinylpyridinium halide) to remove bacteria from water. This insoluble pyridinium-type polymer captures many bacteria alive by contact with them. As an extension of this work, we attempted to use living microorganisms immobilized on this insoluble pyridinium-type polymer for the microbial electrode of the BOD sensor. In this case, the procedure of immobilization is much easier than the entrapping method used by Suzuki et al., the immobilized living cells are kept in direct contact with the sample solution, and various sort of microorganisms can be easily used for the BOD sensor.

A microbial electrode was prepared by injecting suspension of microorganisms into the sensor system, which consisted of the insoluble pyridinium-type polymer and an oxygen electrode. The polymer was used in a beads form. Escherichia coli and Saccharomyces cerevisiae were used as microorganisms for the sensor. Aqueous solution containing glucose (150 mg/l) and glutamic acid (150 mg/l) was employed as a standard solution of five-day BOD of 220 mg/l for the BOD sensor, according to Japan Industrial Standard.

When a sample solution was injected into the sensor system, current of the electrode decreased with time until steady state was reached. A Proportional relationship was observed between the current decrease and the concentration of organic substrates. The sensitivity, i.e., slope of the relationship was found to depend upon the content of pyridinium group in the insoluble pyridinium-type polymer, and the maximum sensitivity was observed when the polymer contained about 2 mmol/g of the pyridinium group.

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S4-14

A PROPOSAL OF INTEGRATING MEASUREMENT OF HYDROGEN IONS IN THE ACID RAIN BY USE OF COPPER(II) OXIDE

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There are many reports about the influence on the natural environment by acid rain [1]. Recently, environmental disruptions by acid rain are reported on masscommunications [2]. The measurement of total acidity in the rain is generally given by titration method [3]. The new method for measurement of total hydrogen ions in the solution was investigated.

Copper(II) oxide is stable in the air and reacted following equation in the acid solutions such as H_2SO_4 or HNO_3.

$$CuO + 2H^+ \longrightarrow Cu^{2+} + H_2O$$

The pH value of acid solution with copper(II) oxide was came up to about 6 with time, and its pH value was stable to this range. This phenomenon means that the dissolving reaction of copper(II) oxide is almost stopped in this pH range. The measured value of Cu^{2+} ion concentration [4] was in proportion to loss of H^+ ions which was calculated from pH change in the solution. Furthermore, loss of H^+ ions in the solution was also in proportion to weight loss of copper(II) oxide. The experiments were carried out in H_2SO_4 or HNO_3 solution. The same results were biven by both solutions.

The weight loss of copper(II) oxide was indicated hydrogen ions in the acid solution. This method is useful for measurement of totalacidity in the acid rain which is due to SO_x or NO_x in the atmosphere. And this method is simple and convenience.

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S4-15

DEGRADATION OF NTA AND Cu(II)-NTA COMPLEX BY THE OXIDATION WITH COMBINED USE OF LEAD DIOXIDE SUSPENSION AND OZONE

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INTRODUCTION

We have recently introduced hydrous lead dioxide (HLD), freshly produced by hydrolysis of lead tetra-acetate, as a collector for trace amounts of metal ions and as a solid oxidizing agent. The adsorption behavior1) of some metal ions on HLD and the redox reaction2,3) of HLD with complexing agents such as EDTA, NTA and IDA have already been reported. In addition, the degradation of these complexing agents and those metal complexes and the collection of metal ions from those metal complex solutions such as Bi(III)-EDTA and Fe(III)-NTA have been also studied.4,5,6)

In this study, the degradation of NTA and Cu(II)-NTA complex by oxidation with combined use of HLD and ozone, and especially the collection of Cu(II) ion from Cu(II)-NTA complex solution at about pH 7 were investigated from the view point of environmental chemistry.

EXPERIMENTAL

The stock solutions of 0.01M NTA, 0.01M Cu(II)-NTA and 0.05 M Pb(II) were prepared from reagent grade NTA, $Cu(NO_3)_2$, and $Pb(NO_3)_2$, and accurately diluted as required. A 0.05M lead tetra-acetate solution and water used were the same as those described in previous paper.4,6)

The polarograph and incubator used were those employed previously.4) Nippon Ozone O-3-2 ozone generator was used with the high purity oxygen gas.

RESULTS

Degradation of Cu(II)-NTA by oxidation with HLD.

The HLD, prepared by hydrolysis of lead tetra-acetate, and an appropriate amount of Cu(II)-NTA in buffered solution at a fixed value of pH were shaken for 1 hr at 30°C, and HLD was filtered off. The concentrations of NTA6) and Cu(II) ion in the filtrate were determined polarographically.

The effect of pH on the decrease in NTA and Cu(II) concentrations (initial value 1×10^{-4} M) is shown in Fig.1. And the curve obtained in the earlier study5) with regard to the degradation of Fe(III)-NTA is also shown in Fig.1.

In the case of the adsorption of cu(II) ion on HLD,1) almost 100 % decrease in Cu(II) concentration was observed at pH higher than 6, while, in the case of Cu(II)-NTA complex, there was only about 70 % decrease in Cu(II) concentration at about pH 7.

On the other hand, in these experiments, we could easily oxidize the

Pb(II) produced in the process of the degradation to lead dioxide by passing the ozone gas into the solution at about pH 7. Therefore, the combined use of HLD suspension and ozone was further examined.

Degradation of Cu(II)-NTA and NTA by oxidation with combined use of HLD and ozone at about pH 7.

A cylindrical tube (33 mm in diameter and 300 mm in height) fitted with a silicone rubber stopper was used as the reaction vessel. A 200 ml of Pb(II) solution in buffered solution at about pH 7 was placed in the tube and the ozone gas (39 mg O_3/l) was passed through the solution for 20 min at a flow rate of 0.7 l/min. After Pb(II) was completely oxidized to lead dioxide, a known amount of NTA or Cu(II)-NTA complex was added into the suspension, and then the ozone gas was continued to be passed through the mixture. An aliquot of the mixture collected at regular intervals was filtered, and the concentrations of NTA and Cu(II) ion in the filtrate were determined polarographically.

The relation between the decrease in NTA or Cu(II) concentration and time for ozonolysis is shown in Fig.2.

In addition, when 1x10^{-4}mole NTA was added to the HLD suspension [1x10^{-4} mole Pb(IV)] and then the ozone gas was passed through the mixture, almost 100 % decrease in NTA concentration was observed after about 10 min.

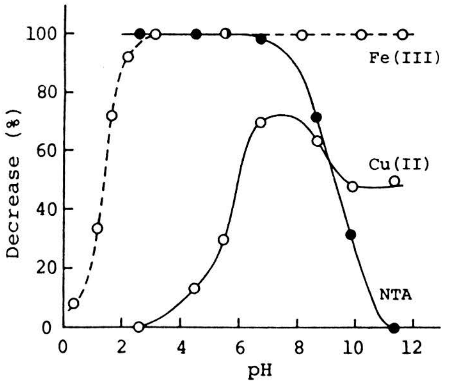

Fig.1 Effect of pH on the decrease in amount of NTA, Cu(II), or Fe(III).

Cu(II)-NTA, Fe(III)-NTA, 1x10^{-4} M, HLD : 5x10^{-4} mole(total vol. : 100 ml), shaking time : 1 hr, temp. : 30 °C

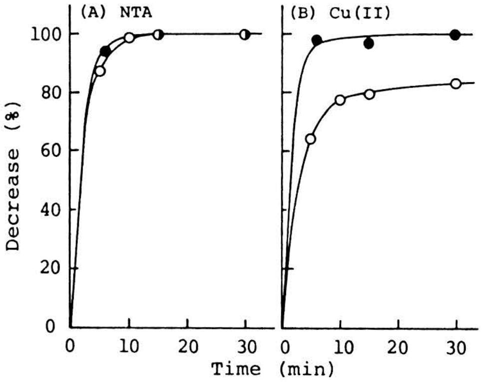

Fig.2 Relation between the decrease in amount of NTA or Cu(II) and time for ozonolysis.

Cu(II)-NTA : 1x10^{-4} M (●), 5x10^{-4} M (○), HLD : 1x10^{-3} mole (total vol. : 200 ml), O_3 gas : 39 mg/l, flow rate : 0.7 l/min

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S4-16 ANALYTICAL CAPABILITIES OF SOLID-BODY DETECTORS BASED ON SOLID ELECTROLYTES FOR DETERMINATION OF LOW CONCENTRATIONS OF HYDROGEN IN THE AIR

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Solid electrolytes with proton conductivity can be applied for development of hydrogen sensor transformers.

In the present paper a number of solid electrolytes with proton conductivity was synthesized, and investigations were carried out with the purpose to obtain comparative characteristics of solid electrolytes and to assess the possibility to develope highly sensitive hydrogen detectors on their basis.

Detectors from solid electrolytes, containing $ZrO_2 \cdot P_2O_5 \cdot H_2O \cdot Li_2O$, etc. were made by cool pressing. Pt and Pd of various grain sizes were applied as catalytic covers. Measurements of the analytical signal of detectors were carried out in the mode of current generation. The value of the signal amplitude, the current integral value, the signal duration were recorded by an automatic instrument, the gas sample being introducted in the impulse manner. The recorded data were further computerized. Hydrogen concentration in the air varied from 0.1 to 10000 ppm, temperature changed from 20° to 80°C. The investigations have allowed to establish, that the analytical signal parameters,,formed by detector(amplitude, stability in time, reproducibility, etc.) are essencially determined by the state of water, contained in the structure of the solid electrolyte membrane, and on its surface. The observance of certain conditions of the technology of the sensors' production has made it possible to develope detectors determining hydrogen in the air with the maximum sensitivity of 0.1 ppm, linear range of 0.1-1000 ppm, selectivity in relation to CO, CO_2 and CH_4 - not less than 10^3, The detector works at a temperature of 20-50°C, with the inertia varying from 30 to 40 c.

In the conclusion reasons and possible mechanisms of the formation of the potential barrier for proton transfer, determining time degradation of detectors based on solid electrolytes with proton conductivity, are discussed.

S4-17

MICROBIAL RESPIRATION SENSORS FOR ENVIRONMENTAL CONTROL

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A wide range of microbial sensors consisting in immobilized whole cells coupled to amperometric oxygen electrodes has been developed /1, 2, 3/. These biosensors use the assimilation of organic substances by the microorganisms reflected by an increase of the respiration rate. The change of respiration rate after substrate addition is followd with oxygen electrodes. The principle of the microbial sensor was successfully used for the determination of peptides /4/ (e.g. peptide hormones and the new dipeptide sweetener aspartame), of ammonium ions, alcohols, glutamic acid, alpha-amylase activity /5/ as well as for determination of complex parameters like the amount of assimilable substances in bioreactors /3/ and the biological oxygen demand (BOD) of waste water.

BOD is a widely used parameter for the determination of biodegradable organic compounds in waste water. The conventional BOD-test takes 5 days to be carried out making it unsuitable for real process control. Rapid BOD-estimations are only possible using microbial sensors. The first BOD-sensor was developed with Trichosporon cutaneum by Karube et al 1977 /1/ showing a response time of 20 min.
In contrast, our respiration sensor reveals response times of 8 and 15 s, respectively, using immobilized cells of Bacillus subtilis and Trichosporon cutaneum. A good correlation was observed between the current change of the respiration sensor and the 5-days-BOD (glucose-glutamic acid-standard).

The minimal measurable BOD was 2.2 mg/l for the sensor with B. subtilis and 4.4 mg/l for Trichosporon cutaneum sensor (dilution of the sample 1 : 25).

Future directions of development of microbial BOD sensor for environmental control might be:

- the use of mixed populations of immobilized microorganisms
- the use of new immobilization techniques (e.g. entrapment with prepolymer methods /6/)

- development of enzyme-microbial-hybrid sensors/5/ for measurement of high-molecular substrates in waste water

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S4-19

PRECONCENTRATION OF IONS INTO A LANGMUIR-BLODGETT FILM-MODIFIED-GLASSY CARBON ELECTRODE

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In the last decade, the chemical modification of electrode surfaces has been intensively investigated as a means for making various functional electrodes.[1,2] In these modified electrodes, a high density of the immobilized functional species, a regularity in the molecular organization, and a ultrathiness of the coated film on the electrode surface are crucial importance. Very recently the LB method has been utilized to fulfill these requirements by us.[3-5] Among them the study of metal clusters formed by reduction of the corresponding metal ions which were originally confined in the form of counter ions in the ionic LB film has been one of the most interesting subjects, for the metal clusters can be used as highly efficient electrocatalysts.[3]

In the present work, we have applied such an electrochemical reaction of ions concentrated in the LB film to the selective detection of metal ions in solution.

An anionic amphiphile, an arachidate anion, was used to concentrate polyvalent cationic metal ions such as Cd^{2+} in the presence of monovalent Na^+ ions. An alkyl derivative of imidazole, 2-heptadecylimidazole (HDIZ) was also used to concentrate Cu^{2+} and Ag^+ ions by taking advantage of its chelating ability to these ions. As a substrate material, glassy carbon (GC) was used because of its wide potential window.

First of all we have tried to see whether Cd^{2+} ions could be concentrated selectively against Na^+ ions into an arachidate monolayer, whether the resulting monolayer could then be transferred on a GC surface, and whether Cd^{2+} ions in the LB film can be readily detected by cyclic voltammetry. Fig. 1 shows a cyclic voltammogram of a GC electrode covered with a monolayer which was formed by spreading an arachidic acid chloroform solution on a water subphase containing 10 μM $CdCl_2$ and 50 μM $Na_2B_4O_7$ (pH 9). In spite of a low concentration ratio, i.e. 1/10, of Cd^{2+} against Na^+ in the subphase, both cathodic and anodic waves for the cadmium redox reactions were clearly observed. Especially the reoxidation of Cd metal deposited exhibited a typical surface wave with a sharp peak whose height was proportional to the sweep rate. Even in the case for the subphase with 1 μM $CdCl_2$

and 50 µM $Na_2B_4O_7$, the cathodic peak height at ca. -0.8 V vs. SCE was still comparable to that observed for the subphase with 0.1 mM $CdCl_2$ and 50 µM $Na_2B_4O_7$. These results indicate that the monolayer of arachidate could concentrate Cd^{2+} ions selectively against Na^+ ions and that the method may be applied to determine Cd^{2+} concentration less than 1 µM in the presence of 0.1 mM Na^+.

In Fig. 2 is shown a cyclic voltammogram of HDIZ monolayer deposited from the subphase which contained the same concentration of 0.1 mM of Cu^{2+} and Na^+ ions at pH 9. A sharp cathodic peak of Cu^{2+}- imidazole complex was observed at ca. -0.3 V vs. SCE. This cathodic peak will be applicable to detect selectively Cu^{2+} in the presence of other ions whose stability constants are much lower than Cu^{2+}. Ag^+ could also be detected by HDIZ monolayer.

Effect of interfering ions, pH, and a number of layers of the LB film will be also presented.

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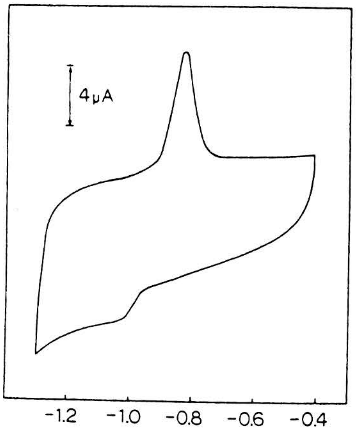

Fig.1

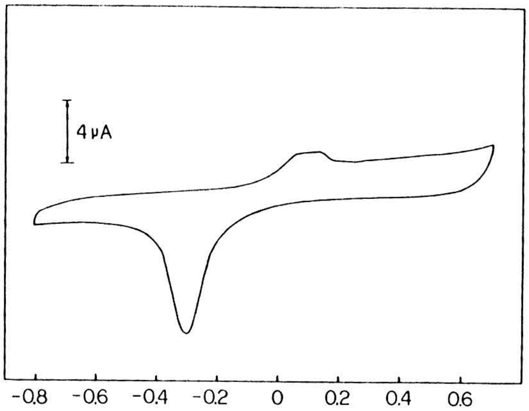

Fig.2

S4-20

X-RAY FLUORESCENCE ANALYSIS USING PVC MEMBRANE

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Energy-dispersive X-ray fluorescence analysis (XRF) has the great advantage of allowing the simultaneous determination of many elements in samples. However, a suitable preconcentration procedure is necessary for the determination of trace metals in environmental water samples.

In the present study, a rapid and simple preconcentration method using a PVC membrane containing a chelating reagent was proposed and applied to the simultaneous determination of copper, manganese, cobalt, nickel, and zinc ions in the waste water. The analytical results of the present method were compared with those obtained by flame atomic absorption spectrometry.

Procedures

For the determination of copper, the PVC membrane (diameter; 15mm, thickness; 13mm) composed of 5% Kelex 100, 70% DOP, and 25% PVC was shaken for 90min in 10ml of sample solution adjusted to pH 5 with 0.2M acetic acid-0.2M sodium acetate buffer. For the determination of manganese, cobalt, nickel, and zinc ions, the PVC membrane composed of 50% Kelex 100, 25% DOP, and 25% PVC was shaken for 150min in 10ml of sample solution adjusted to pH 7.5 with 0.2M hydrochloric acid-0.1M sodium borate buffer. These membranes were then washed, dried, and analyzed by X-ray fluorescence spectrometry. $K\alpha$ lines were used throughout the measurement.

Effects of pH

The optimal pH range for the extraction of each element into the membrane was examined with a universal buffer solution over a range of pH values from 1.0-10.0. The PVC membranes used here were the membranes containing 5% Kelex 100 for copper and 50% Kelex for other metals. Copper was quantatively extracted in the pH range of 4.0-7.0. Manganese, cobalt, nickel, and zinc ions were quantitatively extracted in the pH range of 7.0-9.0, 5.5-8.5, 6.5-8.5 and 6.0-8.0, respectively.

Effects of shaking time and Kelex 100 concentration

The effects of shaking time and Kelex 100 concentration in the PVC membrane were examined. It was observed that 5% Kelex 100 in the PVC membrane and shaking for 60min were sufficient for the complete extraction of copper.

Nickel was extracted quantitatively into the PVC membrane containing 50% Kelex 100 after shaking for 120min. Under these conditions, the shaking times required to attain complete extraction were 30min for zinc and 60min for manganese and cobalt.

Composition of Cu-Kelex 100 complex in PVC membrane

In order to compare the extraction mechanism of the present method with that of the usual liquid-liquid extraction, the extraction behavior of copper ion with the PVC membrane containing Kelex 100 was studied by slope analysis.

The log D vs. pH plots exhibited a slope of 2. The analogous log D vs. log$[HK]_o$ plots were also linear with a slope of 2. These results suggest that a 1:2 chelate, CuL_2 is present in the PVC membrane, which indicates that the extraction behavior of copper ion with the PVC membrane containing Kelex 100 is similar to that of copper ion in a chloroform solution of Kelex 100.

Determination of trace metals in waste water samples

The present method was applied to the determination of copper, manganese, cobalt, nickel, and zinc ions in waste water samples from the university campus. The results were in good agreement with those obtained by flame atomic absorption spectrometry, which is currently used for ordinary waste water analysis. The results for copper, manganese, and zinc ions are shown in Table, while cobalt and nickel could not be detected by both methods. To 500ml of waste water samples were added 50μg of cobalt and nickel and recovery of both metals was examined. Cobalt and nickel were almost completely recovered. The detection limits were as low as the values obtained by flame atomic absorption spectrometry.

From these results, it is concluded that the present method can be used as a simple and rapid preconcentration method in energy-dispersive X-ray fluorescence analysis.

TABLE

Comparison of analytical results for Cu, Mn, and Zn in waste water (ppm) obtained by XRF and atomic absorption spectrometry (AA).

Sample	Cu		Mn		Zn	
	XRF	AA	XRF	AA	XRF	AA
A	0.056	0.072	0.025	0.029	0.18	0.20
B	0.064	0.068	0.058	0.054	0.23	0.29
C			0.039	0.039	0.13	0.14
D			0.024	0.017	0.041	0.039
E			0.064	0.065	0.11	0.13

S4-21

SENSITIZING EFFECTS OF ACETALDEHYDE ON THE COLORIMETRIC DETERMINATION OF METHANOL, METHYL ESTERS AND 2-PROPANOL

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INTRODUCTION

In the colorimetric determination of methanol, the procedure is first oxidized to formaldehyde by potassiun permanganate-sulfuric acid and then colorized by the reaction with chromotropic acid.[1] However, it has been known that the calibration plots of the absorbance vs. the amounts of the alcohol do not give straight lines because the oxidation reaction proceeds only incomplete.

Recently, the author found that an addition of acetaldehyde to the oxidizing agents accelerates the oxidation reaction so highly to bring it to completion, and thence highly improves the sensitivity of the determination of the alcohol.[2,3] The recommended procedures for the improved method will be presented, together with the extended applications of the method toward methyl-esters and 2-propanol.[4,5]

RESULTS

Role of aldehyde-compound added.

When methanol contents in formaline was determined by two different methods, i.e., colorimetry using chromotropic acid and volumetric titration using sodium sulfite as the titrant (JIS K 1502 standard method), there noticed a certain difference between the analytical results of the two methods. The former method gave a methanol content as 14.0% in formalin, whereas the latter 8.8%.[6] To explain the difference in the results, the author presumed that formaldehyde in formalin participates with oxidation process of methanol. In fact, an addition of aldehyde compounds such as acetaldehyde in H_2SO_4-$KMnO_4$ medium accelerate evidently the oxidation reaction, and in conseguence, the sensitivety of the determination of methanol was highly improved.[2,3]

Determination of methanol.

Oxidize 1 ml of sample solution containing 1 ∼ 15 μg of methanol by adding 0.1 ml of 0.004 g/ml acetaldehyde-ammonia solution, 0.1 ml of 0.5 M sulfuric acid and 0.012 g/ml of potassium permanganate solution. Swirl the mixture and keep it at the room temperature for 10 min. Reduce the excess of permanganate by adding 0.1 ml of 0.03 g/ml sodium sulfite solution. Then, add 0.2 ml of 0.02 g/ml aqueous chromotropic acid solution and 4 ml of 75 v/v% sulfuric acid. Heat the mixture at 80 ∼ 85 °C for 10 min with occasional swirling. After cooling to the room temperature, measure the absorbance at 575 nm against the reagent blank solution prepared by the same procedure.

The improved method showed 5 times higher sensitivity compared with the conventional method, and the calibration curve was straight enough in the concentration range of 1 ∼ 15 μg/ml of methanol. The molar extinction coefficient at 575 nm was 7.2×10^3 ℓ.mol^{-1}. cm^{-1}.³⁾

Determination of methyl esters.

A sample gas containing methyl esters is passed at a rate of 0.5 ℓ/min through a midget impinger (with fritted glass beads attached to the tip of bubbler) containing 20 ml of 0.5 N sodium hydroxide solution. The solution is allowed to stand for 20 min or longer at room temperature until the esters are hydrolyzed to methanol and acids. The methanol thus resulted is determined colorimetrically as described above.4)

Determination of 2-propanol.

According to the conventional colorimetric method for 2-propanol, it is oxidized to acetone with $K_2Cr_2O_7$-H_2SO_4 solution, and the acetone resulted is reacted with furfural to form difurfurylidene-acetone. It was found again that the oxidation reaction of 2-propanol to acetone was accelerated by the addition of acetaldehyde-ammonia in potassium permanganate medium. On the basis of these observations, the procedure was developed for the colorimetric determination of 2-propanol using furfural.5)

DISCUSSION

Other related papers are shown in references.7,8,9)

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S4-22

DETERMINATION OF RARE EARTH ELEMENTS,THORIUM AND URANIUM IN PHOSPHATE MINERALS BY SOLVENT EXTRACTION-ICP ATOMIC EMISSION SPECTROMETRY

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Inductively coupled plasma(ICP) atomic emission spectrometry was applied the determination of rare earth elements(REE), thorium and uranium in phosphate rare earth minerals such as xenotime, monazite and apatite.

