

DEVELOPMENT OF HIGH RESOLUTION TIME/SPACE MONITORING IN THE ENVIRONMENT

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The detection and verification of variability within the Earth system at regional and global scales requires the establishment and maintenance of long-term measurement capabilities. The development of time/space sampling will be of critical importance on providing the data bases to conduct process-related studies. These strategies will be particularly important to the maritime environment, where areal magnitude and observational accessibility render most sampling schemes impotent. It is in this particular arena that the attributes of satellites will play a major role. Although they typically provide less accurate data, their synoptic coverage over large extents is unique measurement capability. The reduced spatial observational coverage provided by buoy and drifter platforms complements satellites by providing Eulerian and Lagrangian measurements as a function of depth at high temporal frequencies and over moderate time scales. The combined potential of complementary measurements and time/space observations from these platforms will provide the communities a robust observational system for global analyses. The concentrations (mixing ratio) we want to measure are described as the following equation ;

$$\frac{dC}{dt} = -\text{div } F + S + R \quad F_x = \overline{U_x} \cdot C - D_x \cdot \frac{\partial C}{\partial x}$$

C : concentration, t : time, F_x : flux, U_x : average current speed,

D_x : turbulent diffusion coefficient, S : source,

R : producing and scavenging rate by chemical and biological reactions

From this equation, it is clear that we should design the monitoring network to collect the concentration data for being able to analyse these factors separately. In the course of global atmospheric simulation models, very sensitive and highly dense data are required to make clear their diurnal, seasonal and local variation, so that an appropriate design of monitoring networks would be capable to get the data at every 100 km horizontally, every 1 km vertically and every 4 hours periodically. On the other hand, the spatial size of the oceanic turbulences are small about 100 km to 10000 km as compared with the atmospheric turbulence the size of which are over 1000 km, so that higher dense monitoring design should be required. Moreover, the biological reactions might give significant

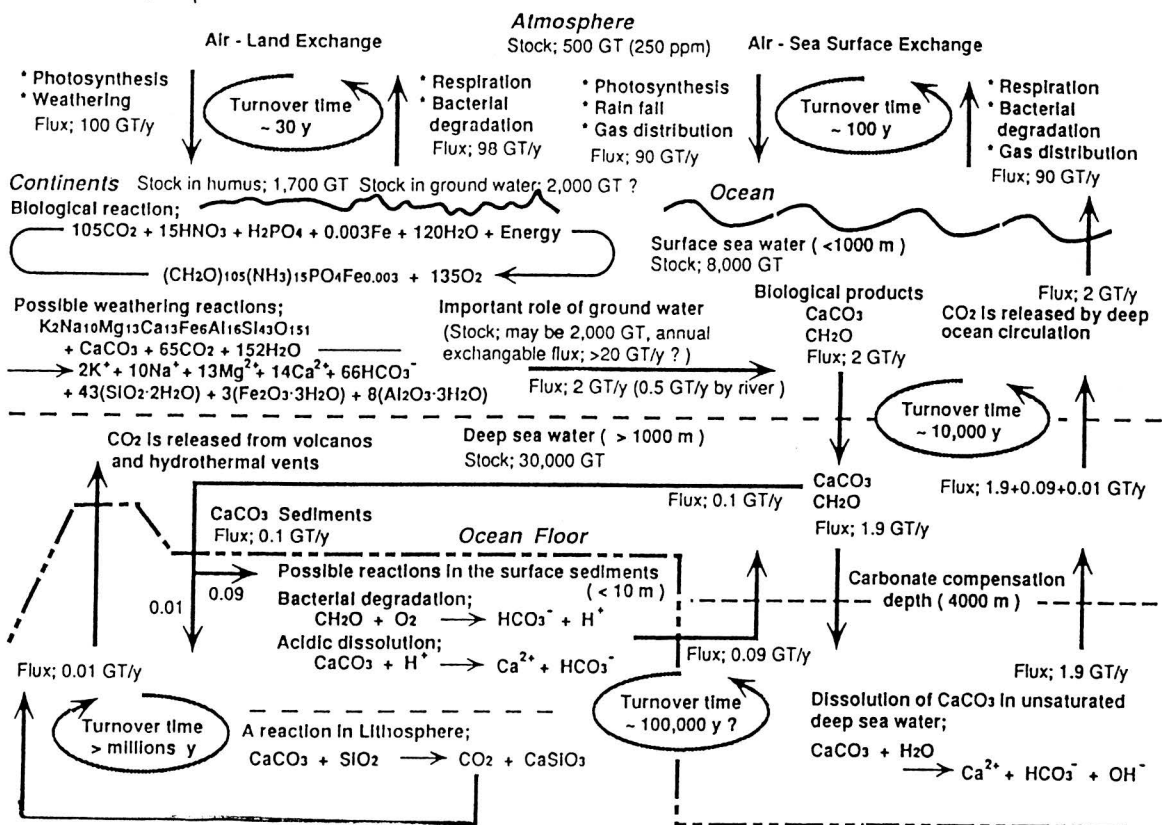
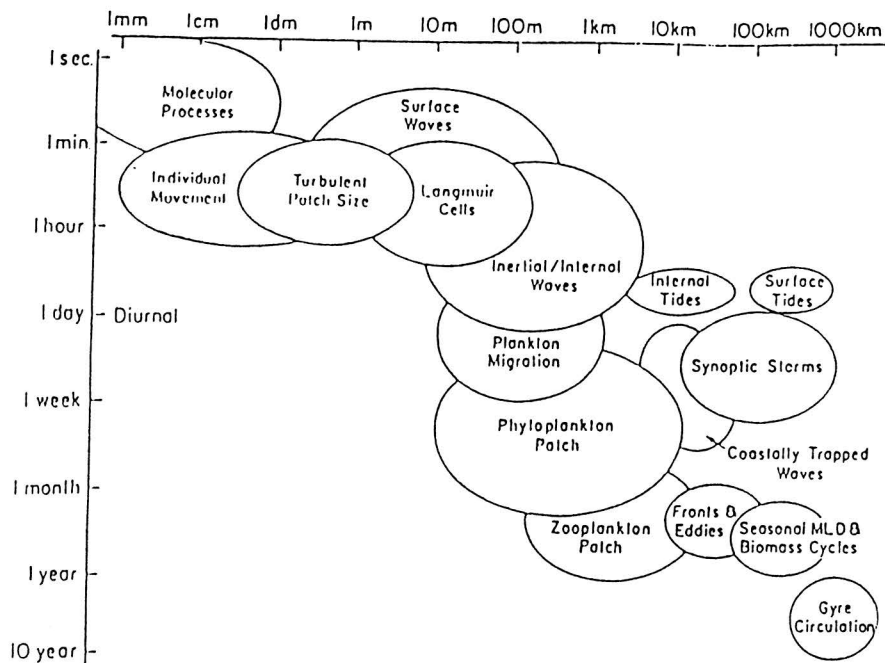