A Japan Jarrell-Ash model ICAP-500 inductively coupled plasma emission spectrometer was used. The detection limit of REE, thorium and uranium were given concentration in the range ca.1–100ppb. These was no influence of the inorganic acids in the concentration range from 10^{-2} to 2X10^{-1}M, but signal suppression was observed at concentrations above 1M of these acids. No significant change in intensities of REE was observed for sodium ion in the concentration range between 10 and 10^{3}ppm. Xenotime and Monazite were dissolve with hot concentrated sulfuric acid. After insoluble residue was filtrated,the solution were diluted with water to give concentration in the range 10–500μg/ml. These sample solutions were directly injected into the plasma.Determination of several REE in phosphate mineral solutions necessitated correction of spectral interferences from coexisting REE. The corrections were easily made from the contents of coexiting elements which were already known. REE,thorium and uranium contents in the phosphate minerals were measured by calibration curve method. The contents of REE(Dy,Yb,Sm,Tb,Eu) obtained ICP atomic emission spectrometry were in good agreement with those obtained by atomic absorption spectrometry or fluorometry. The results in Figure 1 indicated that REE distributed in xenotime and monazite following the Odd and Harkins law.

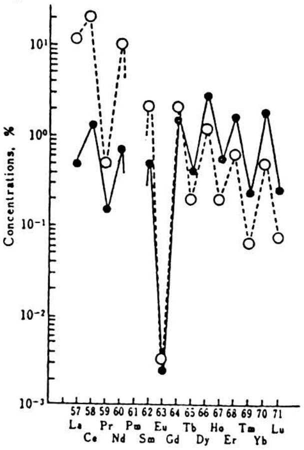

Fig. 1 Distribution patterns of rare earth elements in phosphate minerals

• Xenotime (I), ○ Monazite (I)

Then,solvent extraction – ICP atomic emission spectrometry was applied to the determination of samarium in calcium apatite minerals. The effect of coexisting elements on the samarium emission intensity was scarcely observed at 443.43nm. However,a large amount of calcium phosphate showed high spectral interference and signal suppression. Hence, the separation of samarium from the matrix by solvent extraction was studied. Di-(2-ethylhexyl)-phosphoric acid(HDEHP) as a chelating agent and cyclohexane as an organic solvent are usually used for this solvent extraction system. However, cyclohexane extinguished the plasma flame soon after the introduction. Therefore, the solvent was selected from alkanes and cycloalkanes etc. as the organic solvent which affected plasma stability. The experimental results were showed in Table 1. The stability of the plasma flame was higher for higher hydrocarbons. Intensity and detection limit on samarium extraction with various organic solvents are shown in Table 2. Thus, cyclooctane was used as an extraction solvent in the present work. Samarium was quantitatively extracted into cyclooctane phase contaning 0.1M-HDEHP, and separated from matrix such as calcium phosphate. Apatite minerals was dissolved with concentrated nitric acid. The samarium content in the apatite was found to be $(0.26-1.81)\times10^{-3}\%$.

Table 1 Stability of the plasma to the organic solvents

Organic solvents	Plasma†	Carbon deposition
Cyclopentane	extinguishment	—
Cyclohexane	〃	—
Cycloheptane	unstable	fair
Cyclooctane	stable	none
n(*iso*)-Pentane	extinguishment	—
n(*iso*)-Hexane	〃	—
n(*iso*)-Heptane	〃	—
iso-Octane	〃	—
n-Octane	unstable	fair
n(*iso*)-Nonane	stable	slight
Decane	〃	none
Undecane	〃	〃
Dodecane	〃	〃
Tridecane	〃	〃
Tetradecane	〃	〃
Pentadecane	〃	〃
Hexadecane	〃	〃
Decalin	stable	none
Tetralin	〃	〃
HDEHP††	〃	〃

† R. F. power : 2.0 kW, Coolant gas : 20 l/min, Carrier gas : 0.48 l/min, Plasma gas: 1.2 l/min; †† Di-(2-ethylhexyl)-phosphoric acid

Table 2 Intensity and detection limit of samarium in various organic solvents[a]

Solvents	Intensity ratio (I_o/I_w)	Detection limit[c] / μg ml^{-1}
Distilled water[b]	1.0	0.66
Decane	2.17	0.33
Undecane	1.96	0.48
Dodecane	2.05	0.38
Tridecane	1.72	0.96
Tetradecane	1.75	0.90
Pentadecane	1.11	1.47
Hexadecane	0.96	1.80
Cyclooctane	1.47	0.30
Decalin	1.39	0.78

a) Carrier gas : 0.48 l/min, R. F. power : 2.0 kW; b) Carrier gas : 0.51 l/min, R. F. power : 1.6 kW; c) $S/N=3$, wavelength : 443.43 nm

Similarly, when the aqueous solution of xenotime and monazite were used without any separation for scandium, the correction of spectral interferences from coexisting elements were necessitated. However, the correction was difficult because the amounts of coexisting elements were generally unknown. In order to separate scandium from matrix elements, therefore, the solvent extraction using 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone–n-butylether system was adopted. Furthermore, this system was used to determine of thorium and uranium in those phosphate minerals.

S4-23

MICROCOMPUTER-AIDED CATHODIC-STRIPPING VOLTAMMETRY IN THE PRESENCE OF DISSOLVED OXYGEN

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Cathodic-stripping voltammetry utilizing various preconcentration procedures is becoming more and more popular in environmental trace analysis. It is applicable to highly sensitive and selective determinations of both inorganic and organic substances. But in most cases complete deaeration is necessary before the voltammetric measurements. In the present study, a method in which the effect of the oxygen wave is subtracted by the aid of a microcomputer was tested for cathodic-stripping voltammetry in the presence of dissolved oxygen.

APPARATUS

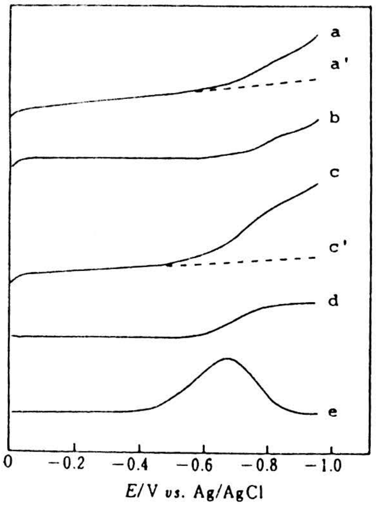
For voltammetric measurements and data processing, a potentiostat and a microcomputer were used in combination. The microcomputer (CPU: 8086, RAM: 256KB, FDD: 1.2MBx2) was equipped with 12 bit A/D and D/A converters and a preamplifier for the A/D converter. A programmable staircase voltage could be applied to the cell with a scan rate of up to 100 V s^{-1}. The current and voltage outputs from the potentiostat were converted to digital data, stored in the memory and used for further data processing.

1. DETERMINATION OF TRACE URANIUM IN THE PRESENCE OF DISSOLVED OXYGEN AND ITS APPLICATION TO SEA WATER

The voltammetric method for the determination of trace uranyl ions after preconcentration on the trioctylphosphine oxide(TOPO)-coated glassy carbon(GC) electrode has been proved to be highly sensiitive and selective [1] and has been applied to sea water samples[2]. In the method, uranyl ions are concentrated into the TOPO layer on the GC electrode at 0 V vs. Ag /AgCl reference electrode, and give a reduction wave when the electrode potential is scanned to a more negative poteniitial. In the present study, the method was applied in the presence of dissolved oxygen, by eliminating its interfering effect with the aid of a microcomputer. Fig. 1 is a schematic presentation of voltammograms. The voltammogram for the reduction of dissolved oxygen was obtained just before the preconcentration of uranyl ions. It was subtracted from the voltammogram measured after the preconcentration, in which the reduction wave for the concentrated uranyl ions and that for the dissolved oxygen were overlapped. The resulting voltammogram was then differentiated, and the peak current for the derivative curve was measured. For the determination, a standard addition method was employed. The method could be applied to sea water samples (UO_2^{2+}: 1.37×10^{-8} M (M = mol dm^{-3})) only by adjusting their pH to 4.0. The relative standard deviation was ca. 5%.

2. DETERMINATION OF TRACE COBALT IN THE PRESENCE OF DISSOLVED OXYGEN

Brainina[3] developed a cathodic-stripping method for cobalt(II). Co(II) between 10^{-6} and 10^{-8} M was determined after its preconcentration with 1-nitroso-2-naphthol on the graphite electrode. In the present study, her method was tested in the presence of dissolved oxygen. A GC indicator electrode was used. The voltammogram for [Co(II) + oxygen] (curve A in Fig. 2) was taken after the preconcentration of Co(II) at -0.33 V for 5 min from the NH_4Cl-NH_3 (pH 10) solution containing 1-nitroso-2-naphthol. The voltammogram for dissolved oxygen (curve B in Fig. 2) was taken in the same solution at 30 s after the measurement of curve A. The peak area of curve 1, obtained by subtracting curve B from curve A, was in a linear relation with the concentration of Co(II) between 2 and 20×10^{-10} M. The relative standard deviation for 1×10^{-9} M Co(II) was 4.2% (n = 7).



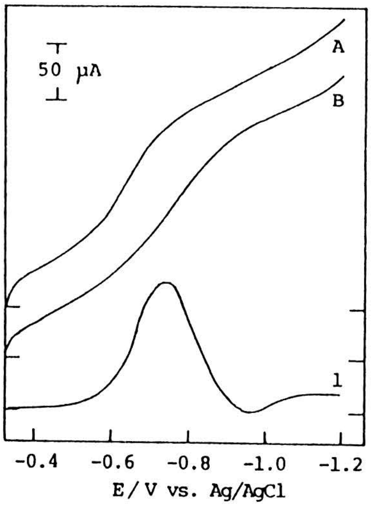


Fig. 1 Schematic presentation of voltammograms for the determination of UO_2^{2+} in the presence of dissolved oxygen. Curve a, voltammogram for dissolved oxygen before preconcentration; b, after correction for the residual current (a') from curve a; c, voltammogram for O_2 + UO_2^{2+} after preconcentration; d, obtained from curve c after corrections for the residual current (c') and curve b; and e, derivative curve of curve d.

Fig. 2 Voltammograms for the determination of Co(II) in the presence of dissolved oxygen. Solution: 1×10^{-9}M Co(II) + 3×10^{-7}M 1-nitroso-2-naphthol + 0.2M NH_3 + 0.05M NH_4Cl (pH 10.0). Curves A and B, after preconcentration at -0.33 V for 5 min and 30 s, respectively, and curve 1, 4 x [A - B]. Scan rate: 16 V s^{-1}.

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S4-24 SIMULTANEOUS DETERMINATION OF TRACES OF FORMALDENYDE AND METHANOL IN AIR BY DIFFERENTIAL PULSE POLAROGRAPHY

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There are lots of methods used to analyse formaldehyde and methanol in air, for instance, spectrophotometric (1) and GC. (2) Unfortunately both are lack of sensitivity at trace level, compared with other method the differential pulse polarographic method is quite sensitive, selective.

Formaldehyde can be determined polarographically in acidic media. (3,4,5) In acidic media the direct reduction of formaldehyde at DME is unusable analytical process. While the hydrazone which is formed by the reaction of hydrazine with formaldehyde is electroactive species, the reduction of the hydrazone at DME is diffusion-controlled and a two-electron process.

$$N_2H_4 + HCHO \text{ ---- } H_2C = N\text{-}NH_2 + H_2O$$

$$H_2C = N\text{-}NH_2 + 2H^+ + 2e^- \text{ ---- } H_3C - NH - NH_2$$

Methanol is not electroactive compound at DME, it's determination is based on formaldehyde reduction through oxidation of methanol by potassium permanganate in sulphuric acidic media.

EXPERIMENT

A PARC Model 384 Polarographic Analyzer and Model 303 Static Mercury Drop Electrode (SMDE) with Ag/AgCl reference electrode and platinum wire counter-electrode are used. The main Instrument setting as follows: Electrode: DME, Mode: DPP, Drop Time: 1 sec, Scan Rate: 4mv/sec, Modulation Amplitude: 50mv, Initial Potential: -0.7v vs Ag/AgCl, Final Potential: -1.3V vs Ag/AgCl, Deaeration Time: 10min, Supporting Electrolyte: 0.2M acetate-0.02M acetic acid, buffer soln pH=5.5, 0.2% hydrazine hydrochloride, 0.016M Citric acid (in cell) Potassium permanaganate: 5mg/ml, Sulphuric acid: 8N.

RESULTS:

It was found that peak current of HCHO and CH_3OH are sensitive to pH change and affected by modulation amplitude, scanning speed, concentration of hydrazine, oxygen in solution etc.

Many organic and inorganic compound which may be occured in air such as: alcohol, phenols, aceton., F^-, Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, NH_4^+, S_x^{2-}, NO_2^-, CH_3COO^-, $HCOO^-$, Zn^{2+}, Cu^{2+}, Cd^{2+}, show no serious interferences; the higher aliphatic aldehydes give polarogram after formaldehyde potential, while aromatic aldehydes do before formaldehyde potential, but the acrolein, butyraldehyd can interfere, it appears that the concentrations of montioned aldehydes greater than three and one time the concentration of formaldehyde.

The lower limit of determination for formaldehyde is 5ppb in cell solution 80ppb for methanol. The concentration range is 5-200ppb for formaldehyde; 0.08-7ppm for methanol in cell solution, the correlation coefficient (r) is 0.999 for formaldehyde, 0.995 for methanol. The precision of determination is within 5% at 60ppb level. The recovery is from 87% to 109% for 40ppb fromaldehyde in electrolyte.

Compared with AHMT colorimetric method, the differential pulse polarographic method is sensitive,accurate.

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S4-25

ANALYSIS OF NITRATE WITH A METAL-DEPOSITED CARBON COLUMN ELECTRODE

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The application of carbon column electrode to the determination of nitrate in environmental aqueous samples was studied. Column electrode, packed with 60 to 100 mesh glassy carbón grains as working electrode materials, has an extremely large surface area relative to the inner volume of column, this structure consequently enables the rapid and complete electrolysis of various depolarizers in flow system (1), for example, several applications to analysis of seawater samples were reported (2,3).

Well, nitrate, which is a stable anion, needs so large overpotential on its electrochemical reduction that it is difficult to reduce nitrate directly at carbon electrode except in strongly acidic solution. So, the development of sensor using electrocatalytic reduction of nitrate was devised. Some substances, such as U(VI), Mo(VI), Yb(III), Cr-complex and V-complex, have been known as catalyst for electrochemical reduction of nitrate.

In this study, Cu and Cd metals (4), which can be briefly attached to the surface of electrode, were chosen. Cu and Cd metals were deposited on the surface of carbon column electrode simultaneously by flow-electrolysis of solution containing metal ions and supporting electrolyte. The Cu-Cd deposited electrode is a kind of chemically modified electrode, and is an available assembly as a reductor or coulometric detector of nitrate. These functions are briefly presented in this report.

COLUMN ELECTRODE AS A REDUCTOR OF NITRATE TO NITRITE

Column electrode can be substituted for conventional reductor, such as Cd grains coated with Cu or powdered Zn, used in the colorimetric determination of nitrate, if reduction of nitrate to nitrite can be achieved quantitatively by electrochemical reductor. In a series of fundamental studies, it was proved that Cu-Cd deposited carbon column electrode prepared by flow-electrolysis of a few milliliters solution of 10^{-5} to 10^{-4}M Cu and Cd ions, can reduce nitrate to nitrite at pH9 quantitatively by being set to about -1.1V vs. Ag/AgCl. Accordingly, in flow system with a column electrode, nitrate can be determined by indirect colorimetry using diazotisation and coupling reactions between reagents and nitrite produced electrolytically. While, as nitrite cannot be reduced at column electrode under these conditions, total amount of both species is determined in the presence of nitrite.

Compared with conventional reductor column, the electrochemical one can be prepared easily by only an exchange of solutions and control of potentials, and in addition, it is also very preferable that little waste containing metal is produced, as metal is collected on electrode all through the experiment (5).

COULOMETRIC DETERMINATION OF NITRATE WITH COLUMN ELECTRODE

Nitrate is reduced to nitrite(n=2) in analytical conditions described above, and accordingly can be determined coulometrically by flow-electrolysis with Cu-Cd deposited column electrode. But, ordinarily sample contains such electrochemically interfering substances as dissolved oxygen, and so only nitrate cannot be determined directly by injection of sample. So, the electrochemical removal of them by the preliminary column connected prior to the detection one was attempted. In particular, as electrochemical reduction of oxygen at carbon electrode requires more overpotential, the pre-column with electrodeposited Ag or Pt metal was adopted in order to electrolyze it quantitatively at more positive potential. Such pre-column can also eliminate other pre-discharging substances and consequently decreases the back-ground current on detecting nitrate at next column.

The double columns system prepared as mentioned above, is a very useful assembly as a coulometric detector for nitrate. Its preparation or control is so easy that this assembly is very available for monitoring system in environmental analysis.

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S4-26

THE PREPARATION AND PROPERTIES OF THE CREATINE ELECTRODE

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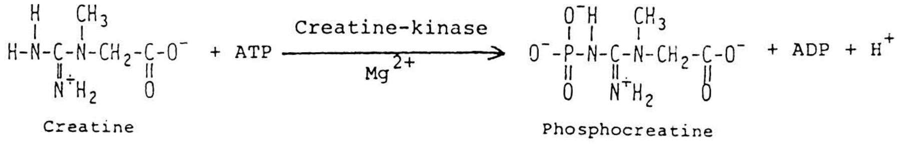
Creatine is contained only a very little in urine, but it is increased by destruction, denaturation, etc. of muscle. In spite of a great recent progress in the study of enzyme electrode, however, a creatine enzyme electrode has not been developed. To determine the creatine, a creatine enzyme electrode has been prepared and tested. The enzyme reaction is as follows:



$$\mathrm{H{-}N(H){-}C({=}N^{+}H_2){-}N(CH_3){-}CH_2{-}C({=}O){-}O^-} + \mathrm{ATP} \xrightarrow[\mathrm{Mg}^{2+}]{\text{Creatine-kinase}} \mathrm{O^-{-}P({=}O)(O^-){-}N(H){-}C({=}N^{+}H_2){-}N(CH_3){-}CH_2{-}C({=}O){-}O^-} + \mathrm{ADP} + \mathrm{H}^+$$

Creatine

Phosphocreatine

EXPERIMENTAL

(Apparatus and Reagents)

A single glass electrode, Model GST-155C (TOA Electronics Ltd.), was employed to prepare the enzyme electrode. PH was measured with a digital pH/mV meter, Model TSC-10A (TOA Electronics Ltd.), connected with an electronic recorder, Model R-102 (Rikadenki Kogyo Co., Ltd.). All measurements were carried out at 37°C ± 0.2°C.

Creatine-kinase was from Boehringer Mannheim Yamanouchi, adenosine-5'-triphosphate (ATP) was from Oriental Yeast Co., Ltd. and creatine was from Wako Pure Chemical Industries.

(Preparation of Creatine Enzyme Electrode)

The electrode was composed of a glass electrode and the immobilized creatine-kinase membrane on its detect end. For the immobilization of creatine-kinase, the cross-linking method was used. On a polycarbonate membrane of 0.1μm caliber, 30μl of

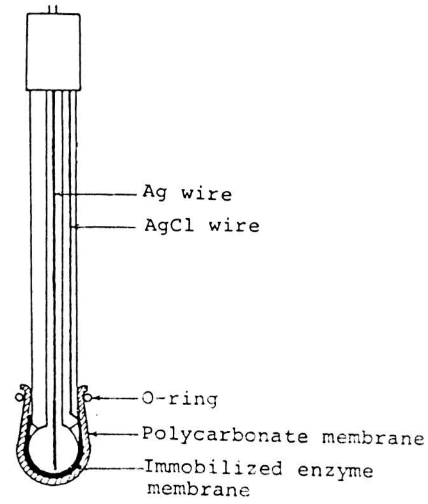


FIG. 1 CREATINE ENZYME ELECTRODE

10w/w% the bovin serum albumin (BSA) solution was spread, then 5mg of creatine-kinase and 4μl of 12.5v/v% glutaraldehyde were added and mixed quickly. The membrane was left to stand for at least 2 hours at 4°C. This immobilized enzyme membrane was attached to a glass electrode by O-ring as shown in Fig.1.

(Determination of Creatine)

Pipet 10ml of 1mM ATP-0.1mM magnesium sulfate (pH 9) solution into the thermostated cell and immerse the creatine enzyme electrode. Inject 2ml of creatine solution into the cell. The evolved hydrogen ions by the enzyme reaction during the first 10 minutes were measured as the variation of pH.

RESULTS AND DISCUSSION

For the preparation of the creatine enzyme electrode, a proper amount of immobilized creatine-kinase was 5mg (enzyme activity was about 800 Units/mg at 37°C) and the variation of pH by the enzyme reaction was constant over 5mg. The electrode response was best in the 0.83mM ATP-8.3mM magnesium sulfate solution. The optimum pH was 8-9 and temperature was 20-38°C. A linear relationship was obtained in the range of 0.42-3.3mM creatine. The calibration curve was shown by the equation of $Y=48.33X+0.003$ (Y is ΔpH and X is creatine concentration/M) and the coefficient of correlation was 0.999. The calibration curve was shown in Fig.2. Effects of concomitant compounds were discussed. The creatine solution was determined in the presence of 3 other compounds. The results are shown in Table 1. Creatine could be determined with a relative error of less than ±1.7% in the presence of 1.7-10 times β-D-glucose, 1-500 times urea and 0.9-3 times L-ascorbic acid.

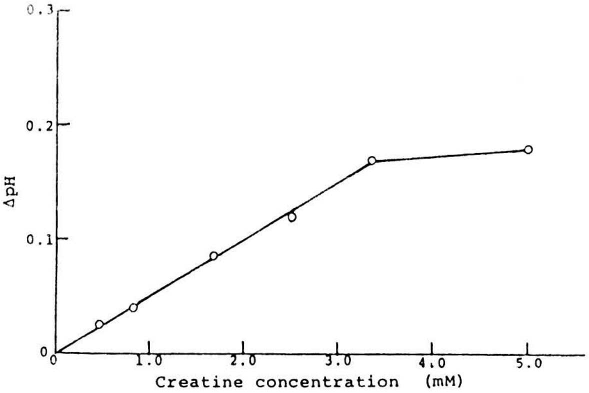


FIG. 2 CALIBRATION CURVE OF CREATINE ENZYME ELECTRODE

Sample, 12ml, of creatine, 0.833mM ATP and 8.33mM magnesium sulfate.
Temp. 37°C.

TABLE 1 EFFECTS OF CONCOMITANT COMPOUNDS ON THE DETERMINATION OF CREATINE

Concomitant compound	molar ratio (creatine : concomitant compound)	R.E.[a] (%)
β-D-Glucose	1 : 1. 66	-0.2
	1 : 5	-0.7
	1 : 10	-1.7
Urea	1 : 1	0.6
	1 : 100	0.6
	1 : 500	0.7
L-Ascorbic acid	1 : 0.85	0.2
	1 : 3	1.2

Sample, 12ml, of 1.7mM creatine, 0.83mM ATP and 8.3mM magnesium sulfate. Temp. 37°c.

a) Relative error.

S4-28

CHARACTERIZATION METHODS OF SELENOCYANATE ION-SENSITIVE FIELD EFFECT TRANSISTOR WITH URUSHI AS THE MEMBRANE MATRIX

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INTRODUCTION A number of studies have been carried out on ion-sensitive field effect transistors (ISFETs) as ion sensors.1) ISFETs with an organic gate coating, however, have short lifetimes and are unreliable because of poor membrane adhesion to the gate of the device.2) We have proposed durable ISFETs with Urushi as the membrane matrix.3)

The characterization of ISFETs has been carried out with a source-follower circuit. However, there is little advantage in using a miniaturized ion sensor device which has a measuring FET amplifier circuit if a source-follower circuit is used. Therefore, a different characterization method based on the drain current was investigated in this work.

EXPERIMENTAL After a mixture composed of 45% of trioctylmethylammonium selenocyanate and 55% of Urushi latex was coated on the gate of the ISFET device, the Urushi membrane was hardened for 10 days at 30°C and 90% relative humidity. The prepared Urushi ISFET was characterized by use of the measuring circuit shown in Fig. 1.

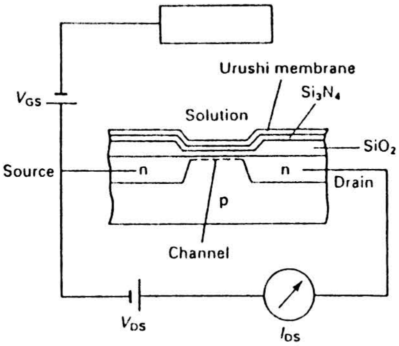

Fig. 1. Measuring circuit of Urushi ISFET

RESULTS AND DISCUSSION

1. Static Characteristics of the ISFET as FET

The I_{DS}-V_{DS} and I_{DS}-V_{GS} characteristics of the Urushi ISFET are shown in Fig. 2.

The ion response drain current of the ISFET was measured under the condition of the saturation region(i.e., V_{GS}=0V, V_{DS}=2.5V).

2. Characterization Method Based on Drain Current of ISFET

The I_{DS}-V_{DS} characteristics in the saturation region of the FET is described by the equation

$$I_{DS} = C_1(V_{GS} - V_{Th})^2 \text{ ------(1)}$$

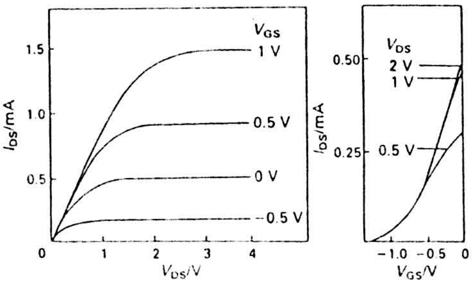

Fig. 2. I_{DS} - V_{DS} and I_{DS} - V_{GS} characteristics of Urushi ISFET in 0.1 M NaNO$_3$

where C_1 and V_{Th} are constants dependent on the FET device. In the ISFET eq.(1) is described as follows.

$$I_{DS} = C_1(V_{GS}^* - V_{Th}^*)^2 \text{ ----(1')}$$

The V_{GS}^* is composed of the voltage applied to the reference electrode V_{GS} (see Fig. 1), the potential of the reference electrode E_{ref} and the membrane potential E at the interface between the solution and ion-sensing membrane. The V_{GS}^* can be described as follows.

$$V_{GS}^* = V_{GS} + E - E_{ref} \text{ -----(2)}$$

Eq.(1') and Eq.(2) can be combined to give

$$I_{DS} = C_1(V_{GS} + E - E_{ref} - V_{Th}^*)^2 \qquad \text{----------(3)}$$

i.e.,

$$\sqrt{I_{DS}} = C_2 \cdot [C_3 + (RT/nF) \cdot \ln a] \qquad \text{----------(4)}$$

when the membrane potential is expressed by the Nernst equation. Eq.(4) indicates that the square root of I_{DS} is proportional to the logarithm of the activity of the ion. The potential response of the ISFET is shown in Fig. 3. $\sqrt{I_{DS}}$ on the vertical axis of the Fig. 3 is converted into potential via eq.(3) and Fig. 2. The selenocyanate ISFET shows a linear response towards ion activity in the range 10^{-5} - 10^{-1} M with almost Nernstian slope.

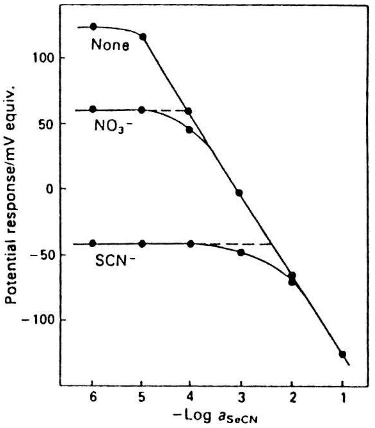

Fig. 3. Potential response of Urushi ISFET with 10^{-2} M interfering ion

3. Characterization of Selectivity Based on Drain Current of ISFET

If the membrane potential is expressed by the Nicolsky-Eisenmann equation, the selectivity coefficients can be calculated by the mixed solution method. The selenocyanate response of the ISFET with 10^{-2} M nitrate or thiocyanate is shown in Fig. 3. The selectivity coefficients against NO_3^- and SCN^- were 1.0×10^{-2} and 4.0×10^{-1} respectively.

4. Durability of the Selenocyanate Urushi ISFET

The prepared Urushi ISFET maintained its potential response for over 2 months.

We thank Dr. Ujihira, Faculty of Engineering, University of Tokyo, for his encouragement throughout these studies and the Central Research Laboratory, Shimadzu Corp., for supplying ISFET devices.

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S4-29

ENHANCED ELECTROCHEMICAL SENSITIVITY AT OXIDE-DISPERSED GLASSY CARBON ELECTRODE

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INTRODUCTION

Glassy carbon (GC) has found applications in a number of electrochemical studies. GC electrodes can be used over a wide potential range, but the apparent rates of electron transfer are slower at the GC surface than at metal surfaces. A variety of pretreatment procedures have been recommended to obtain reproducible results [1]. In general, the GC surfaces are polished with an aqueous slurry of alumina particles to obtain mirror-like finish. Zak and Kuwana reported that alumina on GC surfaces strongly adsorbed ascorbate and catechols, and accelerated their oxidation reactions [2]. We have found that some oxide particles such as Cr_2O_3 show similar effects, which enhances the electrochemical sensitivity for various electroactive species [3].

EXPERIMENTAL

Working electrodes were 3 mm diameter GC rods (GC-30S, Tokai Carbon), press-fitted into a cylindrical Teflon holder by means of a silicone rubber tubing. After polishing GC surfaces with alumina, ordinary electrodes were obtained by cleaning the electrode surface ultrasonically. Oxide-dispersed electrodes were obtained by repolishing with an aqueous slurry of oxides on a wool polishing cloth. A Hokuto Denko Model HA-501 potentiostat and a Model HB-105 programmable function generator were used for cyclic voltammetry.

RESULTS

Figure 1 shows cyclic voltammograms of 4×10^{-6} M uric acid in 0.1 M $HClO_4$. It is known that uric acid gives rise to a 2-electron oxidation peak at the pyrolytic graphite electrode [4]. However, no oxidation wave was observable with an ordinary GC electrode under these conditions (curve a) . Curve b is a voltammogram obtained with a CeO_2-dispersed GC electrode. An oxidation wave was observed with a peak-potential (E_p) of +0.65 V vs SCE at a scan rate of 200 mV/s; the reduction wave was not found in the reverse (cathodic) scan. The E_p shifted to more positive potentials with an increase in scan rate. It was found that the peak current (i_p) increased with an increase in the interval (t_1) while the electrode was immersed in the uric acid-containing solution with an open circuit. As shown in Fig. 2, the i_p was proportional to $t_1^{1/2}$ for t_1 smaller than ca. 180 s, while the i_p was practically constant for larger values of t_1. The maximum i_p was directly proportional to scan rate. It is assumed that the maximum i_p corresponds to that for a saturated uric acid on the CeO_2-dispersed electrode. These results indicate that the electrode process is governed by the strong adsorption of the depolarizer on oxide-dispersed electrodes. It should be noted that the detection limit of uric acid is improved to as low as 10^{-8} M level. Similar effects were found for Cr_2O_3, NiO, CoO and Al_2O_3. Adsorption experiments suggest that the electrocatalysis is due to the interaction between a GC surface and oxides.

Adsorption waves at oxide-dispersed electrodes were observed for the reduction of various aromatic nitro-compounds and the oxidation of biologically important hydroxy-compounds such as Dopamine, Epinephrine and DOPA. In these cases, the overvoltage for the electrode reactions of the species was reduced, and the remarkable improvement in sensitivity was obtained with oxide-dispersed electrodes.

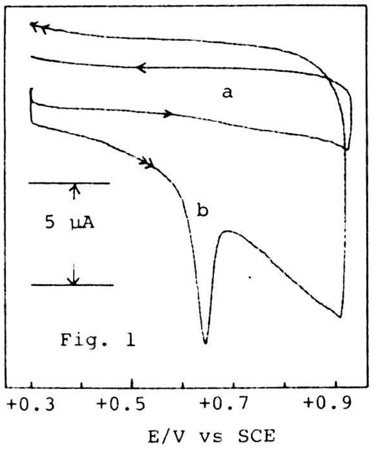

Fig. 1

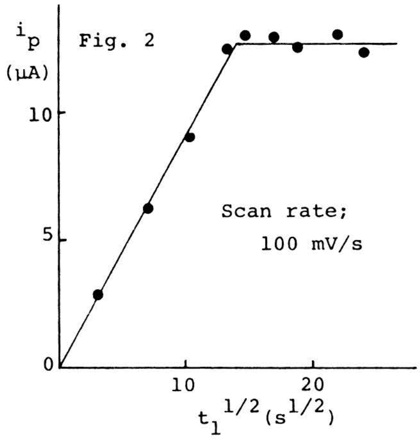

Fig. 2

Support of this study by Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture (No. 61540422) is gratefully acknowledged.

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S4-30 AN IDEA OF A NEW SENSOR BASED ON THE POTENTIAL OSCILLATION

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Imagine the ion transfer at liquid/liquid interface involving processes as follows:

(1) The transfer free energy, ΔG_{tr}, of A^{n+} is less than that of B^{n+}.

(2) The transfer of B^{n+} overcomes when A^{n+} at the interface has been consumed due to the transfer of A^{n+}.

(3) The transfer of B^{n+} results in the change of chemical form of A^{n+} through such a chemical reaction as complex formation, and the transfer of A^{n+} is depressed during the transfer of B^{n+}.

(4) The transfer of A^{n+} resumes when the concentration of A^{n+} at the interface is recovered by the diffusion of A^{n+} from the bulk.

The ion transfer may cause the oscillation of potential difference at the interface, ΔV. In such oscillation, the amplitude corresponds to the difference of $\Delta G_{tr}(=-zF\Delta V^{\star})$ for A^{n+} and that for B^{n+}, and depends on the characteristics of the transferring ions, since ΔG_{tr} is function of the charge and the size of the ion[1]. (* where z and F are the charge of the ion and Faraday constant, respectively)

The period of the oscillation is considered to be controlled by both the rate of diffusion and that of the chemical reaction, and, hence, is affected by the concentration of the ion, diverse substances and media.

Such potential oscillation mentioned above may provide informations to sense ions and/or diverse substances.

The following system is an example to realize the oscillation.

	W	Org	
Ag-AgCl	1M $MgSO_4$	2×10^{-4}M Cs^+TPhB^-	Ag-AgCl
		0.1M TBA^+TPhB^-	

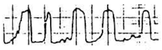
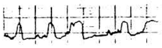
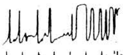
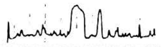
When a constant current, which was less than the diffusion controlled limiting current for the ion transfer of 2×10^{-4}M Cs^+ at the aqueous(W) and organic(Org) solutions interface, was flowed from Org to W using two Ag-AgCl electrodes, the ΔV at the W/Org interface oscillated as illustrated in Table 1.

The oscillation mechanism was elucidated based on the current-scan voltammetry for the ion transfer[2] as follows; At the beginning, Cs^+, of which ΔG_{tr} is less than that of TBA^+, carries the constant current. When the concentration of Cs^+ at the interface has been decreased, TBA^+ takes part in the current flow. During the TBA^+ transfer, the transfer of Cs^+ is inhibited. The inhibition can be clearly demonstrated by the potential-scan voltammetry for ion transfer[3].

Using 1,2-dichloroethane as Org, the amplitude of the oscillation was 0.28V, which is nearly equal to the difference between ΔV for Cs^+ and that for TBA^+. The period of the oscillation significantly depends on the magnitude of the current, concentration of Cs^+, coexisted ions and the solvent, as seen in Table 1 and 2.

Tetramethylammonium(TMA^+) ion and H^+ used instead of Cs^+ gave the oscillation whereas tetraethylammonium(TEA^+) and tetrapropylammonium($TPrA^+$) ions did not. The ΔVs for Cs^+, TMA^+ and H^+ lie at the other side of those for TBA^+ and tetraphenylarsonium($TPhAs^+$) ion across the point of zero charge of the W/Org interface, though ΔVs for TEA^+ and $TPrA^+$ are at the same side. Hence, the change of chemical forms of Cs^+, TMA^+ or H^+ to those which hardly transfer at potentials where TBA^+ or $TPhAs^+$ transfers may be strongly correlated with the change of the double-layer structure at the W/Org interface.

Table 1 Potential oscillation at the liquid/liquid interface and composition of organic solution

solvent	supporting electrolyte	depolarizer	amplitude (mV)	figure of ΔV-t curve
1,2-dichloroethane	TBA^+TPhB^- (0.1M)	Cs^+TPhB^- (2×10^{-4}M)	280	
		TMA^+TPhB^- (2×10^{-4}M)	200	
	$TPrA^+TPhB^-$ (0.05M)	Cs^+TPhB^- (2×10^{-4}M)	120	
	$TPnA^+TPhB^-$ (0.1M)	Cs^+TPhB^- (5×10^{-4}M)	400	
	$TPhAs^+DPA^-$ (0.1M)	TMA^+TPhB^- (2×10^{-4}M)	200	
		H^+DPA^- (5×10^{-4}M)	200	
nitrobenzene	TBA^+TPhB^- (0.1M)	Cs^+TPhB^- (5×10^{-4}M)	200	
80mol% $CHCl_3$ + 20mol% BuOH	$TPhAs^+DPA^-$ (0.05M)	H^+DPA^- (2×10^{-4}M)	140	

TPnA, TBA, TPrA, TMA: *tetra-pentyl, butyl, propyl, methyl-ammonium*
TPhAs: *tetraphenylarsonium*
TPhB: *tetraphenylborate* ; DPA: *dipicrylaminate*

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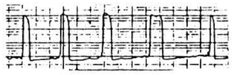
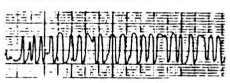
Table.2 Comparison between the period of oscillation and the concentration of electrolytes

Concentration of electrolytes $[TBA^+TPhB^-]$	$[Cs^+TPhB^-]$	Applied constant current (μA)	Mean period (min.)	Figure of ΔV-t curve
0.06 M	10^{-4} M	20	10	
0.06 M	2×10^{-4} M	30	9	
0.06 M	4×10^{-4} M	50	2	
0.04 M	2×10^{-4} M	34	3	
0.05 M	5×10^{-4} M	60	2	

S4-31

SELECTIVE SEPARATION OF METAL IONS WITH LONG-CHAIN 8-QUINOLINOL

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The environmental pollution by heavy metals has been one of a big social problem. The method of the solvent extraction has been widely used for the extraction-spectrophotometric determination and preconcentration of metal ions prio to instrumental analysis. Despite its low selectivity for the extraction of metal ions, 8-quinolinol has proven to be a very valuable extractant for a preconcentration of metal ions. Recently, hydrophobic extractants have become of interest for a selective separation of metal ions. Kelex 100 with a highly hydrophobic substituent at a 7-position of 8-quinolinol is characterized by the large distribution constant and the high selectivity for copper(II) over iron(III) [1]. In this work, a selective separation and determination of copper(II) and molybdenum(VI) with 5-octyloxymethyl-8-quinolinol (HO_8Q) is reported.

1. SELECTIVE SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM(VI)

The effect of pH of the aqueous phase on the extractability of copper(II) cobalt(II), nickel(II), zinc(II), lead(II), iron(III), molybdenum(VI), tungsten (VI), and vanadium(V) with HO_8Q into chloroform was shown in Figs. 1 and 2. The complete extraction of molybdenum(VI) was achieved between 5.0 mol dm^{-3} nitric acid and pH 5.5 The extractability of tungsten(VI) and vanadium(V) at 5.0 mol dm^{-3} nitric acid are 3% and 7% respectively. Metal ions, which are shown in Fig. 1, bismuth(III), gallium (III), tin(IV), zirconium(IV), niobium(IV), and thallium(I) are not extracted at 5.0 mol dm^{-3} nitric acid at all. The extracted molybdenum (VI)-HO_8Q complex absorbed at 380 nm with the molar extinction coefficient of 1.14×10^4 mol^{-1} dm^3 cm^{-1}. Molybdenum(VI) can be separated and spectrophotometrically determined in the presnce of large amounts of such metal ions as iron(III), nickel(II), cobalt(II), zinc(II), cadmium(II), lead(II), niobium(IV), gallium (III), thallium(I), and copper(II). Thus, the effect of diverse ions on the determination of

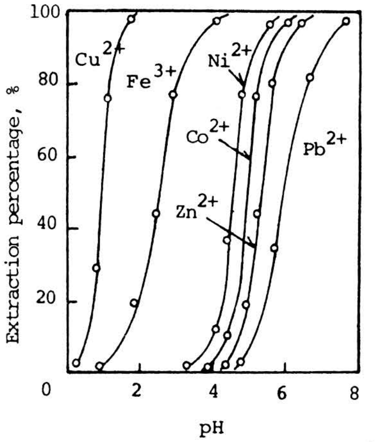

Fig. 1 HO_8Q: 0.01 mol dm^{-3}

molybdenum(VI) by the present method was remarkably reduced even without using masking reagents compared with that by using the thiocyanate method and 8-quinolinol method. The value of the extraction constant, $K_{ex}(=[MoO_2(O_8Q)_2]_o/[Mo(OH)_6][HO_8Q]_o^2)$ was determined to be 1.0 x 10^{10} at 20°C, which is only 1.5 times larger than that for 8-quinolinol. An excellent extractability of molybdenum(VI) with HO_8Q from stronger acidic solution compared with 8-quinolinol may be ascribed to a large hydrophobicity of HO_8Q.

2. SELECTIVE SEPARATION OF COPPER(II) AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II)

The complete separation of copper(II) from metal ions except for iron(III), which are shown in Figs.2 and 3 is possible. The extraction of copper(II) with 0.01 mol dm^{-3} HO_8Q at pH 1.9 by shaking for 5 min was complete. On the other hand, the extractability of iron(III) was less than 5% after shaking for 3 min. The complete separation of copper(II) from iron(III) was not accomplished. But copper(II) was stripped completely with 0.5 mol dm^{-3} nitric acid solution after shaking for 5 min. Even under the same conditions, about 2% of iron(III)-HO_8Q complex was stripped. Thus, copper(II) can be selectively separated in the presence of many metal ions. The molar extinction coefficient of the extracted copper(II)-HO_8Q complex in chloroform was to be 7.9 x 10^3 mol^{-1} dm^3 cm^{-1} at the absorption maximum of 410 nm. Copper(II) can be determined in the range from 2.2 to 57.8 μg/7 cm^3.

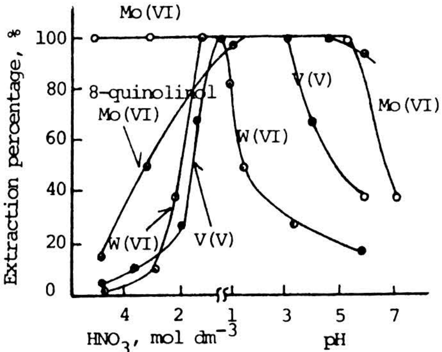

Fig. 2 HO_8Q : 0.01 mol dm^{-3}

3. EQUILIBRIUM OF COPPER(II) EXTRACTION

A plot of log D vs. $\log[HO_8Q]_o$ at pH 1.06 gave the straight line with a slope of 2.0, indicating that two molecules of HO_8Q probably participitate in the extraction of one copper(II) ion. The straight line with a slope of 2.0 was obtained by plotting log D vs. pH in the pH range from 0.5 to 1.5. The extracted species is perhaps a 1 : 2 copper(II) complex, $Cu(O_8Q)_2$.

The effect of the number of carbon atoms of an alkyl group in alkyoxymethyl-8-quinolinol on the extractability of copper(II) was examined. The $pH_{1/2}$ values for 5-octyloxymethyl-8-quinolinol, 5-propyloxymethyl-8-quinolinol, and 5-methyoxymethyl-8-quinolinol, and 8-quinolinol are 1.0, 1.2, 1.4, and 1.8 respectively. The fact that the $pH_{1/2}$ values for 5-octyloxymethyl-8-quinolinol is larger than that for 8-quinolinol should be ascribed to the large hydrophobic character of the substituent.

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S4-32

CATALYTIC DETERMINATION OF COPPER IN PLANTS AND BIOLOGICAL MATERIALS BY IRON(III)-THIOSULFATE REACTION

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Catalytic action of copper in the redox reaction between thiosulphate and iron(III) is used for the detection of trace copper [1]. Some papers have also been published so far on the determination of trace copper by use of the reaction [2-5]. In the papers, iron(III)-thiocyanate was used as the source of iron(III) ions or the oxidant, and was photometically measured to follow the redox reaction, so that the determination was interfered significantly with iron, zinc, lead and others [4,5] and required tedious and time-consuming separation procedure [2,3]. Goto et al. [6] have reported on the determination of copper by measuring the fading time of colored iron(III)-thiosulphate complex without thiocyanate using a Plufrich photometer. However, it was also influenced by the above ions, because a limited concentration of iron(III) was used.

In this present paper, the absorbance of iron(III)-thiosulphate complex has been studied in detail and measured to follow the catalytic reaction using a large excess of iron(III) ion and without using thiocyanate, so that a simple method with little influence of iron(III) and other foreign ions has been developed. The lower limit of determination is about 0.1 μg, and down to 1 ppm of copper in biological samples can be determined without any separation and/or concentration procedures.

The absorption spectra of iron(III)-thiosulphate were constructed from measurements of its time-dependant absorption at a range of wavelengths. The reaction was initiated in a 5-ml solution of 0.162 M ammonium iron(III) sulfate, 0.0208 M sodium thiosulfate and 0.1 M hydrochloric acid at 20°C, and photometically followed at 525 nm. The reaction within 3 min was approximated by a first-order path. A calibration curve of -log(absorbance) at the reaction time of 0.5 min was linear up to 1.5-μg copper with deviation of ca. 0.03 μg. Nitric acid also can be used as the acidic medium. The interference of foreign ions was examined in the determination of 1-μg copper. Up to 10 mg of sodium or potassium, 5 mg of magnesium, 2 mg of manganese(II), 1 mg of aluminum(III), iron(III), cobalt, nikel, chromium(III) or zinc(II), 0.5 mg of lead(II) or vanadium(V), 0.3 mg of cadmium(II) and 0.02 mg of chromium(VI) did not interfere.

Analysis of biological samples : A 50 mg to 1 g of sample was decomposed with 10 M nitric acid and then with a mixture of 4 M nitric acid and 12% perchloric acid. The solution was heated to fume and dryness. The residue was dissolved with 2 ml of 5 M hydrochloric acid and diluted to 100 ml with water. An aliquot (1 ml) was taken for analysis. The analytical result of Bovine Liver from NBS in Table 1 was agreed with the certified value (193±10 ppm). The blank value (<10 ppm) was within the deviation in calibration curve. A 500 mg of Pepperbush was heated to decompose with 10 M nitiric acid and 35% hydrogen peroxide, and then evaporated to remain oily substance. The oily residue was filtered off by a filter paper. The analytical result of the filtrate was agreed with the certified value (12±1 ppm). It shows that the analysis of the oily substance is not required. The analysis of human urine will be also described.