Fig.1 (upper) A schematic diagram illustrating the relevant time and space scales of several physical and biological processes important to the physics and ecosystem of the upper ocean [after Dickey, 1990]. Definitions of terms are given in the glossary. (lower) A hypothetical global carbon cycle for simulating the trends over 100,000 years (Amounts of carbon are estimation of average value over 100,000 years : GT ; 109 tons of carbon, y ; years)

effects to the concentrations. Figure 1 shows a schematic diagram illustrating the relevant time and space scales of several physical and biological processes summarized by Dickey and the BIOGEOCHEMICAL cycles of carbon in the earth system summarized by Kimoto. It is clearly shown that the research for the complexes of natural processes are needed to design the simultaneous observation between physical, chemical and biological processes.

From 1977, one of our main efforts has been to apply new analytical procedures to design of continuous measurement instruments for forecasting the planktonic bloom (red tides) in the inland ocean. The mechanisms of red tides are significantly influenced by physical, chemical and biological processes so that the observation system should be designed to measure the physical, chemical and biological parameters simultaneously. Our continuous monitoring system can measure such items as temperature, salinity, pH, dissolved oxygen (DO), turbidity, chemical oxygen demand, phosphate, total phosphorus, nitrate, ammonia, silicate and chlorophyll-a. The automatic measurement instruments, two sets of diesel electric generators, a computer controlled automatic sampling winch, and wireless telemetering equipments are installed together in a mooring buoy or a barge system. The operational period, without requiring refueling, is approximately two weeks for every one hour measuring period. The sampling depth for each sampling period is automatically set to a definite sampling depth from the surface to 100 m below. Two sets of these monitoring systems were used for continuous observation in Osaka Bay (1988-1991, maximum water depth 20 m) and three sets of them are now operating in Lake Biwa (1990-, maximum water depth 100 m). During these developments, we found some new analytical methods; contamination-free surface polished electrodes (for measurements of salinity, pH, and DO see also Fig. 2), column preconcentration (phosphate) and voltammetric detection (phosphate and silicate), gas permeable membrane for separation and preconcentration (ammonia), and catalytic flow coulometric reduction (nitrate). In this system, two sets of 2 kW capacity diesel electric generator, automatic sampling equipment, wireless telemetering system, data logger are also installed in the semi-submerged type monitoring buoy as shown in Fig. 3. A specially designed automatic washing equipment for the sampling and measuring system overcame the problems due to the growth of algae on the systems. The sampling inlet was automatically controlled and was set to definite sampling depth at every one hour sampling period.

This polished electrode for phosphate analyser consists of glassy carbon working electrode (WE) at the centre of the electrode body. The working electrode is 3 mm in diameter and 10 mm long. It is lowered into the ring-type counter-electrode (CE; 4 mm inner diameter and 6 mm outer diameter), the gap between the working electrode and counter electrode being filled with epoxy resin to provide electrical insulation. A cylindrical polishing magnetic stirrer bar (6 mm in diameter, 7 mm long) is mounted on top of the

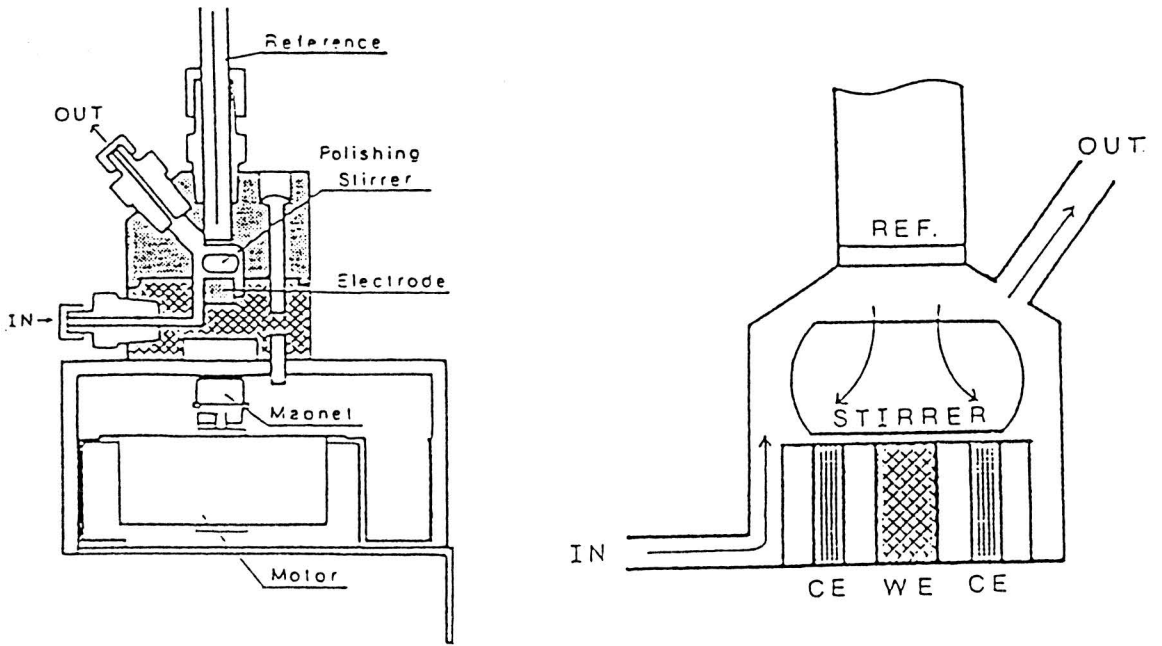


Fig. 2 Polished electrode (left) and the details of the electrode (right)