Table 1 Analytical result of Bovine Liver a)

No	Copper added (μg)	Copper found (μg)	Copper in sample (ppm)
1	0.0	0.50	20_0
2	0.5	0.94	17_6
3	1.0	1.45	18_0
			Av.18_5

a) 250-mg sample was decomposed and 1/100 in solution was taken.

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S4-33

THE OSCILLATING POTENTIAL AS A SENSOR FOR NON LINEAR PHENOMENA IN NATURE

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The Belousov-Zhabotinskii (B-Z) reaction is considered as a model reaction of non linear phenomena in nature and attracts much attention.

In the present report, the oscillating potential in B-Z reaction by various metal ions as catalysts is studied, and the reaction dynamics of various types of B-Z reaction is discussed in terms of the oscillating potential.

The oscillating potential and the reaction process

The B-Z reaction (1) comprises the following four major elementary reactions when RuL_3^{2+} is used as a catalyst, although it involves more than ten complex reactions$^{1)}$.

$$3BrO_3^- + 5CH_2(COOH)_2 + 3H^+ \xrightarrow{catalyst} 3BrCH(COOH)_2 + 2HCOOH + 4CO_2 + 5H_2O \quad (1)$$

$$BrO_3^- + 4RuL_3^{2+} + CH_2(COOH)_2 + 5H^+ \longrightarrow BrCH(COOH)_2 + 4RuL_3^{3+} + 3H_2O \quad (2)$$

$$4RuL_3^{3+} + BrCH(COOH)_2 + 2H_2O \longrightarrow 4RuL_3^{2+} + Br^- + HCOOH + 2CO_2 + 5H^+ \quad (3)$$

$$BrO_3^- + 2Br^- + 3CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 3H_2O \quad (4)$$

$$6RuL_3^{3+} + CH_2(COOH)_2 + 2H_2O \longrightarrow 6RuL_3^{2+} + HCOOH + 2CO_2 + 6H^+ \quad (5)$$

The B-Z reaction is composed of two reaction loops, one is the redox reaction loop shown in eq.[(2)-(3)-(5)], while the other is Br^- generate-consuming loop shown in eq. [(2) -(3)-(4)], as is shwon in Fig. 1.

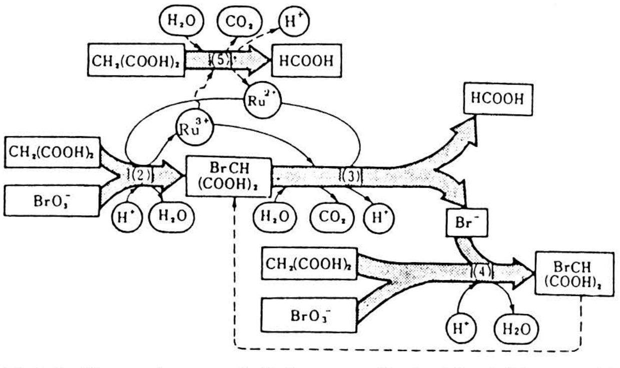

Fig.1 The scheme of Belousov-Zhabotinskii reaction

When a Pt electrode, a Bromide ion selective electrode and a reference electrode are immersed in the solution of the B-Z reaction system, the oscillating potential is observed at each electrode. The oscillating potential at Pt electrode corresponds to the dynamics of the redox loop[(2)-(3)-(5)], while that at Br^--ISE due to the Br^- generate-consuming loop [(2)-(3)-(4)].

The oscillating potential in Ru(II) catalyzed B-Z reaction.

A series of Ru(II) complexes* represented by a general formula of RuL_3^{2+} and $RuL_2X_2^{(2+n)+}$ were examined as catalysts for B-Z reaction. Among twelve complexes studied, six Ru(II) complexes are found to be effective as catalysts, whose oxidation potentials are more positive than 1.00V vs.SCE.

Two types of the oscillation patterns are observed with these Ru(II) complex catalysts, the one (group A) with larger amplitude, longer period and shorter duration time, the other (group B) with smaller amplitude, shorter period and longer duration time. A group catalysts are $Ru(bpy)_2(NO_2)_2$, $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(py)_2^{2+}$, while B group catalysts are $Ru(dmbpy)_3^{2+}$, $Ru(phen)_3^{2+}$ and $Ru(bpy)_3(NH_3)_2^{2+}$. The apparent activation energies of oscillation, E_a, are determined from the Arrhenius plots of the oscillation frequency which corresponds to the over all reaction rate. The E_a is in the order of $Ru(dmbpy)_3^{2+} > Ru(bpy)_2(NH_3)_2^{2+} > Ru(bpy)_2(py)_2^{2+} \fallingdotseq Ru(bpy)_3^{2+} \fallingdotseq Ru(bpy)_2(NO_2)_2$. This result indicates that the catalytic reactivity of A group complexes are larger than that of B group complexes.

The oscillating potential in Mn(II) catalyzed B-Z reaction.

The Mn(II) catalyzed B-Z reaction in phosphoric acid gives an instable oscillating potential. The oscillation damps quickly after 10 to 20 stable cycles. The reaction does not complete at this stage, however, so that the oscillation occurs again when the external condition is changed in the ways such that the stirring is stopped or the temperature is raised. The initial stable oscillations have much larger amplitude and longer period compared with those of the reaction catalyzed with Ru(II) or Ce(III) compounds, while the second oscillation shows chaotic nature.

Conclusion

The variation of the oscillation parameters with time show the self organizing nature of these reactions and the correlation between the potential change at Pt electrode and that at Br^--ISE in one oscillation, that is the limit cycle, gives dynamic relation of two reaction loops. The temperature dependence of the oscillation frequency gives the activation energy of the reaction. These analyses of the oscillating potential give much important informations about the reaction dynamics of non linear reactions.

Reference

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* Ru(II) complexes represented by a general formula of RuL_3^{2+} and $RuL_2X_2^{(2+n)+}$, where L represents 2,2'-bipyridine, 4,4'-dimethylbipyridine and 1,10-phenanthroline; X_2 represents $(NH_3)_2$, $(py)_2$, $(NO_2^-)_2$, $(CN^-)_2$ and etc., n=0 , -1, -2, depending to the formal charge of ligand.

S4-34 STRIPPING METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN AIR WITH LEAD-FILM ELECTRODE

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Suck 15 dm^3 air sample into 5 ml H_2O_2-HAc-NaAC solution for the absorption of sulfur dioxide at rate of 0.5 dm^3 per minutes. Heat on a steam bath for 2 monutes to expel excessive hydrogen peroxide. Add 0.05 mg Pb^{2+}, put in glass-carbon ball-electrode, using silver-film electrode as reference and platinum wire as auxiliaru electrode. Apply electro-deposition at -1.2^V for 30 seconds and at 10.30 V for another 30 seconds. Scan to -1.2 V at rate of 40 mV per second. Record the stripping voltage-amper first derivative curve. There is a peak of stripping on the -0.8 V. The peak-current is proportional to the concentration of sulfer dioxide in air at the range of 0.1-5.0 g in 15 dm^3 air.

S5-01

ELEMENTAL DISTRIBUTIONS AND GEOCHEMICAL FEATURES OF THE 1400-METER SEDIMENT CORE SAMPLES IN LAKE BIWA AS ELUCIDATED BY ICP-AES

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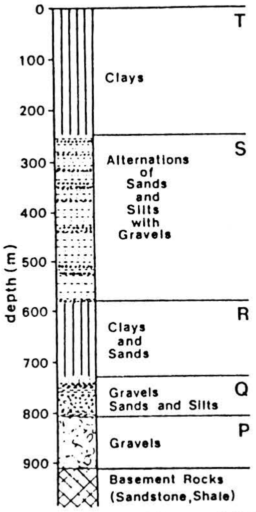
Lake Biwa is the largest lake in Japan, located almost in the center of the Honshu Island, near Kyoto. It has been known that the origin of Lake Biwa is very old because depression has been proceeded during the late Cenozoic era since the birth of the lake. Thus the lake have survived up to the present in spite of a thick pile of sediment on the lake floor. The history of Lake Biwa is, therefore, of interesting subject for the scientists in the various fields.

During 1982-1983, the 1400-meter drilling sediment core samples were taken from Lake Biwa at almost the center of the present lake. This research project has been conducted by Prof. S. Horie in the University of Kyoto, and we have joined the project especially for the distribution analysis of inorganic elements in the sediment core samples.

1. MATERIALS AND EXPERIMENTS

The columnar section of the 1400-meter core sample from Lake Biwa is shown in Fig. 1. As can be seen in the figure, the core sediment is divided into 5 Beds from the geological aspects: T: 0-250 m, S: 250-580 m, R: 580-730 m, Q: 730-820 m, and P: 820-910 m. Below 910 m, it was basement rocks, consisting of mainly sand stone and shale. The sediment samples from the beds T-Q were collected at about each 5 m from the bottom surface to 820 m, and then about 150 samples were analysed by ICP-AES (inductively coupled plasma atomic emission spectrometry). The samples were digested by HNO_3-HF-$HClO_4$, after drying at 110 C for 4 hours, and finally dissolved in HCl. Major, minor, and trace elements (Al, Fe, K, Mg, Na, Ca, Ti, Mn, P, Ba, Sr, V, Cr, La, Cu, Ni, Y, Sc, and S) were determined simultaneously by ICP-AES.



Yokoyama and Takemura (1983)

Fig. 1. Columnar Section of the 1400-Meter Sediment Core Samples from Lake Biwa.

2. ELEMENTAL DISTRIBUTIONS OF SEDIMENT CORE SAMPLES

In Fig. 2, the vertical elemental distributions of Fe, Mn, and P are shown as representative examples. Some remarkable changes of these three elements in concentration can be seen between the boundaries of the T-S beds (near 260 m) and the S-R beds (near 580 m). This suggests that some geological variations occurred in these regions, which correspond to about 600,000 and 2,500,000 years ago, estimated from fission-track dating. The elements such as Mg, V, Cr, Cu, Ni, Sc, and S showed the similar distribution patterns to those of Fe, Mn, and P. On the other hand, the distributions of Al, K, Na, Ti, Sr, Ba, La, and Y showed small changes through the whole sediment core samples.

Iron and Mn are known as aquatic elements which easily change the chemical oxidation states under reductive aquatic environment. Further, the concentrations of P and S in the sediment samples have significant relationships with biological activities in water. Therefore, it can be speculated that during the period of the T bed Lake Biwa have been in aquatic environment. From another experimental results,it is noticed that the Mn concentration in the sedimentis a good index of water depth of the lake. In addition, the elements which showed the similar distributions to Fe, Mn, and P are known to be bio-elements. From these facts or results, the present Lake Biwa has been at the present location since about 600,000 years ago as a quite deep and large lake (water depth of about 40-100 m). The decreases of the concentration of bio-elements in the S bed may suggest that Lake Biwa was a shallow lake or on the land surface with or without water sometime before 600,000 years. This is supported by the facts that the distributions of the rock-forming elements such as Al, Ti, Na, K, Ca, Sr, Ba, and La as well as those of quartz showed small concentrationchanges or rather larger contents in the sediment in the S bed. The period of the R bed may be also in an aquatic environment. In addition, the concentrations of S were not more than 600 ug/g. This suggests that Lake Biwa has not been in marine environment at the present location since its birth. Further detailed investigations will be discussed.

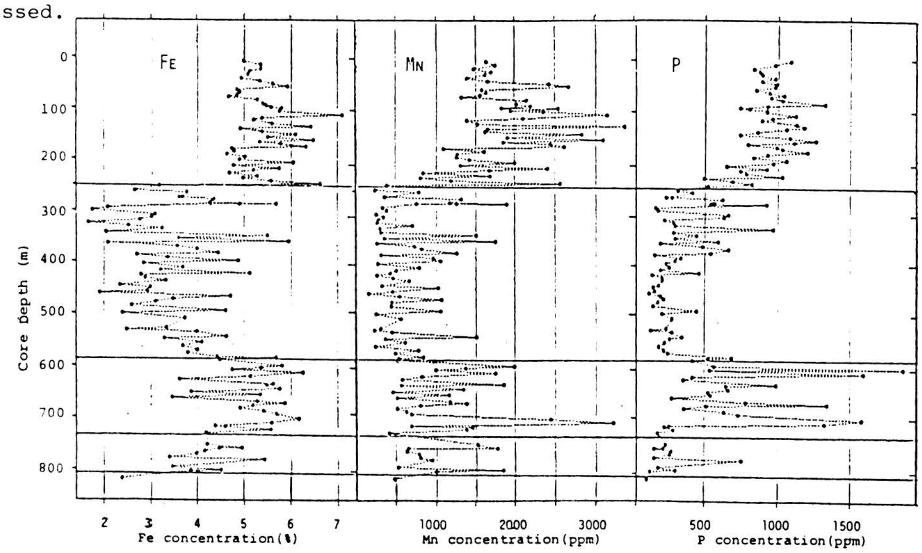


Fig. 2. Vertical Distributions of Fe, Mn, and P in the 1400-Meter Sediment Core Samples

S5-02

CONTINUOUS MEASUREMENT OF EVAPORABLE ORGANIC HALOGEN COMPOUNDS IN WATER WITH STRIPPING AND SURFACE IONIZATION SENSOR

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Japan

In recent years, the pollution of tap water and underground water by organic halogen compounds of trichloroethylene etc. have been noted. Therefore the simple and continuous monitoring method of these environmental water is desired. The authers studied the method combining stripping and a surface ionization sensor of halogen-sensitivity, which was modified in accuracy and precision with the intermittent conduction of sample gas based on the study of the detection mechanism by the authers.

EXPERIMENTAL

The apparatus of stripping and detection was showed in Fig.1. The sample water was continuously conducted into the column in which air was bubbled at 50 ml/min to transfer disolved organic halogen compounds into itself. The sample and reference air were induced alternatively to the sensor with a sequential access micro valve. The sensor was composed of an anode of platinum filament of 0.1 mm in diameter wound on ceramic bobbin of o.d.1 mm and a cylindrical cathode (Fig.2). The current of the orders of 0.1 to 1 uA between the electrodes supplied the voltage of 200 V was amplified with FET and recorded on a chart (Fig.3). The rate of air flow in the sensor was 50 ml/min; The sample air was conducted for 3 sec. at an interval of 30 sec. or above. The anode was heated by delivering 750 mA (about 850°C).

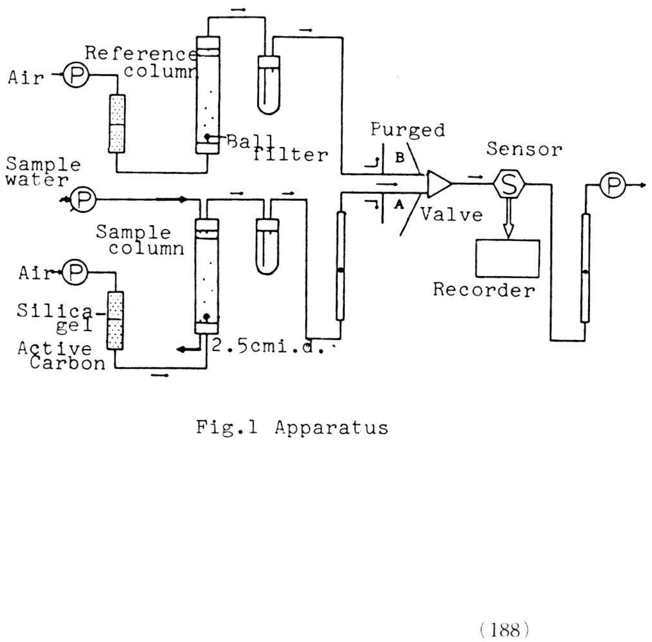

Fig.1 Apparatus

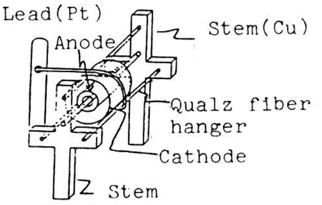

Fig.2 Halogene sensor

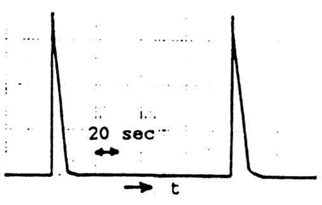

Fig.3 A example of chart

RESULTS AND DISCUSSION

Area of gas-liquid contact and concentration of gas-phase: Air bubbling with a fritted glass filter of 20 to 30 um in pore size at flow rate of the water of 200 ml/min, the ratios of operating concentration to equilibrium one in gas-phase were measured at the various depth of the column in trichloroethylene(TCE) solution of 0.365 in Henry constant of 20°C. Where the contact area is directly proportional to the depth. Figure 4 shows that the long column is required for the equilibrium concentration in the stripping condition. The column of 40cm was used to get the ca. 0.6 in the ratio in the subsequent experiment. The ratio of chloroform of small Henry constant(0.158) was 0.63 in agreement with that of TCE. On the other hand the relationship between the ratios and the flow rate of the water was at a plateau at 100 ml/min or above.

Effect of temperature: The out-put for TCE of 100 ug/l was measured at the various temperature of the air and the water. Figure.5 shows that the temperature of water governs the ratio. The data was reproducible and agreed with the theoritical value(0.6) at 25°C or bellow,respectively. The concentration in the water is measured exactly with making temperature corrections.

Calibration curves: The out-put in Fig. 6 was governed by the product of the Henry constant and the sensitivity of the sensor. The limit of quantitation was a few ug/l; The co-efficient of variance in 30 ug/l was 5.7 %.

Interference from co-existence: The sensitivity of free chlorine at pH 6.5 and chloride ion of 0.1 mg/l was a nine hundredth as small as that of chloroform; The co-existence of sodium chloride brought the error of +7 %. These interference was negligible in practice.

This system can be used in practice by calibrating with chloroform and TCE in tap water (drinking water) and ground water,respectively.

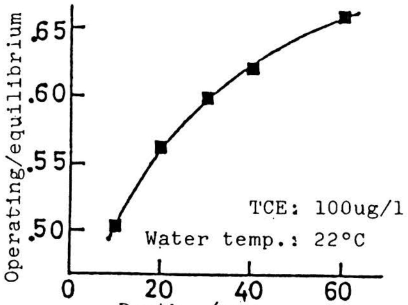

Fig.4 Contact area - conc. of gas phase

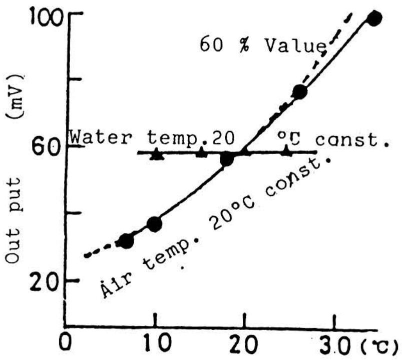

Fig.5 Characteristic of temp.

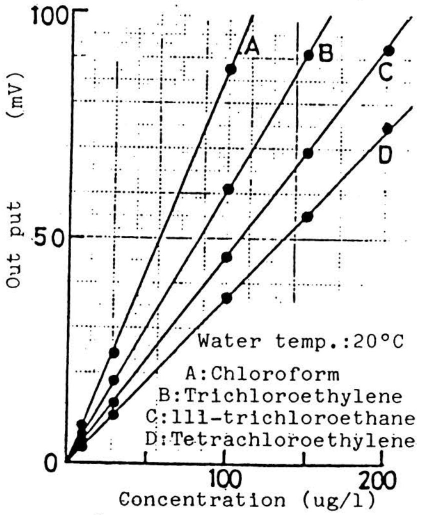

Fig.6 Calibration curves

S5-03

HEAVY METAL ANALYSIS IN SEA WATER SHELLFISH AND RIVER WATER SHELLFISH IN KOREA

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According to the industrialization in many countries, river and sea water are contaminated with various kind of pollutants including heavy metals. Shellfish is usually living on the sediment area where influent metals are accumulated. As the result shellfish could be a indicator of metal pollution in the river and sea water.

Authors investigated heavy metal contents in shellfish which are living in Han River, the largest river passing through Seoul city, by comparing the metal contents in sea shellfish.

Eight kind of the river shellfish, Cipangopaludina chinensis malleata, Semisulcospira amurensis gottschei, Unio douglasiae, Cristaria plicata, Anodonta woodiana, Solenaia triangularis, Lamprotula gottschei, Corbicula fluminea, and three kinds of sea shellfish, Meretrix lusoria, Cyclina sinensis, Mactra veneriformis, were chosen as the sample specimen.

The samples were digested with nitric acid and perchloric acid, and metals were analyzed by Atomic Absorption Spectrophotometer and cold vapor generator.

The metal contents in the river water shellfish were 5.12 ppm of Cd, 31.74 ppm of Zn, 5.56 ppm of Cu, 251.28 ppm of Mn, 124.70 ppm of Fe, 4.29 ppm of Ni, 0.34 ppm of Hg, and 5.59 ppm of Pb. In the sea water shellfish the metal contents were 0.37 ppm of Cd, 9.34 ppm of Zn, 1.93 ppm of Cu, 1.84 ppm of Mn, 21.24 ppm of Fe, 1.84 ppm of Ni, 0.07 ppm of Hg, and 1.82 ppm of Pb, whose values are less than the river water shellfish.

In the analysis process shellfish were divided into five sections; mentel, foot, gill, viceral organ, and adductor muscle. Gill had the highest concentration of metals among above five sections in shellfish.

The five point sediments in river were analyzed to compare metal contents with shellfish and got the following results ; Fe 97.16 ± 59.84 ppm, Mn 59.23 ± 11.58 ppm, Cd 0.05 ± 0.04, Cu 1.05 ± 0.79 ppm, Zn 5.82 ± 4.42 ppm, Ni 1.45 ± 0.73 ppm, and Pb 1.81 ± 0.90 ppm.

The river waters were also digested with nitric acid and analyzed with AAS. The highest concentration metal was Fe as 50.40 ± 42.61 ppm and the Cd concentration was 0.13 ± 0.08 ppm.

As the above results river shellfish contained much higher concentration of metals than sea shellfish.

S5-04

THE FLUCTUATION OF WATER QUALITY AND SUCCESSION OF PHYTOPLANKTONS IN THE BRACKISH LAKE NAKANOUMI.

-YONAGO EMBAYMENT-

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1. INTRODUCTION

Lake Nakanoumi is most prominently characterized by its brackish water consisting of fresh and sea water and by the abundance of nitrogen and phosphorus which permits high biological productivity and facilitates water pollution. Since the water quality varies greatly both horizontally and vertically and sewerage system in the river basin had remained backward, eutrophication had remarkably progressed from 1975 to 1978. In addition, the biota of Lake Nakanoumi, species living in the lake, such as zoo- and phytoplanktons, macroalgaes and fishes, is extremely divesified because fresh water and marine species are added to species proper to brackish water. And their distribution shows much variations horizontally and seasonally [1].

Thus, Lake Nakanoumi which is the closed waters on the coast has ecologically unique characteristics together with the phisicochemically complicated water environment. In this lake, there is waters, which is highly closed and is strongly influenced by the influx of sewage from the surrounding city, such as Yonago Embayment waters, where eutrophication progresses more rapidly and water pollution is more conspicious than in the main basin of Lake Nakanoumi. In this waters, the standing crop of phytoplankton is large and the occurrence frequency of red tide is also high. It is not easy to grasp the distribution of water and phytoplanktons or the relation between them in the main basin of Lake Nakanoumi because in the main basin, the stream flows on a large scale and the water is apt to be influenced by the water and phytoplanktons in other areas. In this respect, unlike the main basin of Lake Nakanoumi, Yonago Embayment waters is firmly closed and the stream flows on a very small scale and consequently it is hardly affected by the water of other areas.

Therefore, Yonago Embayment waters has an advantage over the main basin of the lake in that it is easier to seize the distribution of water and phytoplanktons and the relation between them.

The understanding of characteristics of phytoplanktons is highly closed waters like Yonago Embayment seems to offer important information for elucidation of the mechanism of water pollution, for prediction of the water quality after a salt- to fresh-water transition in the feature and for prevention of the progress of water pollution in Lake Nakanoumi which is the closed water area at the coast.

The present report is based on the data obtained from the investigation on dynamics of phytoplanktons in Yonago Embayment waters from 1974 to 1984.

2. GEOGRAPHIC ENVIRONMENT

Yonago Embayment is located at the east end of Lake Nakanoumi, deeply landlocked by the protrusion of the Yumigahama Peninsula and it is shallow with the average depth of about 4.5 m. The embayment is surrounded by urban district (Yonago City) and the sewage from the city directly runs into this waters. The stream in the embayment is anticlockwise and the water is ready to stagnate.

3. WATER ENVIRONMENT

As Yonago Embayment is about 16 km away from the Sakai Channel which is the entrance of the sea water and the depth is suddenly reduced around the mouth of the embayment. Thus, the embayment is not directly influenced by the sea water which flows into Lake Nakanoumi by a tidal movement and consequently a firm halocline observed in the main basin of Lake Nakanoumi is not formed. For this reason, The water in the embayment is more apt to be mixed vertically by winds and waves than that in the main basin. In addition, the concentration of nitrogen and phosphorus in this embayment is higher than those in the other water areas of Lake Nakanoumi, for the amount loaded from the urban sewage and the bottom of the lake is large.

4. DYNAMICS OF PHYTOPLANKTONS

The changes in the amount of Chlorophyll-a (Chl-a) at the depth of 1 m had been monitored from 1974 to 1984 and as a result, the values more than 70 ug/l had been often observed and in March of 1979, a very high values of 334 ug/l was recorded. As to the relationship between the amount of Chl-a and the water temperature or the salinity, it was observed that the amount of Chl-a tended increase when the water temperature and the salinity were low. Besides, the phytoplanktons which had appeared most numerously in Yonago Embayment were *Skeletonema costatum*, *Prorocentrum minimum*, *Cyclotella* sp., *Gymnodinium* and so on, which occupied more than half of the total numbers of phytoplanktons appeared during eleven years (1974-1984).

Among them, the phytoplankton which caused the most remarkable red tide was P. minimum and it appeared frequently from winter to spring, when the water temperature was low. And it was observed that the red tide phenomenon caused by this species tended to occur when a strong seasonal wind blew immediately after the mass appearance of *S. costatum*.

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S5-05

NITROGEN METABOLISM IN THE BRACKISH LAKE NAKANOUMI

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The nitrogen-15 tracer technique is an effective approach for the study of the nitrogen metabolism in aquatic environment. In aquatic field studies, this technique was first applied to the measurement of the nitrogen fixation rate in lake water [1,2].

In this work, we applied the ^{15}N tracer technique [3] to the measurement of ammonium and nitrate uptake rate by the natural phytoplankton communty in the brackish lake Nakanoumi. We also applied the ^{15}N dilution technique [4] for simultaneous determinations of nitrification and nitrate reduction in a water-sediment system.

Here, we report on the seasonal variation of ammonium and nitrate uptake rate and the dynamics of ammonium and nitrate in the phytoplankton standing stocks, and a nitrification-denitrification mechanism in the water-sediment system, as observed in the brackish lake Nakanoumi.

1. WATER ENVIRONMENT

Lake Nakanoumi is connected with Japan sea only via Sakai Channel which is approximately 0.3 Km wide and 7.5 Km long. This lake had a surface area of 97.5 Km^2 and a total storage volume of 5.2×10^8 m^3 at mean water-level of 0.2 m. The mean depth of the lake is 5.4 m and about 70% of this area is shallower than 7 m. Salinity decreases toward the interior of Lake Nakanoumi from 30-35 ‰ at Sakai Channel to 5-10 ‰ at Ohashi Channel. In the deeper basin of Lake Nakanoumi a halocline developes at a depth 3-4 m [5]. Dissolved oxygen (DO) decreased in the water below the halocline in summer. But the dissolved exist about 10-30% saturation, because a seawater with high DO concentration enter directry into the bottom of Lake Nakanoumi through Sakai Channel [6].

At the central basin of Lake Nakanoumi a high concentration of nitrate was observed in winter, while a high concentration of nitrite derived from the nitrification was observed in the overlying water in summer.

2. UPTAKE RATE OF AMMONIUM AND NITRATE BY PHYTOPLANKTON

The uptake rate of ammonium and nitrate by the natural phytoplankton community in Lake Nakanoumi were measured from August 1983 to July 1984 using the ^{15}N tracer technique, Ammonium was assimilated in preference to nitrate, and nitrate use began when ammonium was depleted to about $3\ \mu gN \cdot l^{-1}$. The result of the mutiple regression analysis implied that the uptake rate of ammonium was modified primarily by water teperature, phytoplankton standing stock and ambient concentration of ammonium.

Nitrogen appears to be the most important limiting element for the phytoplankton growth in the euphotic layer at the central basin of Lake Nakanoumi from May to December, because the halocline acts as an effective barrier for the vertical transport of enriched nitrogen nutrient in the overlying water. The seasonal pattern of nitrate concentration in the euphotic layer at the central basin of Lake Nakanoumi was closely related to the nitrate uptake rate by the phytoplankton standing stocks.

3. NITRIFICATION AND DENITRIFICATION IN A WATER-SEDIMENT SYSTEM

Samples of water-sediment from Lake Nakanoumi were incubated in the labolatory under conditions of several dissolved oxygen concentrations. The total inorganic nitrogen (TIN) concentrations decreased with increasing concentration of DO from 4 to 31%.

The rate of nitrification and nitrate reduction in a water-sediment system were simultaneously determined by the ^{15}N dilution technique. The rate of nitrification, nitrate reduction and denitrification at 25°C were 9-15, 22-31 and 15-22 $mgN \cdot m^{-2} \cdot day^{-1}$ respectively. The summer TIN concentrations in the hypolimnion at the central basin of Lake Nakanoumi substantially decreased during the period of 1979-1984. The nitrification-denitrification in the water-sediment system at low DO (10 30%) condition appears to be at least partly responsible for this interesting phenomenon.

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S5-06 THE AUTOMATIC DETERMINATION OF IODINE SPECIES IN SEAWATER BY A NEW ELECTROCHEMICAL TECHNIQUE

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INTRODUCTION

Inorganic iodine species in seawater have been analyzed by various methods such as AgI precipitation method, catalytic method, I_3^- spectrophtometry and pulse polarographic method. In these methods, apart from the AgI precipitation method which is very complicated, iodine species are determined as IO_3^- and total-I, and I^- concentration is obtained as the difference between those of IO_3^- and total-I. Since the I^- concentration is often far lower than that of IO_3^- in seawater, sufficient accuracy for determination of I^- concentration cannot be obtained by these methods. Moreover, there is a possibility that organically-bound iodine is determined as a part of I^- by these methods. We have developed a new electrochemical technique for the automatic determination of iodine species in seawater(1). This method is based on the principle that the I^- is electrochemically oxidized to I_2 and simultaneously adsorbed on a carbon electrode in a preconcentration cell and that the I^- eluted from the carbon electrode is determined at the continuously polished Ag_3SI electrode in the detection cell. With this method iodine species can be accurately determined as I^- and total-I from seawater samples of less than 50 mL.

METHOD

Filtered seawater is acidified with acetic acid. At the same time, tetradecyldimethylbenzylammonium chloride is added. To the sample solution for total-I analysis is added ascorbic acid to reduce IO_3^- to I^-. Then the sample solutions are placed on an auto-sampler and the subsequent operations are automatically conducted in a flow system that is controlled with interlocking 6-step timers. At the first stage, the residual sample solution in the system is exchanged with a new one, followed by changing the potential applied to the preconcentration cell from -0.2 to 0.8 V vs. NSE. The sample solution is passed through the cell for 80s(7mL) for total-I analysis and 400s(34mL) for I^- analysis at the flow rate of 5mL/min. After electrolysis, the cell is rinsed with a cleaning solution to remove interfering materials. The cell potential is again reduced to -0.2 V vs. NSE to elute I_2 from the carbon electrode with eluent containing a reducing agent. The eluent is introduce to the detection cell and I^- is determined at the polished electrode to which the potential of 0.06 V vs. NSE is usually applied. Since a major portion of coexisting materials is separated at the electrolysis stage and the Ag_3SI electrode is highly selective for I^-, there are few interfering materials in this method.

To examine the effect of organically-bound iodine on the determination of inorganic iodine species by this method, alkyl iodide compounds, iodoalcohols and iodotyrosine derivatives, which have been found in marine organisms, were tested. Almost all organic iodine had negligible effects, except that a part of iodotyrosine derivatives and iodoform is detected as I^-.

ANALYTICAL RESULTS

This method was applied to the seawater samples collected from the adjacent seas of Japan and the north Pacific Ocean in 1984 and 1985. In all sea areas investigated, the distributions of total-I were similar to previous observations from the open oceans, that is, its vertical profiles were almost uniform from surface to bottom with slight depletion in the surface waters. I^- distributions were also as expected for all sea areas except for the Japan Deep, which had a relatively high concentration in the surface waters and extremely low concentration below the euphotic zone. The average concentration of I^- in the deep waters of the north Pacific Ocean was 2.5 nM, which corresponds to 0.6 % of total-I. The proportion of I^- to total-I in the surface waters was ca. 12 to 15 % between 35°N and 46°N, and it increased from south of 35°N; 30 % at 30°N and 45 % at 24°N. Besides the surface waters, high concentrations of I^- were observed in the bottom waters of the Japan Sea, the water column of the Japan Deep and directly overlying waters of the north Pacific Ocean. Especially, noticeable amounts of I^- were distributed irregularly from surface to bottom in the Japan Deep. Since the concentration of total-I in these waters is a common value, the increase of I^- concentration is considered to be due to the fact that IO_3^- is reduced to I^-. According to the previous reports, the reduction of IO_3^- in the ocean is caused by nitrate reducing bacteria, and IO_3^- is used to compensate for the depletion of NO_3^- in the surface waters. However, a considerable amount of I^- exists in the surface waters of north of 40°N where the concentration of NO_3^- is more than 10 μM and high concentrations of I^- are observed partly in the deep waters where the concentration of NO_3^- is more than 30 μM. This suggests that the reduction of IO_3^- occurs when the consumption rate of NO_3^- is fairly fast in the presence of a large amount of organic matter, rather than when NO_3^- is depleted.

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S5-07

ON-BOARD AUTOMATED SYSTEM FOR MONITORING LAKE ENVIRONMENT

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INTRODUCTION

We developed the on-board automated monitoring system, which enables us to measure the time series of 13 physical/chemical components (water temperature, pH, conductivity, dissolved oxygen, turbidity, chlorophyll-a, COD, TN, NO_3-N, NH_4-N, TP, PO_4-P, SiO_2) at any time interval greater than one hour. We applied this system to the estimation of the vertical diffusivity near the bottom and the release rate of ammonium nitrogen from the bottom in the Southern Basin of Lake Biwa.

The release rate of ammonium nitrogen from the sediment in the Northern Basin of Lake Biwa was estimated by Kamiyama et al. (1), and they found that the release rate is 1.6 mg-N/m^2/day. Their result was, however, derived from the vertical distributions of ammonium nitrogen in the sediment and it does not necessarily mean the real flux of ammonium nitrogen from the bottom to the water. Moreover, their method is not available for a shallow lake like the Southern Basin, because the sediment of a shallow lake is often disturbed by wind-waves and the distribution of ammonium nitrogen may be not stable enough to determine the release rate.

Our main concern of this study is to establish the method to estimate the vertical diffusivity and the release rate of chemical components near the bottom of a shallow lake such as the Southern Basin.

DISCUSSION

We set the on-board automated monitoring system on the dredged area (depth 12 m) in the Southern Basin from 16th to 30th of October in 1984. The sampling water of each depth of 7 m and 11 m was pumped up at every one hour, alternatively. In Fig.1, the circles show the time change of turbidity, the solid line does the wind speed at Yabase island and the hatched area indicates the precipitation at Otsu. It is easily found that we had weak wind and no rain from 23rd to 28th. In order to estimate the release rate of ammonium nitrogen from the bottom, we used the data on these calm days.

Fig.2 illustrates the observed values(circles) and the predicted values (solid lines) of ammonium nitrogen. This prediction was performed on the assumption that the distributions of ammonium nitrogen are governed by the one-dimensional diffusion equation. After the calculations of several cases, we succeeded in obtaining the optimum values of the vertical diffusivity and the release rate. The vertical diffusivity is compared with the values estimated the different method(2) in Fig.3.

CONCLUSION

We estimated the vertical diffusivity and the release rate of ammonium nitrogen in the Southern Basin of Lake Biwa with the data of the automated monitoring system. As the result, it is found that the vertical diffusivity is 0.13 cm²/sec and the release rate is 39.2 mg-N/m²/day. We can conclude that the method of this study is reasonable to estimate the vertical diffusivity and the release rate in a shallow lake.

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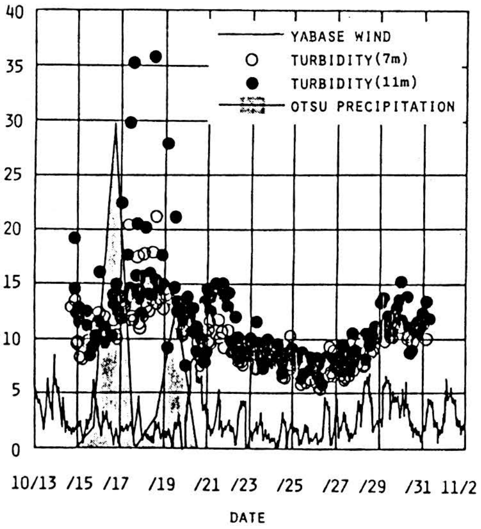

Fig.1 Time change of turbidity, wind speed and precipitation.

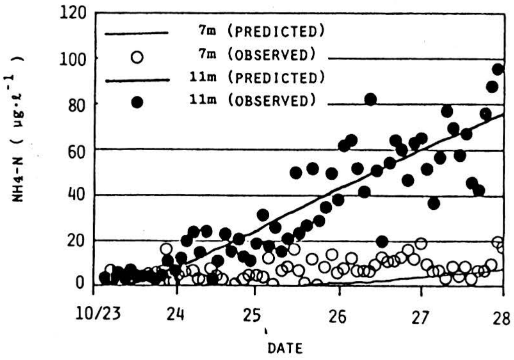

Fig.2 Prediction of the concentration of ammonium nitrogen.

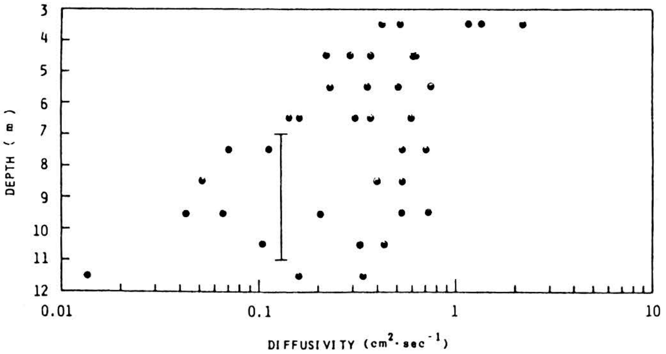

Fig.3 Comparison of diffusivities derived by the different methods. ● are estimated from the profile of water temperature and the vertical solid line shows the result of this study.

S5-08

DEVELOPMENT OF CONTINUOUS MULTI-ELEMENTS MONITORING SYSTEM FOR THE ENVIRONMENTAL WATER CHARACTERIZATION

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INTRODUCTION

Recently, red tide occurs very often in coastal sea areas and in lakes in Japan. It is considered that one of the main reasons of occurrence of red tide is the eutrophication of waters. For the elucidation of mechanism of red tide occurrence and for the purpose of foresight of its occurrence it is necessary to develop automated measurement techniques of eutrophic substances and other water quality parameters. Therefore, a new continuous multi-elements monitoring system for the environmental water characterization has been developed.

DEVELOPMENT OF AUTOMATED MEASURING APPARATUS OF EUTROPHIC SUBSTANCES

Automated measuring apparatus of phosphate, total phosphorus, nitrate, ammonia and total nitrogen were developed. Dissolved inorganic phosphate was measured with phosphomolybdate-electrolytic detection method1). Total phosphorus was determined by autoclave digestion of phosphorus compounds following the phosphomolybdate method. Ultraviolet dual wavelengths spectrophotometric method was applied to the measurement of nitrate2), enrichment with a gas-permeable membrane and measurement of conductivity were to ammonia3), and the autoclave digestion method and the ultraviolet spectrophotometry to total nitrogen4).

AUTOMATED MEASURING APPARATUS OF OTHER WATER QUALITY PARAMETERS

Temperature, pH, dissolved oxygen, salinity and turbidity were measured with the conventional apparatus. An automated apparatus for the measurement of chemical oxygen demand with the permanganate oxidation method was developed. Silicate was measured with the silicomolybdate-electrolytic detection and chlorophill a with the fluorometric method.

CONSTRUCTION OF CONTINUOUS MULTI-ELEMENTS MONITORING BUOY

A monitoring buoy of which size was 6.0m long, 4.5m wide and 4.7m high was constructed. All above mentioned automated measuring apparatus were equipped to the buoy. Fig. 1 shows the construction of the buoy. Two diesel electric power generators of 2kW capacity, an automated sampling apparatus, a wireless telemetering system and data logger were equipped to the buoy.

A specially disigned automated washing equipment for the sampling and measuring systems overcame the problems due to the growth of algae on the systems.

Another monitoring buoy which could transport on a traller from water to water, was constructed. The size of the small buoy was 5.4 x 2.8 x 2.2m. Fig. 2 shows the construction of the buoy.

EVALUATION OF THE MULTI-ELEMENTS MONITORING BUOY

The automated measuring apparatus could measure automatically the water quality parameters without any serious problem. It was found that the concentration of eutrophic substances in waters was changing very rapidly.

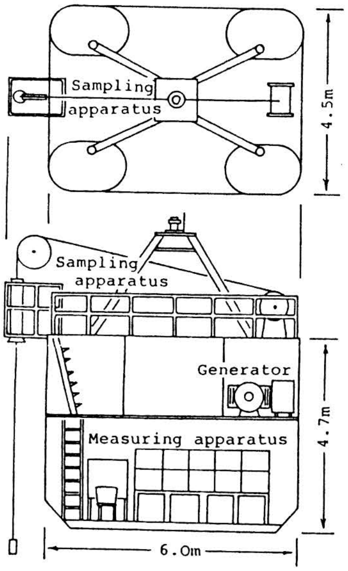

Fig. 1 Construction of large buoy

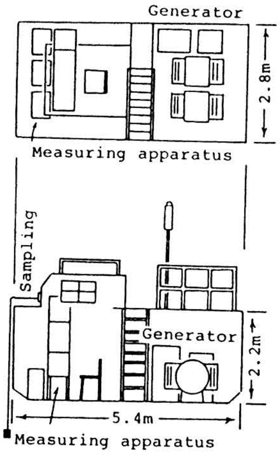

Fig. 2 Construction of small buoy

ACKNOWLEGEMENT

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S5-09

CONTINUOUS MONITORING METHOD OF ENVIRONMENTAL WATERS USING CONTINUOUS MICRO FLOW

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Environmental scientists are aware of the increasing need for automated methods which are suitable for continuous measurements of chemical oxygen demand (COD), total phosphorus and nitrogen, which can also determine such trace toxic metals as mercury in wastewater and other water samples. Two classes of the continuous flow analyzers are in use today for such purpose; the air-segmented analyzer (Technicon AutoAnalyzer) of Skeggs and the flow injection analyzer of Ruzicka and Hansen. The former employs air-segmentation of sample, thus dividing the flowing sample stream into a number of compartments separated by air bubbles to prevent broadning a sample zone. The latter is based on the injection of sample into a moving, continuous carrier stream, thus using the dispersion of sample zone by laminar flow. The disadvantage of conventional flow analyzers is that analytical results tend to deviate from those obtained by the standard method, because the reaction time is usually too short and large amounts of reagents are required for continuous measurement.

We have been developed the completely continuous flow analyzer for COD, total phosphorus, total nitrogen and total mercury in wastewater and environmental waters. Our analyzer differs from conventional continuous flow analyzers in only one respect. The sample is continuously injected as a stream into a continuous reagent stream at a lower flow rate(less than 100 µl/min) without air segmentation.

1. CONTINUOUS MONITORING METHOD OF COD

A sample, an acidic reagent (10 % sulfuric acid containing 40 % phosphoric acid), a catalytic reagent (0.5 % siver nitrate) and an oxidizing reagent (1.6 mM potassium permanganate) are continuously pumped with a peristaltic pump at the low flow rate of each 50 µl/min. The sample stream is mixed in order with the acidic, catalytic and oxidizing reagents. The mixture is introduced into a reaction tube (18 m x 0.6 mm i.d.) in a boiling water bath, where the sample is oxidized for 30 min under continuous flow. Following the reaction, the mixture stream passes through a micro photometric flow cell (10 mm light pass, 8 µl volume) and then a thin layer electrolytic cell. The absorbance at 525 nm and the reduction current at 0.50 V vs. Ag/AgCl of permanganate unreacted are continuously recorded to monitor COD in water sample.

2. CONTINUOUS MONITORING METHOD OF TOTAL PHOSPHORUS

A sample, an oxidizing reagent (1 % potassium persulfate in 0.1 N sulfuric acid) and a color developing reagent (1.5×10^{-4} M malachite green, 1.7×10^{-2} M ammonium molybdate, 0.06 % polyvinyl alchol in 2.5 N sulfuric acid) are continuously pumped at the flow rate of each 60 µl/min. The sample stream is first mixed with the oxidizing reagent and introduced into a hydrolysis and oxidation reaction tube (4 m x 0.6 mm i.d.) inserted a platinum wire (4 m x 0.2 mm o.d.) in an aluminum bath (120°C), where the organic phosphorus and condensed phosphates are converted to orthophosphate. The mixture stream is then mixed with the color developing reagent and introduced in to a reaction tube (5 m x 0.5 mm i.d.), where the orthophosphate is converted to the ion-association complex of $(\text{malachite green})_3(PMo_{12}O_{40})$. Following the reaction, the stream passes through a micro photometric flow cell. The absorbance at 600 nm is continuously recorded to monitor total phosphorus in water sample.

3. CONTINUOUS MONITORING METHOD OF TOTAL NITROGEN

A sample, an oxidizing reagent (1.8 % potassium persulfate in 0.6 N sodium hydroxide) and an acidic reagent (0.62 N hydrochloric acid) are continuously pumped at the flow rates (µl/min) of 100, 50, and 50, respectively. The sample stream is first mixed with the oxidizing reagent and introduced into a oxidation reaction tube (8 m x 0.5 mm i.d.) inserted platinum wire in an aluminum bath (150° C), where all nitrogens in ammonium, nitrite and organic forms are converted to nitrate within 9 min. The mixture stream is then mixed with the acidic reagent and introduced into a reaction tube (2.5 x 0.5 mm i.d.) in an aluminum bath (30°C), where the sample is neutralized to be pH 2 to 3. Following the reaction, the stream is passes through a micro photometic flow cell. The absorbance at 220 nm is continuously recorded to monitor total nitrogen in water sample.

4. CONTINUOUS MONITORING METHOD OF TOTAL MERCURY

A sample, an acidic reagent (9 N sulfuric acid), an oxidizing reagent (1.5 % potassium persulfate) and a reducing reagent (1 % stannous chloride in 1.2 N hydrochloric acid) are continuously pumped at the flow rates (µl/min) of 600, 65, 35 and 35, respectively. The sample stream is mixed first with the acidic reagent and then the oxidizing reagent, and introduced into a reaction tube (1 m x 0.5 mm i.d.) in an air bath (80°C), where the organic mercury is converted to mercuric ion. The mixture stream is mixed with the reducing reagent and then with an argon gas stream of 7.5 ml/min, and introduced into a reaction tube (60 cm x 1.3 mm i.d.), where the mercuric ion is reduced to elemental mercury and extracted into the gas phase. The mixture is then introduced into the home-made gas-liquid separator and the mercury vapor is carried by the argon stream through a condenser, where the water vapor is removed from gas phase. The dried mercury vapor passes through a photometric flow cell (40 mm light pass, 1.13 ml volume). The absorbance at 253.7 nm is continuously recorded to monitor total mercury in water sample.

The details of experimental results will be presented in the posters.

S5-10

RAPID DETERMINATION OF PHOSPHORUS IN AQUEOUS SYSTEMS BY FIA COUPLED WITH CAPILLARY TYPE CATALYTIC DIGESTOR

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Flow infection analysis (FIA) is expected to offer the prospect of fast, sensitive, high quality and automating analysis in diverse application fields [1]. As to phosphorus analysis, Motomizu et al [2] reported FIA method for determing trace amounts of phosphate in river water. In order to extend this method to total phosphorus (TP) determination, a compatible process of digestion for converting various phosphorus compounds to orthophasphate (OP) has to be developed.

The official digestion process for TP in water [3] requires as much as 90 minutes digestion time including heating and cooling of an autoclave. In the course of our study on improving the official digestion process, it was found that the digestion could be carried out in 4 minutes,using a capillary type catalytic digestor (MB-10 unit), which is directly connectable to a FIA system. By combing the MB-10 unit with FIA, we have developed a novel system to determine TP and OP rapidly.

EXPERIMENTAL

Analytical scheme is as follows: (1) Add oxydizing reagent ($K_2S_2O_8$) to the sample (2) Heat for 4 min. at 160°C under presence of Pt catalyst; Phosphorus compounds $\longrightarrow PO_4^{3-}$ (3) Add reagents to form a colored complex; $PO_4^{3-} + (NH_4)_2MoO_4 +$ Malachite Green $\longrightarrow$ (Malachite Green)$_3$($PMo_{12}O_{40}$) and (4) Determine the phosphorus concentration by measuring absorbance at 650 nm.

A Sumigraph P-2000 system equipped with the MB-10 unit was used for this work. The MB-10 unit consists of 10 meter length of Teflon tubing of 1.0 mm i.d., containing a Pt wire in it as catalyst. The tubing is wound upon an aluminum bobbin with fins which is to be set in a thermostat. By skipping the MB-10 unit, OP can be measured. For multi-channel process control application, two sets of the automated sample selecting rotary valve with four-way were incorporated in the sampling line.

RESULTS

A calibration curve (absorbance vs. P-concentration) indicates a linear dynamic range of about 5×10^2 of magnitude. A detection limit of 5 P-ng/ml was obtained by optimizing the sample injection volume in the range from 250 to 1000μℓ for given analyte concentration.

Phosphorus compounds, such as metaphosphate, pyrophosphate, tripolyphosphate, and adenosine 5'-triphosphatre (ATP), are digested in 4-5 minutes for full phosphorus recovery.

Enhanced oxidizing ability due to the platinum catalyst is manifested when other organic substances coexist in the sample. For example, 500 ng/ml of disodium phemyl phosphate (DSPP) is digested in 4 minutes for full phosphorus recovery, with coexistence of 200 ng/ml of potasium biphthalate.

Determinations of TP and OP were performed at five different locations of Lake Biwa, without any trouble.

One of the drawbacks of this method with respect to environmental applications is "color fading" of Malachite Green due to chlorine ion occuring in seawater. Chlorine ion reacts with potasium persulphate to produce chloric acid ions (ClO_n^-) which, at elavated temperatures, cause fading of Malachite Green, resulting in negative error. The other is "density fluctuation" due to difference in density between carrier and seawater. This causes "ghost peak" on FIA response curve, resulting in error. Those errors are not negligible at low phosphorus concentrations.

A solution to the chlorine ion problem is found to add a reducing agent such as sodium thiosulfate. Concerning the ghost peak problem, it is practically useful to add known amount of orthophosphate to the seawater sample so that the range of total analyte concentration will be properly accommodated in the dynamic range of calibration curve. Examples of the determination of TP and OP in diverse seawaters will be presented.

A sumigraph P-2000 equipped with an automatic process sampling system has been used for more than two years to monitor phosphorus concentration in industrial wastewaters. Since this system was intended for use with the process of dephosphorization in a chemical plant, six samples included (a) raw wastewater (b) treated wastewater (c) final wastewater and (d) three standard solutions. The system is operated automatically under the CPU control so that the measurements for six samples are completed in one hour with five runs for each sample and repeated 24 times a day.

The system remains stable and has regularly been operated for periods of 7 days without attension. The details will be presented.

CONCLUSION

A novel FIA system directly coupled with the capillary type digestor has been developed for rapid TP analysis. This system can provide us with a versatile means for fast, sensitive, high quality analysis and monitoring of phosphorus in environmental waters and industrial wastewaters.

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S5-11

MEASUREMENT OF ELECTROKINETIC POTENTIAL ON THE FINE MUD PARTICLES APPLIED WITH COMPUTER VISUALIZATION SYSTEM

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1. Introduction

The sediment transport phenomenon with regard to a cohesive mud layer is one of the most important factors for the water quality assessment in river, lake and sea. By reason of the complicated phenomenon, it is generally attempted to symplify the mechanism to make use of the experimental and empirical data.

In this paper, the visualized computer analysis system is applied into the measurement of electrokinetic potential for the fine mud particles. This method will be able to record a large quantity data immediately and to analyze them without difficulty.

2. Apparatus and Experiment Procedures

The system of apparatus is composed with two parts, which are the record part and the treatment part, shown in Fig.1. The first part is taken upon the record on the mobirlty of fine particles, and in the second part, the ζ-potencial is calculated with the recorded pictures, as shown in Photo.1 and 2 respectively.

The sell used in the present work is an acryl-glass sell of 2mm in clearance and is settled by electrode bottles on both side. The light source is a 5 mW He-Ne laser beam leading with glass fiber tube and the detector is a CCD (Change Coupled Divice) type video camera equiped with optical microscope (×80). As in the electophoresis through the cell, the actual number of particles in the statical layer will show random variations about the mean flowing speed, in proportion to the transmitted voltage intensity. Hereupon, the samples poured into the sell are made of deionized water with a small amount of particles. In practical mearsurements, the rate of voltage sellected in 5 steps from 100V to 300V in every 50V interval are corresponded to particle velocity of a few millimeters per second through the cell and, under these conditions, Brownian

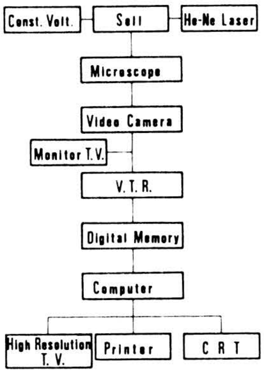

Fig.1 System diagram.

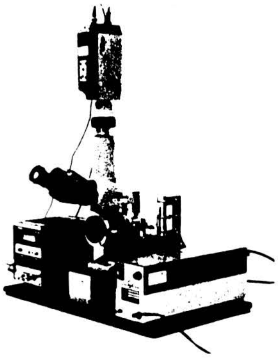

Photo.1 Apparatus of record part.

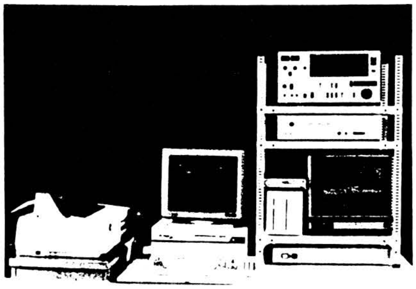

Photo.2 Apparatus of computer treatment part.

diffusion will have a quite negligible effect on the mobility.

The mobility of particles will occur on a time scale which depend on the phase boundary potential, since changes would only be expected if measurments are made at intervals sufficient to give some displacement of the previous sample. These informations of VTR pictures are modified into two gradients with the computer, and ζ-potential is estimated with the displacement of particles at arbitrary intervals of two frames in VTR.

The results, modified psudo-colour picture, the compounded picture relating to the displacement of each particles and ζ-potential values, are displayed on CRT or in print.

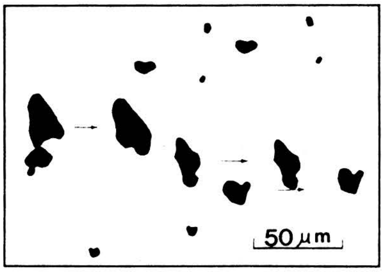

Fig.2 Displacement of mud particles for one second.

3. Results and Discussion

Materials used in this experiment are river mud particles, Hanta valley coal and bentonite, and are appeared reasonably monodisperse in distilled water. The displacement of particles is illustrated with two different frames at intervals from 2 to 12 seconds as shown in Fig.2, applying the compounded picture method, and ζ-potential is estimated in eq.(1) by the displacement in unit time on each voltages.

Table 1 Characteristics of experimental data

Materials	Diameter (μm)	Specific Gravity	ζ (mV)
Hanami River Mud	237	2.72	−35.0
Hanta Vally Coal	130	1.61	−44.9
Bentonite	88	2.73	−65.8

$$\zeta = \frac{4\pi}{\varepsilon} \cdot \frac{V}{(E/L)} \cdot (300)^2 \cdot 1000 \qquad (1)$$

Where, ζ; ζ-potential (mV), V particle velocity (cm/s), ε;dielectric constant of liquid, E;voltage added to electrodes (V), L;distance between electrodes (cm). It will be charactristically indicated in Table 1 that the ζ-potential is only depend on the particle diameter.

The settling velocities which are connected to the phenomena of deposition and resuspension are measured for the deposit particles in Fig.3, and in this figure, the solid and dotted lines are simultaneously indicated as the Rubey's theory and the Allen's theory in individual. It will be accepted that the settling time on experiment data is taken longer than it of theories, and this tendency is evidently appeared in so fine as powder.

Since, the discrepancy in settling velocities is increasing in proportional to the ζ-potential as shown in Fig.4, it will be considered that the increasing of ζ-potential induces the virtual volume in around the particles, and the excessive resistance appeared in resuspension along the prticles.

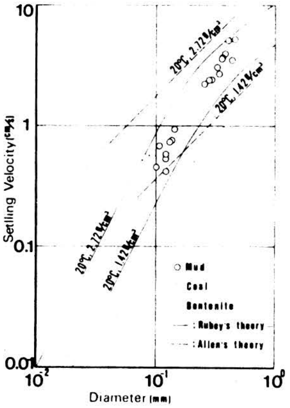

fig.3 Settling velocity on various particles.

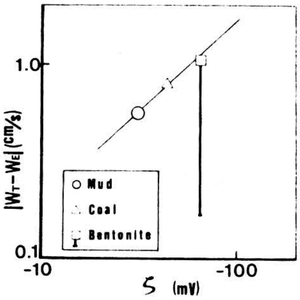

Fig.4 Relationship between ζ-potential and difference of settling velocities.

4. Conclusion

The mobility of flowing particles can be earsily mearsured with the computer visualization system and represented as the ζ-potential value. The quantity of ζ-potential shows very different dependence on particle size, and is proportional to settling velocities in fine particles. The results in this paper will be useful to apply in the water quality assessment.

S5-12

THE ENVIRONMENT CHARACTERIZED AS NATURAL PROCESSES: AN ECOLOGICAL BASIS FOR ENVIRONMENTAL PLANNING IN JAPAN

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INTRODUCTION

An "ecological approach" to environmental planning means that the environment is first characterized as natural and social processes,each with intrinsic opportunities and constraints for all prospective land uses.[1] The uses which take the greatest advantage of the opportunities while avoiding the greatest number of constraints are considered to be the most suitable for any particular location. Plans based on the synthesis of these suitably located uses are considered to be ecologically sound,contributing to sustainable development.[2]

DISCUSSION

In this paper, an approach to urban planning based on the above mentioned concept is introduced. Since safe, comfortable/pleasant and healthy cities are among the most desirable ones for human habitation, criteria for their location as well as for their planning should be central in their environmental planning. Each of these criteria,however, merely represent the functioning of natural and social processes. For instance:[3,4]

1. SAFETY CRITERIA

(a) Flood Hazard Vulnerability:- Flooding is primarily a result of the operation of the hydrological cycle and occurs when precipitation runnoff exceeds the capacity of the ground to absorb it. Coastal areas subject to high tides from typhoons may also be equally hazardous. Areas vulnerable to such flooding should be avoided or especially adapted to by urban uses,while areas which absorb flood waters, steep slopes, permeable lowlands, wetlends etc. should be protected and/or developed for non-urban,non-facilities uses.

(b) Earthquake Hazard Vulnerability:-Earthquakes are a result of the operation of geological mountain-building processes,especially plate tectonics. Areas/cities on or near active faults, on soft ground with deep unconsolidated sediments, or near the coast and thus vulnerable to tidal waves, are all highly hazardous. Special precautions should be taken to protect such areas from intensive urbanization. Within those areas, safety features such as evacuation plans,routes and sites etc. may also be required.

2. AMENITY/COMFORT CRITERIA

(a) Asthetic Values:- Aesthetic values can be seen as being a function of the socio-cultural protection process. These values vary from nation to nation or even from place to place. They may include natural elements, such as mountainous areas, coastal areas and wetlands, or water surface areas etc. Social elements such as attractive buildings, structures, street scenes etc. may also be included. These all require special protection and care if they are to be maintained and their value increased.

(b) Historical-cultural Values:- These areas likewise reflect the functioning of the socio-cultural protection proess. They record the historical development of an area as well as man's cultural adaptations to it in the forms of religious edifices,traditional customs or festivals etc. These tend to form key elements in the regional identity of a place,and as such should be preserved and integrated into all future plans.

3. HEALTH CRITERIA

(a) Aquifer Recharge Areas:- These areas reflect the functioning of the hydrological cycle where surface runoff is stored in subsurface geological strata or aquifers. These aquifers provide valuable sources of clean groundwater as well as fresh water inflow to coastal areas. To protect these vital sources of water in a healthy state, permeable strata outcrops must be protected from intensive urban impermeable surfaces and groundwater pollution etc.

(b) Areas of Self-purification Potential:- The nutrient recylcing process is reflected in soil areas upon which organic matter is broken down be micro-organisms and returned to the ecosystem. These organisms are particularly active at the water's edge which,along with highly productive soils, should be protected from destructive uses or intensive urbanization. The other process is the O_2-CO_2 process of the atmosphere in which both terrestrial and aquatic plants absorb CO_2 and produce the oxygen essential for all life. These areas also need to be protected, and only uses which insure the sustainability of these processes and thus the health of life on earth should be permitted in both urban and non-urban locations.

CONCLUSION

These are but a few of the many criteria that need to be considered when undertaking ecological planning. In the slide presentation, as example of how these criteria are developed and used in environmental planning will be shown.

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S5-13

ENVIRONMENTAL CHARACTERIZATION APPLYING EMISSION PROPERTIES OF THERMOLUMINESCENCE FROM NATURAL QUARTZ GRAINS

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In the course of thermoluminescence (abbreviated to TL here) studies of sliced granite specimens exposed to gamma-rays, the authors have noticed that the thermoluminescence color images (referred to TLCI) provide meaningful information about the origins of white mineral constituents with different colorations (1). In subsequent TLCI-experiments of natural quartzs, a noticeable finding was of two different color images, which were readily distinguishable into red and blue TL-emitting grains on TLCI. The quartz sands from volcanic ash layers always revealed a red TLCI, whereas the quartz rocks from pegmatite vein as well as the plutonic origins gave a typical blue TLCI, being consistent with the well known quartz TL-color (2,3).

In the present studies, two typical TL-emission spectra have been measured for the quartz minerals. Furthermore, quartz fractions from the beach sands are verified to consist of a mixture of both red and blue TLCI, probably characterizing the origins of respective quartz grain. The ratios of integral red TL (using red-filter) to all TL counts (total-TL) sensitive for the measuring system are apparently dependent on each quartz origin and on Eu and Sm contents.

1. TLCI-observation from quartzs with known origin

From the thermoluminescence color imaging (TLCI)-patterns, it was also confirmed that there appear two distinct colorations, distinguishable to red and blue, among different origins of quartz samples with excellent reproducibility. Among the examined samples, a Mozambique quartz, which is originated from an epithermal vein, has the highest sensitivity among typically blue TL-emitting quartzs. In this sample all TLCI-patterns indicated blue color alone over wide ranges of absorbed doses. On the other hand, Tazawa-Lake quartz sands, which has been represented to a volcanically originated quartz, is always bearing representative red TLCI-patterns in the absorbed ranges. Three typical TL-spectrograms of the samples exposed to 8.8 kGy are demonstrated in Fig. 1. It is ensured that the blue TL ((a)-Mozambique) in the TLCI proves a broad emission-band having a peak at around 470 nm, whereas the red one ((b)-Tazawa-Lake) has a similarly broad emission-band having a peak around 620 nm.

2. TLCIs from quartz of beach sands

The dominant emissions from the quartz grains from beach sands are red and blue when the samples were exposed to 9.42 kGy with X-rays. These colorations were verified as significantly dependent on the origin of containing respective quartz grains as described in the preceding section. Ten beach samples, collected from the northern part of Niigata district, could be distinguished into four main groups from the TLCI-patterns. Three beach sands, presumably supplied from Shinano-River, are having nearly similar proportions of red and blue TL-grains. One sample gives the strongest red-TL among all beach sands examined, coinciding to great contribution of quartz grains originated from surrounding volcanic mountains. Two specimens have an abundant red fraction relative to blue-TL grains, supporting the origin from Agano River. On the other hand, three remaining beach sands from most northern part seldom contain the red fraction, implying main quartz origin due to granitic rock bodies from geological background in this area.

More quantitative analyses of the TL and TLCI patterns have been carried out by using two color glass filters or spectrometer fixed at desirable wavelengths combined with the glow-curve analysis and by applying the color-image analyzer.

3. Search for cause of red-TL

The cause of red-TL in 12 kinds of natural quartzs is searched from aspects of the impurity elements, particularly Eu and Sm contents, as predicted in the preceding paper (3). Hence, the TL-intensities are converted to the ratios of red-TL to total-TL and checked as a function of Eu-contents, determined by the non-destructive neutron activation analysis. The results are illustrated in Fig. 2, suggesting there exists a certain relationship between red-TL and Eu-contents.

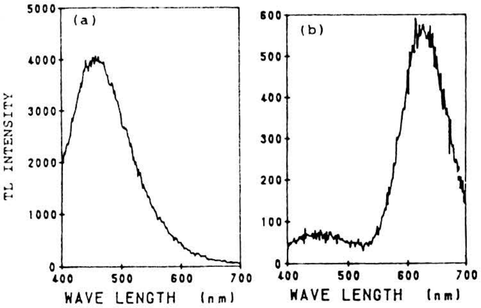

Fig. 1 Spectrograms of blue-TL (a) and red-TL (b) from natural quartzs

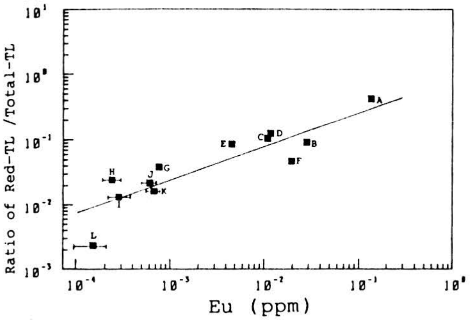

Fig. 2 Eu-contents versus ratios of red-TL to total-TL

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S5-14

VERTICAL DISTRIBUTION OF CHEMICAL COMPOUNDS AT METEOROLOGICAL OBSERVATION TOWER(213 m) II

- TOTAL AND WET DEPOSITION -

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In order to get the informations on the vertical differences of the chemical components in the deposition samples, the Meteorological Observation Tower(213 m) was utilized at the same time as getting aerosol and gaseous samples.[1)]

From June,1985, polyethylene funnels of 30 cm dia. were fixed at the northwest and northeast corners of the 213 m stage to obtain the wet deposition. Polyethylene bottles of 5 l were connected to the funnels and changed after each event rain or snow. The same arrangements of funnels and bottles were also set on the roof of the Meteorological Research Institute (ca. 25 m) and in the observation field (the height of the sampler was ca. 0.5 m). Every event rain sample or composit rain sample of 2-4 days was collected simultaneousely at all the heights.

To obtain the total deposition, polyethylene cylinders of 10 cm dia. were used as deposition gages which were set at 213 m, 175 m, 125 m and 62 m stages of the tower, on the roof of the institute and at the observation field. Each cylinder was filled with 400 ml distilled water at the begining of the week and the sample solution was collected at the end of the week.

The amount of sample collected at 213 m and 0.5 m by the funnels of 30 cm dia. is shown in Fig. 1 for each month from June,1985 to May, 1986. The variation of the amounts at the two heights showed similar pattern, however, the amount collected at 213 m was 60 - 80 % of that at 0.5 m. The wind speed was always higher at 213 m, which might have caused the different amount collected.

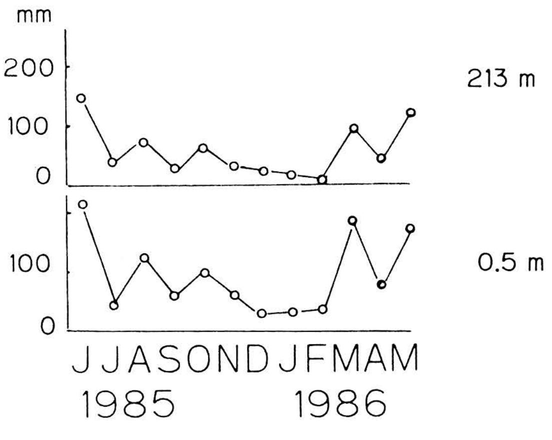

Fig. 1 Amount of sample collected

The wet and total deposition samples were filtered through Millipore filters(pore size, 0.45 µm), immediately after the collection of samples. The filtrate was used for the direct determination of chemical compounds using the following methods; Chloride, nitrate and sulfate were determined by ionchromatography using a YEW 100 Ion Analyser of Yokogawa Hokushin Co.Ltd. Sodium and ammonium were also determined by ionchromatography using a Wescan Cation column No.269-004 connected to a Reactor Motor NSP(55K25GKA) of Oriental Motor Co.Ltd., and a Wescan Conductivity Detector Model 213.$^{2)}$ Potassium was determined by flame emission spectrometry and calcium and magnesium were determined by atomic absorption spectrometry using a Hitachi 170-50 Atomic Absorption Spectrophotometer. A Jarrell-Ash Model 975 ICP Emission Spectrophotometer was also used for the multi-element determination, programmed for Be, B, Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sb and Pb.$^{3)}$

An example of the chemical composition of the rain sample obtained at 213 m and 0.5 m is shown in Table 1. One of the typical differences of the rain of two heights was found to be the lower pH at 213 m than at 0.5 m. In this sample, it can be apparently explained that the lower concentration of ammonium ion at 213 m was one of the major causes for this lower pH.

Table 1 Concentrations of soluble chemical compounds in the rain obtained at 213 m and 0.5 m

Sample	Amount collected ml	pH	Cl	NO_3	SO_4	NH_4	Na	K	Ca	Mg
						µg/ml				
850715 213 m	1950	4.21	0.73	2.11	1.94	0.19	0.22	0.13	0.30	0.06
0.5 m	2200	4.32	0.41	2.05	2.19	0.63	0.07	0.09	0.15	0.02

Sample	B	Al	Si	Mn	Cu	Zn	Sr
					ng/ml		
850715 213 m	1.8	28.4	23.8	4.9	2.9	51.5	0.6
0.5 m	3.5	9.9	5.4	3.7	1.8	10.7	0.4

The seasonal variation of these chemical components were also determined. The results should be discussed in relation to the meteorological conditions such as wind speed, wind direction, relative humidity etc. as well as to the problems how to obtain the true representative samples of a certain site, considering the differences caused by the vertical position of the samplers.

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S5-15

POSSIBLE APPLICATIONS OF AUTOMATICALLY RECORDED BUFFER CAPACITY CURVES TO ENVIRONMENTAL PROBLEMS

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Background of Study

The theory of buffer capacity presents several interesting features of buffer capacity curves (β-pH curves), which are, when the buffer capacity of the medium is disregarded, 1) monobasic Brønsted acids make bell-shaped peaks on pH axis, whose positions are determined by their pKa values, 2) the peak heights depend only on the acid concentration, and 3) the heights of the curves are additive for mixtures of acids, like the spectra of mixtures. The curves for polybasic acids may be regarded, to first approximation, as those of monobasic acid mixtures.

Biological, food, clinical and environmental chemists have often utilized buffer capacity curves for characterization or semiquantitative analysis of complex weak electrolyte mixtures for these features of the curves, but the curve drawing has never become a popular tool. A reason for this has been the inconvenient plotting method that produces disappointingly scattered and irreproducible results.

Nevertheless, the potential merits of the curves need not be neglected and seem to warrant more attention, because of their unique advantages not expected of modern analytical methods.

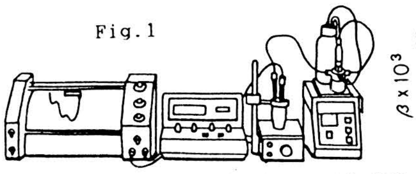
Apparatus and Method

The automatic recording apparatus developed by the author (now commercialized; Fig.1) is one of the possible versions, and comprises an amplifier of the pH meter output, an analogue differentiator, a reciprocator, and an divider. An X-Y recorder whose Y input is connected to the amplifier ouput and X input directly to the pH meter output draws the buffer capacity curve, when standard alkali is added at a constant rate to a stirred vessel containing an acidified sample solution and electrodes. Typically a curve is drawn taking 10 to 15 min. Buffer capacity (β) is obtained by calibration using acidic AcOH/Tris mixture. Recorded curves match well with the computed curves, except in extremely low buffer capacity region. Buffer capcity curve and conventional titrations curve are compared in Fig. 2. Sometimes the addition of water-miscible solvents helps to reveal peaks hidden in the buffer capacity of the medium.

Results and Future Approach

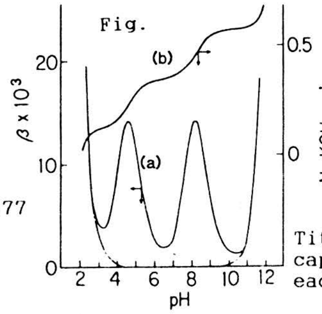
Most of the past studies using the automatically recorded β-pH curves has been in the field of food chemistry, and no systematic application to environmental chemistry proper has been made. Yet the several successful examples achieved in food chemistry, and the presence of interesting examples of application of the curves (obtained by conventional method) in the past make the application of the newer method to environmental chemistry seem very attractive and promising. Several examples are shown as Figs. 3 to 6 with explanations.

Fig.1



K. Tsuji, Agr.Biol.Chem.,46,677

Fig.



Titration and buffer capacity curves, 0.05 M each AcOH and Tris

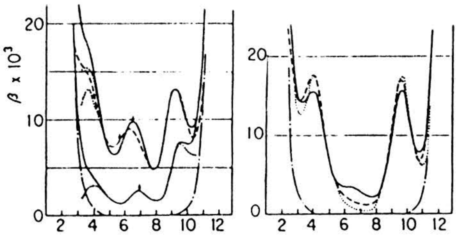


Fig.3. Curves of natural (left) and synthetic (right) flavoring agents K. Tsuji, Nihon Nogei Kagakkaishi, 56, 769 (1982)

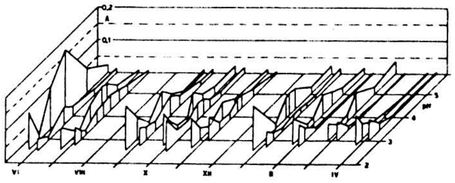


Fig.4. Seasonal change of conifer leaf extract buffer capacity, polluted and unpolluted (E.Wind, Phyton(Austria), 19, 197 (1979)

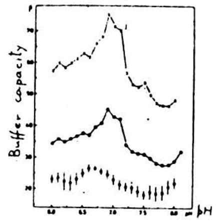


Fig.5. Curves for cell-contg. and cell-free ascites fluid (C.Albers, P.Vaupel, Respn.Physiol. 45, 287(1981))

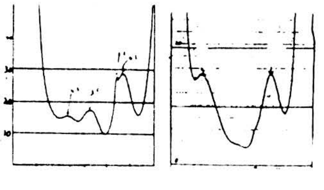


Fig.6. Urines, normal person (left) and leukemia patient (K. Tsuji, unpublished data)

Successful applications in food chemistry includes correlation of curve data with sensory evaluation data for miso, shoyu, and green tea (see review, New Food Ind, 27,51 (1985)).

S5-16

ACCUMULATION OF TRACE ELEMENTS IN PLANTS AND COORDINATION CHEMISTRY

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The purpose of the present study can be summarized as follows.

i) To search plants accumulating particular chemical elements speciffically.

ii) To examine the relations between environmental conditions(mostly chemical characteristics of soils) and concentrations of chemical elements in plant leaves.

iii) To examine the possibilities of finding indicator plants which can accumulate toxic or useful elements including radioactive isotopes in environments.

iv) To obtain macroscopic data which will give us hints for elucidating mechanisms in molecular levels or inorganic chemistry levels by which selective uptake of inorganic ions take place.

v) To examine if any correlations exist between the tendencies of accumulating inorganic ions in plants and botanical taxonomy.

1. MATERIALS

Sampling

Leaves: Twigs with leaves were collected and packed in polyethylene bags.

Soil : In case it was possible, surface, A, B and C layers of soil were collected in polyethylene bags.

Sampling Site: Sampling sites cover sub-frigid, temperate and sub-tropical zones in Japan, i. e., from Hokkaido to Ryukyu Islands.

Sample Treatments

Leaves: At the earliest chance, leaves were cleaned by rubbing gently with gauze damped with deionized water and finally by pouring redistilled water on them. Cleaned leaves were packed in a sheet of filter paper and dried for 48 hrs. at 80°C.

Soil: After dried at room temperature, soil samples were sieved and a fraction less than 100 mesh was collected and dried further at 80°C for 48 hrs.

2. ANALYTICAL METHOD

All the measurements of elemental concentrations in both plants and soil were performed by neutron activation analysis.

Irradiation: All the irradiations were performed with the pneumatic facility Pn-2 of KUR(Kyoto University Reactor) operated at 5MW.

Neutron flux: ϕ_{th} $2.75\times10^{13} n\cdot cm^{-2}\cdot sec^{-1}$
ϕ_{epi} 1.1×10^{12} "
ϕ_{fast} 6.0×10^{12} "

Short lived Nuclides: Al, V, Mg, Ca, Ti, Mn, Na, K, Dy, Cl, I, Cu

50-100mg leaf samples and 50-70mg soil samples were irradiated for 5 to 10 sec and measured for 100 to 200 sec with a pure Ge detector immediately after irradiation.

Long lived nuclides: Na, K, Rb, Cs, Ca, Sr, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Sc, Hf, Th, U, Cr, Fe, Co, Ni, Zn, Cd, Sb, Se, Br, Ag, Au

400-1000mg leaf samples and 100-200mg soil samples were irradiated for 60 min and cooled for 7 to 9 days. Measurements were performed for 2 hours on each sample and further measurements were carried out for 12 hours after 20 to 30 days cooling with a low background Ge detector system.

Flux monitors used: Na, Mn for short irradiation, Cr, Co, Sb and U for long irradiation.

3. CONCLUSION

i) A number of new accumulator plants have been found.

Co: One third of *Euphorbiaceae* plants so far examined were found to accumulate Co ions up to 100μg/g(D.W.)

Zn and Cd: All of willow (*Salicaceae*) species and plants belonging to the *Ilex* family accumulate these ions.

Rare earth elements, Ba, Ra and Ac: Some species of ferns such as those belonging to *Gleicheniaceae* and *Struthiopteris Weiss* accumulate these ions up to 1000μg/g(D.W). Plants belonging to *Fagaceae* accumulate these ions to a certain extent.

ii) No simple direct correlation has been found between elemental concentrations in plants and in soil in general for such ions as Fe, Co and Mn.

iii) Concentrations of so called essential elements such as K, Mg, Ca and Fe converge into narrow ranges regardless of soil compositions and of plant species.

iv) Concentrations of rare earth elements in plant leaves are obviously dependent on the acidity of soil and on the concentrations of those in soil.

v) Plant species belonging to *Theaceae* and *Fagaceae* both of which accumulate rare earth ions to a certain degree were found to accumulate preferentially heavier rare earth ions to the lighter ones up to 100-1000 times as much.

Some species of ferns (*Gleicheniaceae* and *Struthiopteris*) accumulate rare earth elements intensively but the preferential accumulation within rare earth elements has not been observed except for anomalies on Ce and Eu.

vi) These facts suggest that complex formations and membrane transports are playing imortant roles on uptake of inorganic ions in plants. Rare earth ions may become good tracers for such kinds of studies.

vii) It is often the case that these preferentialities or selectivities are not confined in a given species but are extended to other species belonging to the same genus or family.

viii) Following to the Pearson's concept of classifying metal ions and ligands into hard and soft ones, it is possible to classify botanic species into hard, soft and intermediate ones in which the last ones occupy the majority.

Willows and Ilex plants are the examples of soft plants which tend to be rich in Zn, Cd, and Se and poor in Al, rare earth elements.

A number of species of *Theaceae* are the other extremes, that is, hard plants which accumulate intensively Al and F and other hard ions.

ix) The macroscopic studies as described here would offer important clues for conducting microscopic or molecular level studies such as those on mechanisms of accumulation of inorganic ions from chemical point of view and on elucidating physiological roles of inorganic ions in living things.

x) *Metasequoia* was found to accumulate ^{131}I from the Chernobyl accident!

S5-17

DETERMINATION OF TRACE AMOUNT OF TRIBUTYLTIN COMPOUNDS IN ENVIRONMENTAL SAMPLES BY GAS CHROMATOGRAPHY

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Many kinds of organotin compounds have been shown to be active against various marine organisms. For example, tributyltin compounds of the type Bu_3SnX are used to antifouling paint (A/F) which was applied primarily to ship and boat hulls to inhibit the growth of marine organisms such as algae and barnacle.[1,2] The use of the organotin compounds as antifoulant , however, may cause leaching of the compounds into the marine environment.[3] Cooksley has shown that tributyltin compound in antifouling paint leaches into seawater at a rate of 1.5-2.0 $\mu g/cm^2/day$.[4] Due to the increasing development and use of a wider variety of organotin compounds in antifouling paint , it is important to elucidate about the behavior and distribution of the tributyltin compounds that are produced in seawater when the antifoulant leaches into marine environment.[5.6]

In this paper, we shall describe the determination of trace amount of tributyltin compounds in environmental samples such as seawater and sediment by gas chromatography equipped with electron-capture detector (ECD-GC).

Apparatus:

The gas chromatographic conditions were as follows: column packing, 10% Thermon-HG on Chromosolb W 60/80 mesh; column size , 3m×3mm i.d. stainless steel column; Column temp., 160°C; injection and detector temp.,300°C; carrier gas , nitrogen, 60 ml/min; detector ,ECD (^{63}Ni).

Procedure:

Seawater: To 1000ml of seawater sample was added 1ml of 12M hydrochloric acid , and the solution was extracted with two 40ml portions of n-hexane. The extract was washed twice with 25ml portions of 0.006M hydrochloric acid, dried over anhydrous sodiun sulfate, and filtered. The resulted solution was concentrated, if necessary, as the sample for gas chromatography.

Sediment: Tributyltin compound in sediment was extracted with 100ml of methanol and 1ml of 12M hydrochloric acid using Soxhlet's extractor (70°C/2h). The extract was concentrated to about 10ml, and diluted by 100ml of saturated sodium chloride solution. The resulted solution was extracted with two 30ml portions of n-hexane, and the n-hexane layer was treated in the same way as the case of seawater sample.

Results

The recoveries of the overall performance of this method were (84-91)% for seawater samples and (89-94)% for sediment samples. The detection limits of TBTC were 0.6 μg/l in seawater and 0.03 μg/g in sediment.

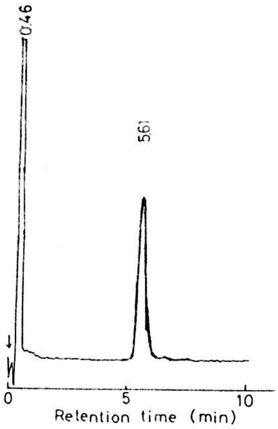

Fig.1 Gas chromatogram of TBTC
(TBTC: 1.2 μg/ml)
(Sample volume: 3 μl)

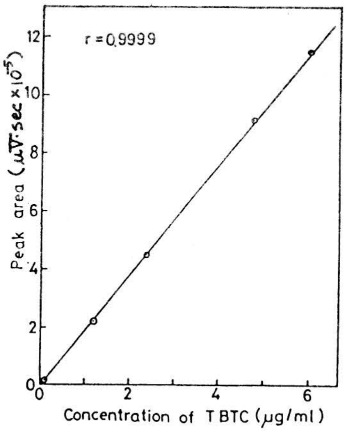

Fig.2 Working curve of TBTC
(Sample volume: 3 μl)

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S5-18

A tephra layer gives us the best time-control planes in paleoenvironmental research

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We can accept a magma chamber under a volcano as a kind of gigantic crucible. During his every eruption a huge volume of pyroclastics is released, blown high up in the air, spread widely with westerlies and sometimes transported to more than 1,000 Km. In the magma chamber some kind of minerals are crystallized, but major part of magma is transformed to amorphous materials in its rapid cooling. Volcanic glass is a such end member of magma product and has a homogeneous chemical composition. Each volcanic activity gives us a characteristic information through volcanic glass composition. So we can define a specific tephra layer in a stratigraphic columnar section over all dispersed area. Some times a tephra layer is dated by radiometric techniques, that is, zircon crystall included in the same tephra gives a fission truck age and if a tephra layer is intercalated in peaty sediments, radio-carbon ages of both peaty beds are available. Consequently we can commonly get two important time-controls through a tephra in a same time. Wide spread specified tephra undoubtedly gives us a definite and reliable datum plane. Through the specified tephra layer we can safely compose the natural history which is an indispensable basic data on a research of paleoenvironment. Stratigraphical and geohistorical information must be more evaluated in the field of environmental research. Present state of environment is the final re-representation of the natural history.

For a long time ordinary tephra identification was accepted as a very skillful technique and sometimes gave subjective interpretation regardless of its theoretical stability. The present method improved this weak point and serves for Quaternary stratigraphy.

In this time a latest Pleistocene and two Holocene wide distributed thephra in Japan are reconfirmed with an energy dispersive spectrometry (EDX). The oldest one is called as Aira (AT) tephra which was erupted in Aira caldera of Kagoshima, southern Kyushu and dated as 24 Ka by radio carbon method. Present age falles to the mid-time of the last glacial age. Second one is named as Oki tuff which was originated from Ulreung-do Island, Korea in the earliest Pleistocene time and dated about 9.3 Ka. Akahoya tuff is third one which was blown up from Kikai caldera in the southern sea of Kyushu and dated 6.3 Ka also by radio carbon method. This age is correspond with the Holocene climatic optimum and the highest level age of eustatic movement.

Preparation: Crude sample was soaked in calgon, dispersed in ultrasonic bath, rinsed repeatedly with distilled water to eliminate contaminated clay minerals, sieved with a stainless steel mesh, dried on a heater, adhered on a clean glass chip and coated with carbon in a vacuum evaporator.

Analytical method: Clean volcanic glass shards, that is, clean surface and fresh fracture was desired, was confirmed under a SEM and followed by spectrum acquisition under the next condition; EO=20 Kv, Ref=200 μμA, Z=15 mm and 500 KI count/all channel. Each quantitative analitical result was got compairing with standard spectra and adopted ZAF correction. Commonly we acquired 20 to 100 spectra on a tephra sample and represented their average values with standard deviation. Analyzed major elements of glass shard were Na, Mg, Al, Si, K, Ca, Ti and Fe, and represented their relative percentages in oxide form. Analytical condition and element list were fixed through the course of the study for the reason of guarantee of consistent results.

Results: After a statistical calculation, results were shown in a form of table, scatter diagram and comparison chart with corresponding chemical composition which was analyzed in the past.

For the reason of stable results, the present method should be accepted as an easy and reliable tephra identification technique. Stratigraphical and chrolological data suport the present tephra identification and has not any discrepancies.

S5-19 SERS OBSERVATION OF THE ADSORPTION BEHAVIOR OF SO_x AND NO_x ON THE SILVER POWDER AT NEARLY REAL ENVIRONMENTAL CONDITIONS.

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1. INTRODUCTION

Under real environmental conditions, adsorption of gases on metals take place under atmospheric pressure and presence of oxygen, water vapor and other gases. However many studies on gas adsorption have been carried out with electron spectroscopy under vacuum conditions with so called clean surfaces. The behavior of adsorbed gases under atmospheric pressure may be different from those under vacuum conditions. In order to observe the behavior of adsorbed gases under natural conditions, surface enhanced Raman scattering (SERS) can be a useful analytical tool.

In the present report, adsorption behavior of the principal air pollutants of SO_2 and NO_2 on silver powder produced from aqueous solution of $AgNO_3$ were studied by SERS. The silver powder surface produced by this method was adopted as a model of the real surface. SERS spectra of SO_x and NO_x on the silver powder were measured at both nearly environmental conditions and vacuum conditions.

2. EXPERIMENTAL

Nine wt.% aqueous solution of $AgNO_3$ was reduced with $NaBH_4$ and the precipitated silver powder was washed with re-distilled water. The silver powder was first dried either in air or under low vacuum conditions and then stored in dry Ar atmosphere. We will call the former powder air dried silver powder (ADSP) and the latter vacuum dried silver powder (VDSP). The silver particle was of $\approx 1 \sim 10\ \mu m$ in diameter[1]. Raman spectra were recorded at room temperature with a 1m double monochromator with a conventional photon counting system. The Ar^+ ion laser beam of 50mW with a wavelength of 488.0nm was used and the beam was focused by a cylindrical lens to form a line image on the sample. The details of the vacuum system for the Raman measurements will be described elsewhere [1].

3. RESULTS AND DISCUSSION

3.1 Adsorption behavior of SO_2 on silver powder surface [1]

When both ADSP and VDSP samples were first exposed to air and then placed in various gas mixtures containing SO_2, SERS peaks at 625, 925 and 960 cm^{-1} were observed. These peaks seem to be due to surface species such as SO_3^{2-} and SO_4^{2-} [2]. However when both ADSP and VDSP samples were first placed under high vacuum conditions and then exposed to similar gas mixtures containing SO_2 as performed in the previous experiment, only the VDSP sample exhibited SERS peaks of surface species such as SO_3^{2-} and SO_4^{2-} for a gas mixture of H_2O of $\sim 10^3$Pa, O_2 of $\sim 10^5$Pa and SO_2 of 10^2Pa from the various performed. AES and XPS spectra showed that the surface of the VDSP has a higher contamination of carbon than that of the ADSP. The different adsorption behavior of SO_2 on the silver powder seems to be partly due to the effect of surface contamination on the stability of the SERS active sites in vacuo. The presence of both H_2O of $\sim 10^3$ Pa and O_2 of $\approx 10^4 \sim 10^5$ Pa is necessary to observe SERS peaks of the surface species such as SO_3^{2-} and SO_4^{2-}.

Adsorption behavior of O_2 and H_2O on the silver powder surface will be discussed elsewhere [1].

3.2 Adsorption behavior of NO_2 on silver powder surface [4]

Both VDSP and ADSP samples were first placed under high vacuum conditions and then exposed to 10^2Pa of NO_2. The total pressure was raised up to 10^5Pa with dry Ar, N_2 or O_2. Observed SERS spectrum is shown in (a). Observed peaks at 1040 and 815 cm^{-1} seem to be due to surface species such as NO_3^- and NO_2^- ions, respectively [3]. When the total pressure was decreased, the specturm changes from (a)($\sim 10^5$Pa) to (b)(1.3Pa), (c)($\sim 10^{-4}$Pa). This spectral change is reversible ($a \rightleftarrows c$) by changing the pressure by pumping and addition of dry gases of any kind. The peak at 2315cm^{-1} and other peaks in (c) seem to be due to NO^+ and NO_3^-, respectively, but the NO_3^- seems to be adsorbed at different sites from those under atmospheric pressure [4]. The surface reaction may be expressed as follows.

$$2NO_2^- \rightleftarrows NO_3^- + NO^+$$

Once the silver powder with adsorbed nitrogen oxide was exposed to moistened gas or air of $\sim 10^5$Pa, the reversible change was interrupted, and NO_3^- and NO_2^- ions were observed on the silver surface, as shown in (d). Other pesks in (d) will be discussed elsewhere [1].

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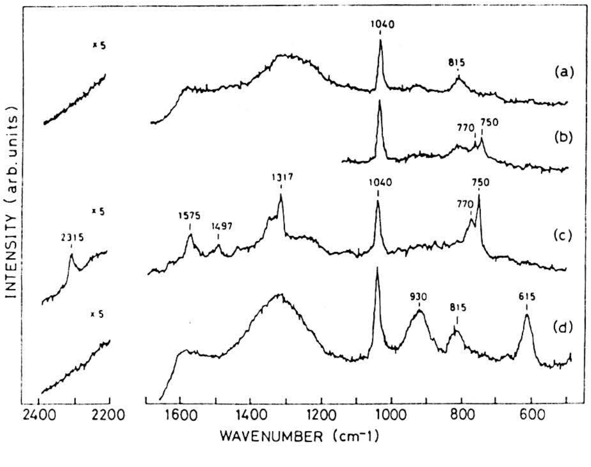

Raman spectra of adsorbed nitrogen dioxide on the silver powder surface. (a) Addition of both NO_2 of 10^2Pa and Ar of $\sim 10^5$Pa; (b) Evacuation up to 1.3Pa; (c) Evacuation up to $\sim 10^{-4}$Pa; (d) Addition of moistened Ar of $\sim 10^5$Pa.

S5-20

SOME FACTORS INFLUENCING COPPER(II)-COPLEXING CAPACITY OF RIVER WATERS

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1. INTRODUCTION

Copper(II)-complexing capacity(CuCC) of a water sample is defined as an ability of a sample to remove added copper(II) from the free ion pool [1]. Various methods for the measurement of the CuCC have been proposed and reviewed by Hart, Neubecker and Allen [2,3]. However, the chelate extraction has not been proposed so far for this purpose. In the course of a study on the CuCC, a rapid and simple method using back-extraction technique was established, which enables one to measure the CuCC-value as well as the conditional formation constant for the resulting copper(II) complex without any preliminary treatment [4]. By using the present method, some factors influencing the CuCC of a water sample from the Kiryu River were discussed.

2. EXPERIMENTAL

A water sample is filtered using a 0.45 µm membrane filter. Twenty cubic centimeters of the resulting sample is taken in a separatory funnel, and the equal volume of benzene containing 5.00×10^{-5} mol dm^{-3} bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)copper(II) [$Cu(bfa)_2$] is added. The mixture is then shaken vigorously for 30 min. After the phases are allowed to separate, the aqueous phase is filtered, and copper(II) in the aqueous phase is determined with an atomic absorption spectrometer. The CuCC-value of a water sample is defined as the concentration of copper(II) back-extracted into the aqueous phase.

3. RESULTS and DISCUSSION

By employing EDTA as a typical ligand, the CuCC-value obtained by the present method was confirmed to indicate the complexing ability as well as the concentration of a ligand. The possible existence of HCO_3^- and CO_3^{2-} in natural waters did not affect CuCC-values in the pH region between 7.0 and 9.0, if the total concentration of HCO_3^- and CO_3^{2-} is below 1.0×10^{-3} mol dm^{-3}. Among many coexisting cations, iron(III) which is the only possible interfering ion, did not interfere with the determination of the CuCC in the case of its concentration less than 1×10^{-5} mol dm^{-3}.

The present method is applied to the Kiryu River. Water samples were taken at two points (point A is situated 5 km above point B and Kiryu city is in-between A and B) on 12 th of May, 1986. Although only slight differece was observed in the CuCC-values of points A and B at midnight, the values obtained at point B were observed to be higher than those at point A in the daytime. Hourly variation of the CuCC-value was found to correlate with the ABS (alkylbenzene sulfonic acid) concentration, strongly suggesting that the CuCC-value may be influenced by the waste water containing ABS.

The conditional formation constant for the copper(II) complex estimated by the present method is given in Table 1. Among various samples listed in Table 1, commercial detergent possibly contains a certain ligand as an additive, because ABS does not have any complexing ability. By comparing β-values of the Kiryu River and detergents, we can estimate that the complexing ability of this river water is mainly due to synthetic detergents derived from human activities.

Table 1. Conditional formation constants for various ligands

Sample	log β
Kiryu River	
point B (12 o'clock)	9.24
point B (14 o'clock)	9.58
EDTA	12.05
Soap	
No. 1	10.90
No. 2	13.00
Synthetic detergent	
No. 1	8.03
No. 2	9.22
Dye	11.62

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S5-21

GC/MS ANALYSIS OF POLYHALOGENATED COMPOUNDS IN FLYASH FROM MUNICIPAL INCINERATORS OF DIFFERENT COUNTRIES

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Exposure to polyhalogenated compounds in environment is particulary crucial because some isomers such as polychlorodibenzodioxins and polychlorodibenzofurans have extraordinary toxicities to animals. However, separation and chemical analysis of a number of isomers are of great difficulties experimentally.

Several reports and publications show the exposure from all municipal incinerators around the world. There is considerable difference, however, in the levels of toxic polyhalogenated compounds analyzed in the flyash samples from the various incinerators. The formation of the toxic polyhalogenated compounds in incineration in considered to be a universal phenomenon and incinerators as threat to a clean environment. This understanding has been reassesed because under certain conditions some incinerators show a negligible amount of the toxic isomers in the flyash and fall within guidelines of environmental agencies. Thus, it is of importance to analyze the flyash from different incinerators and determine the operational conditions and factors involved in the formation of the toxic compounds that can eventually result in safe operation of incineration with minimum environmental risks from the toxic compounds.

A fully computerized system consisted of gas chromatography and mass spectrometry(GC/MS) is a powerful analytical tool for the analysis of complex samples of homologous isomers of polyhalogenated compounds.

The results of the GC/MS analysis of polyhalogeneted compounds in flyash samples from municipal incinerators of different countries such as of Toronto, Oslo, Paris, Kyoto, Hiroshima and Machida showed a characteristic pattern of isomer distribution in the flyash samples from different places. This observation simplies that the basic pathways and mechanism for the formation of the toxic isomers of polyhalogenated compounds could be similar in all incinerators regardless of difference in design and operating conditions of the incinerators. The levels of the toxic isomers were different in all flyash samples amoung which Machida's flyash samples showed lowest levels of the toxic compounds. The formation mechanism is discussed.

S5-22

REGULATION MECHANISM OF TRACE ELEMENT DISTRIBUTIONS IN ESTUARINE AND COASTAL WATERS, ELUCIDATED BY X-RAY PHOTOELECTRON AND FLUORESCENCE SPECTROSCOPY

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In order to estimate human impact on ocean environment, behaviors of trace elements in estuary are an important and interest subject to be elucidated. Many studies dealing with trace elements in the coastal and estuarine areas have been carried out and the progresses of such studies were well summarized in some papers [1]. These studies have noticed the importance of adsorption and desorption of trace metals with suspended particles (SPs). We have also performed various studies on naturally occurring SPs in estuary for the better understandings of the mechanisms regulating trace element distributions, using some modern analytical techniques. The experimental results will be presented and discussed from the viewpoints mentioned above.

The estuarine and coastal water samples were collected from the Tamagawa River and the Tokyo Bay area in the middle of November, 1982 and end of June, 1984. The analytical instruments used were X-ray photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF), and X-ray difruction (XRD) for studying surface compositions, total compositions, and mineral identification, respectively. In addition, inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for determination of dissolved trace metals in waters [2-4].

The distributions of dissolved trace metals in the study area showed charasteristic patterns for each element [5]. From such experimental results [5], it has been noted that selective reactions between dissolved metals and SPs should be taken into consideration.

The anlytical results for surface composition of SPs, which are important as an interface for physical phenomena such as adsorption and desorption of trace metals, are summarized in Table 1. The values in the table are shown in molar fractions for elements. As can be seen from the table, surface compositions of SPs varied with the sampling positions and depths. It should be noted that the molar fractions of C and N increased with the distance from the river mouth and depth, while those of O, Si, K, Al, and Fe decreased. From comparison of surface compositions of SPs with those of naturally-occurring substances, it was found

Table 1. Molar Fractions for Surface of Suspended Particles. (Sampling:Nov., 1982)

Distance /km[a]	-2	5.7
Depth/m	0	25
Salinity /‰	6.7	34.1
C	22	64
O	52	25
Si	9.9	2.8
N	2.2	3.2
Al	5.5	0.49
Fe	1.4	0.19
Mn	0.17	0.15
Zn	0.02	0.05
Cu	0.04	0.11
Ti	0.06	-[b]

a) Distance from the mouth of the Tamagawa River to the Tokyo Bay. b) Not detected.

that surface compositions of SPs near the river mouth were similar to those of clay minerals such as illite and montmorillonite. On the other hand, that at the center of the bay showed clear similarity to that of humic acid.

The results for total compositions of SPs by XRF are shown in Fig. 1 for Si and S, representatively. The Si content was largest at the river and gradually decreased with the distance from the river mouth. The distributions of Al, Ti, Fe, K, and Ca in SPs were similar to that of Si. The contents of Al, Ti, and Fe were, however, found to decrease more rapidly than that of Si, while the contents of K and Ca decreased rather in similar manner to that of Si. As can be seen in Fig. 1(b), the sectional view of S was much different from that of Si. The distribution of S was maximum at the surface of Station 4, about 2 km far from the river mouth, and generally S showed the larger contents at the surface.

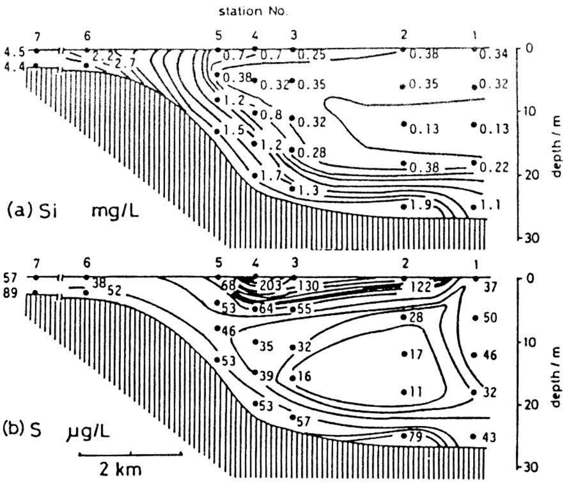

Fig. 1. Sectional views of Si (a) and S (b) contents of suspended particles in 1 L water. (Sampling: July, 1984)

From the experimental results described above, the following conlusive remarks can be noted. Tamagawa River water primarily carries silicate and clay minerals which are rich in Si, K, and Ca, and in Si, Al, Ti, and Fe, respectively. During the flow into the Tokyo Bay area, such minerals are deposited on the sea floor, while some organic matters were adsorbed onto the mineral-rich SPs. The clay minerals may be more rapidly deposited than silicate minerals. The mineral analysis of SPs by XRD supported the remarks above.

Then we intended to clarify some controlling factors for the distributions of dissplved trace metals in relation with the SPs. A kinetic model was examined, where adsorption and desorption mechanisms of trace metals through the surface of SPs were taken into account. From such studies, it was found that N-rich organics may have large contributions to adsorbtion of many heavy metals such as Al, Ti, Mn, Fe, Ni, and Zn. Clay minerals were more likely to adsorb Al, Ti, Mn, Co, Zn, and Y. More detailed studies'on physicochemical prperties of SPs will give a clue for further understanding of regulation mechanisms for the distributions in the estuarine and coastal areas, and trace metals in marine environment.

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S5-23

CHARACTERIZATION OF THE SUSPENDED SOLIDS IN THE LAKE, RIVER AND RAIN WATERS.

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1. Introduction

The study on the suspended solids (SS), which consist predominantly of inorganic colloids, such as clays, hydrous metal oxides, and of organic colloidal matter of detrital origin, as well as living microorganisms (algae and bacteria), is of great importance in transporting and distributing materials in natural waters. SS also play a certain role in circulation of dissolved substances by chemical adsorption.

The present paper summarizes the variation and the distribution of the concentrations of elements such as Si, Al, Fe, K, Mg, Ti, Mn, Ca, P, S and others in SS collected from Lake Biwa. The elemental composition of SS from the lake was compared with those of SS in the river and rain waters as well as those of the lake sediments.

2. Experimentals

The lake waters were sampled monthly since April, 1985 from two fixed stations of Lake Biwa. The river waters were collected from the major twenty-four rivers flowing into Lake Biwa in April, 1986 and the rain waters on the roof of Shiga University in Otsu after September, 1985. All the sampling sites are illustrated in Fig.1. Immediately after sampling, SS were collected on the filter(0.45μm Millipore). The elements in SS trapped on 0.45μm filter were treated as the particulate form. SS were dried at 110°C for two hours, and measured by the wave length dispersive X-ray fluorescence spectrometry (Shimadzu Model VF-320). Ten elements such as Si, Al, Fe, K, Mg, Ti, Mn, Ca, P and S were analyzed quantitatively in a few milligrams of SS , which is the maximum amount fiterable by 0.45μm filter. Then, the nondestructive neutron activatation analysis of SS was performed by the flux monitor method using the Reactor of Kyoto University.

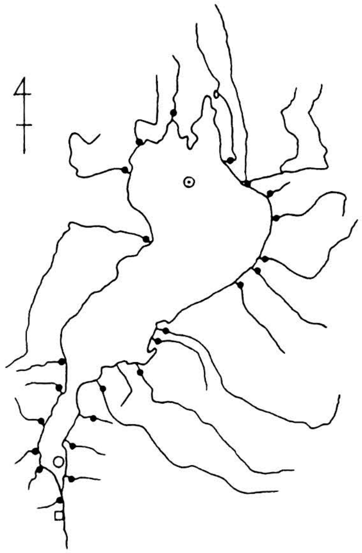

Fig.1 Sampling Sites
(⊙,○;Lake, ●;River
□;Rain)

3. Results and Discussion

Fig.2 shows the monthly variations of the concentrations of the elements in SS and of chlorophyll a, and the weight of SS in the surface water of the lake. 1) The particulate-Si, Al, Fe, K, Mg and Ti showed almost the similar variation patterns to each other. There are good correlations ($r > 0.92$) hold among these elements and these correlation curves give the straight lines which pass closely through the origin of the coordinates. These facts demonstrate that the concentration ratios of these six elements did not change through the year. The composition of SS in the lake water was close to those of SS from the rivers and rain and of the lake sediments. 2) In the southern basin, where the level of eutrophication is much higher than in the northern, the particulte-P and S varied in a similar manner to the variation pattern of chlorophyll a. P and S in algae account for the large portion of the paticulate-P and S, respectively. 3) The variation pattern of the particulate-Ca was very close to that of the weight of SS. It is interesting that the concentration of Ca in SS is constant regardless of the kinds of SS. 4) The pattern of the particulate-Mn showed poor correlations with the other components. It is necessary to consider the precipitation mechanism for Mn independent of the other species. We suggested that the microbial oxidation of Mn(II) to the oxides in the water column is important for the precipitation mechanism of Mn in Lake Biwa as well as the other lakes. 5) In SS from rain, it is worthy of note that the ratio of Al is a little lower than that in the lake and river, and that the concentration of Mn correlated strongly with those of Si, Al, Fe, Mg, K and Ti ($r > 0.95$).

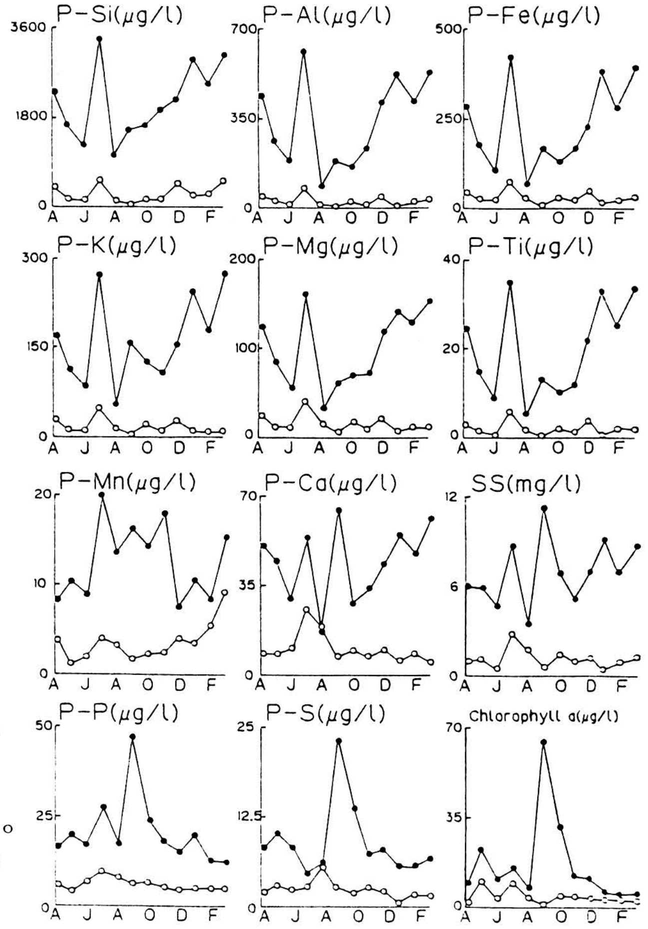

Fig.2 Monthly variations of the concentrations of the elements in SS and chlorophyll a, and the weight of SS in Lake Biwa (● ; northern basin, o ;southern basin).

S5-24

VERTICAL DISTRIBUTION OF CHEMICAL COMPOUNDS AT METEOROLOGICAL OBSERVATION TOWER (213m). I
- SUSPENDED PARTICLES AND GASES -

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The chemical compounds in the suspended particles and gases were continuously determined at the various heights of the Meteorological Observation Tower(213m) of Meteorological Research Institute, Tsukuba, Japan in various seasons. The concentration of the suspended particles near the ground was found to be influenced by the atmospheric stability, which imposed major effect on the seasonal variation of the concentration of the suspended particles. It was found to be useful to know the vertical distribution of the chemical compounds of the suspended particles for elucidation of sources of them. Discussion were done on their sources and the meteorological conditions to explain the typical distributions.

EXPERIMENTAL

We performed simultaneous sampling of the suspended particles at different heights in different seasons. Suspended particles were collected with low volume air samplers, high volume air samplers and cascade impactors, and the concentrations of the suspended particles were continuously measured by particle counters. The concentrations of the chemical components were determined using X-ray fluorescence spectrometry, Nutron activation analysis, X-ray microanalysis, atomic absorption spectrometry and ion chromatography. Three Dashibi ozone monitors and three Monitor Labs NOx monitors were also used at the same time.

RESULTS AND DISCUSSIONS

The concentration of the suspended particles collected by the high volume air samplers at 1m above the ground was generally high in winter, and low in summer with some high peaks in spring. This trend was very consistent for the three years though there were some differences in the concentrations depending upon the meteorological conditions of the year.

On the other hand, it is interesting that the concentration was almost invariable at 175m with some slight increase in spring, which would be associated with wind blown dust presumably including the dust coming from Asian Continent.

The most typical vertical difference was seen with chloride in winter, that is, the chloride concentration was substantially high near the ground and it gradually lower and evenly distributed at any height. Bromine showed similar tendency as chloride.

Potassium, calcium, aluminium, and iron showed similar tendency but the difference between the different heights in winter was not so pronounced as chloride. Sulfate and nitrate concentrations were high in winter and low in other seasons, but their vertical differences were meager.

Sodium remained constant throughout the year at any height, which could be utilized as a promising indicator for uniform vertical distribution.

The CMB method was applied to the data obtained by low volume air samplers. The concentrations of Na, Al, K, Ca, Sc, V, Mn, Fe, Zn, Br, and Pb were evaluated as the index for the sources as follows; 1) soil, 2) marine aerosols, 3) iron and steel industry, 4) refuse incineration, 5) fuel oil combution, 6) gasoline automobile, using the ratio refered from Mamuro et al.[2,3] except soil data.

The contribution of marine aerosols was found to be around 10% in summer and only 0.5% at 1m in winter. The rate of contribution of these sources for the amount of Na and Cl were also calculated using the same ratios, the chloride concentration at 1m in winter could be explained only upto 18% of the total by this calculation. This means that some strong sources for the chloride other than sea salt and refuse incineration should exist in winter near the ground at Tsukuba.

On the other hand, from spring to summer, the chloride was supposed to come from the sea salt. The deficiency of chloride compared with sodium in the suspended particles of these seasons might be explained by the mechanism of so call chlorine loss during the transportation process of the sea salt.

CONCLUTIONS

In the present study, the seasonal variation of the concentration of the suspended particles, high in winter and low in the other seasons, was found to be confined only near the ground, and it was almost constant at 175m. The main cause of this seasonal variation was supposed to be the stability of the air near the ground.

The various distribution of the chemical components varied widely depending upon the species, their origins etc.. In the present observations, the distribution could be divided into the following groups;
1) Cl, Br, 2) Na, 3) SO_4^{2-}, Fe, K, and Ca, 4) NO_3^-.

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S5-25

CONTINUOUS OBSERVATION OF EUTROPHIC SUBSTANCES IN THE BAY

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INTRODUCTION

Phosphorus, Nitrogen and Silica are three major checical elements for the eutrophication in sea and fresh water. The concentration of such chemical compounds as phosphate, nitrate, nitrite, ammonia, silicate et al in sea water are significantly influenced by such locations, depth, transportation of the water, photosynthesis and respiration of the planktons et al. Therefore, for chacterizing the sea water, it is important to measure the chemical compounds horizontally, vertically and continuously. Recently we developed a new continuous monitoring system for eutrophic substances.1) This system can measure temperature, conductivity, pH, dissolved oxygen (DO), turbidity, chemical oxygen demand (COD), phosphate (PO_4), total phosphorus, nitrate (NO_3), ammonia (NH_3), total nitrogen, silicate (SiO_4) and chlorophyll a. In this system, two sets of 2 kw capacity diesel electric generator, automatic sampling equipment, wireless telemetering system, data logger are also installed. The specially designed automatic washing system solves the contamination problem of the sensors due to the growth of algae in the equipments. All the items can be measured automatically in every one hour cycle. This paper presents the results of some field studies using this system in Osaka Bay (1983 - 1985) and Tanabe Bay (1986).

RESULTS

Table 1 shows the comparison of the measuring data of this system with the data which are analysed the same samples in the laboratory.

Figure 1 shows the comparison of the continuous measuring data (bottom curve in figure 1 : left side scale) with the data at 10:00 am in every day (upper curve in figure 1 : right side scale). In the continuous monitoring, it is clearly observed the sharp peaks at July 28 to 29, however, in only one measurement in every day, it is difficult to detect such daily peaks. Therefore, the continuous monitoring for such eutrophic substances are significantly important to find the characterization in sea water.

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Table 1. Comparison of continuous monitor with manual analysis

Items	Principle of the manual method	Measuring range of continuous monitor	Variation of measuring results	Correlation coefficient	Difference between two method (FS:Full Scale)
pH	Glass electorde method	2 ～ 12 pH	7.8 ～ 8.7 pH	0.95	−0.06 ～ +0.06 pH
DO	Winkler method	0 ～ 20 mgO/L	4.7 ～ 11.8 mgO/L	0.97	−5% ～ +2% / FS
COD	Permanganate method	0 ～ 10 mgO/L	1.2 ～ 6.9 mgO/L	0.81	−14% ～ +13% / FS
PO_4	Phosphomolybdate (blue) method	0 ～ 0.2 ppm-P	28 ～ 115 ppb-P	0.87	−11% ～ +10% / FS
SiO_4	Silicomolybdate (blue) method	0 ～ 2 ppm-Si	0.1 ～ 0.9 ppm-Si	0.88	−10% ～ +6% / FS
NO_3	Cu-Cd reduction method	0 ～ 1 ppm-N	80 ～ 510 ppb-N	0.95	−4% ～ +5% / FS
NH_3	Indophenol method	0 ～ 0.5 ppm-N	60 ～ 410 ppb-N	0.97	−14% ～ +13% / FS

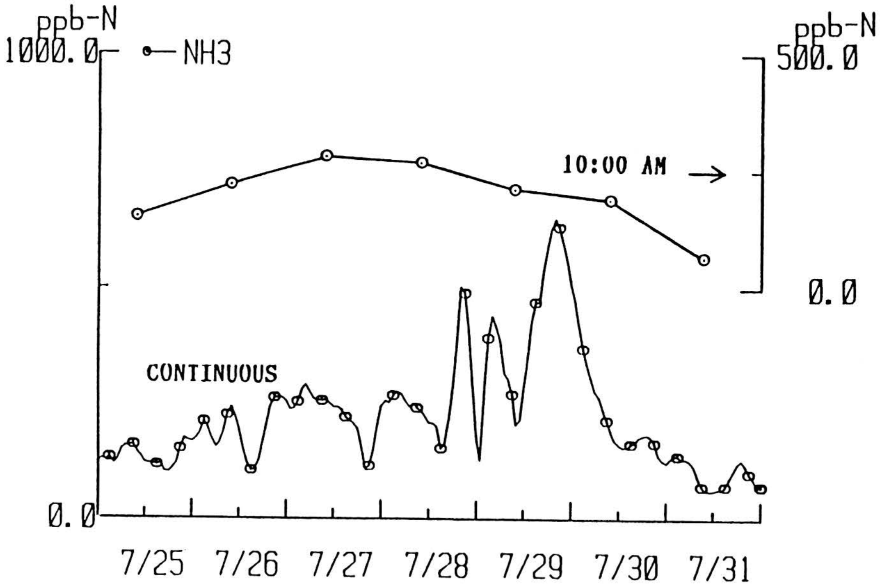

Fig. 1. Comparison of the continuous data with the batch data at 10:00am in every day (Osaka bay, 1984)

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