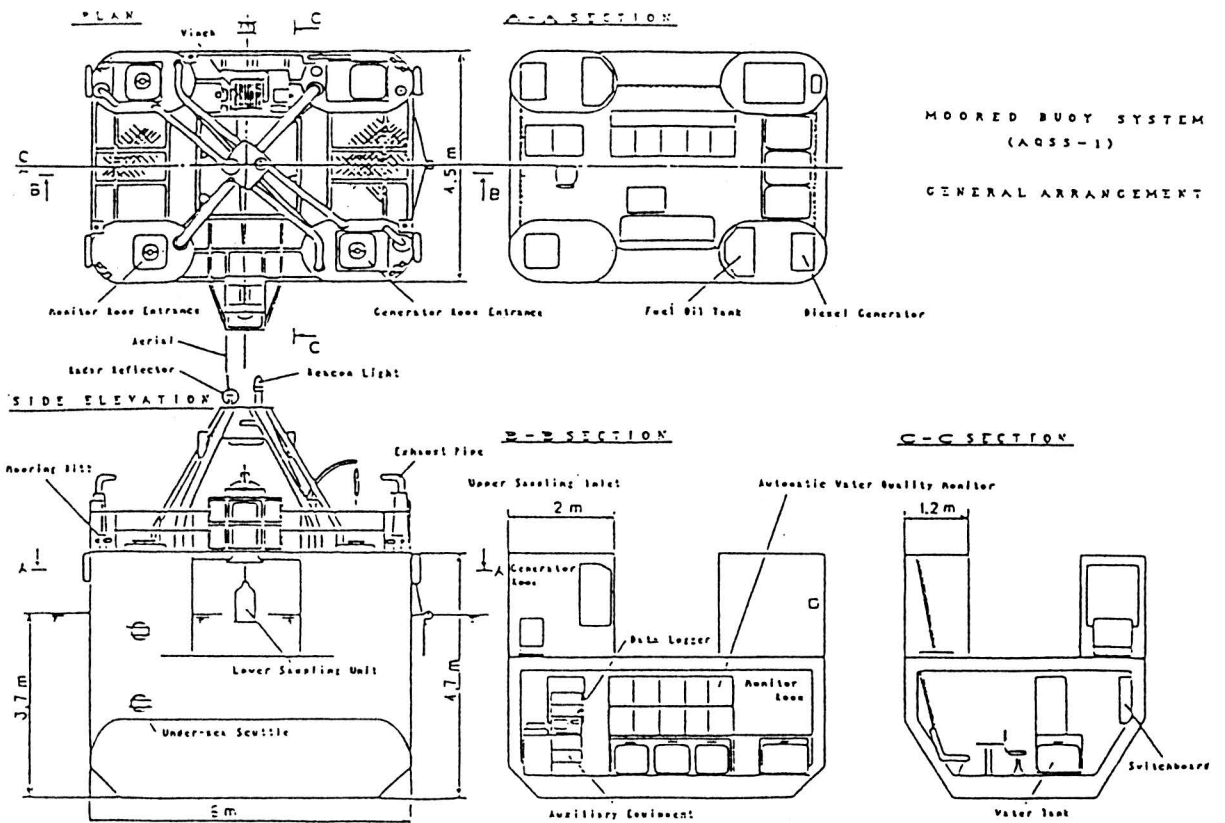


Fig. 3 An assemblage of the semi-submerged type continuous monitoring buoy

combined working and counter 600-mesh silicon carbide power and epoxy resin. The bar is rotated at 600 rpm by the motor-driven magnet under the electrode, thus continuously polishing the electrode surface. The sample flows from the working electrode to the counter electrode because of the action of the stirrer. The electrode surface is thus kept clean and free from any contamination. An Ag/AgCl electrode in 1 M potassium chloride solution is used as reference electrode installed above the stirrer bar.

The details of automated measuring apparatus were as follows. An automated measuring apparatus for inorganic phosphate was based on the formation of phosphomolybdate, preconcentration and separation of phosphomolybdate by the column and measurement with a voltammetric detector. Total phosphorus was digested by a acidic persulphate solution to inorganic phosphate in an autoclave at 120 °C. Nitrate was measured with specially designed dual wavelengths spectrophotometer. Absorbance difference between 223 nm and 232 nm had a good correlation with the concentration of nitrate plus nitrite. Automated measuring apparatus for ammonia was based on preconcentration and separation of ammonia with gaspermeable micro-porous membrane, and measurement of the ammonia-enriched acid solution by the conductivity sensor. Total nitrogen was digested to nitrate by a basic persulphate solution in an autoclave at 120 °C. Chemical oxygen demand was measured with permanganate oxidation method in an alkaline solution. Silicate was measured with the formation of silicomolybdate and the measurement of it with a voltammetric detector. Chlorophyll-a was measured with a spectrofluorometric method. Temperature, pH, dissolved oxygen, salinity and turbidity were measured with the conventional sensors. For developing these automatic continuous monitoring equipments, preconcentration and separation techniques for automatic analyser were quite important. So we describe later as an example of the applications of preconcentration and separation techniques for phosphate measuring equipments.

Continuous measurement method for phosphate with voltammetric detection system

Voltammetry for the analysis of phosphate is based on the measurement of cathodic current at the electrochemical reduction with phosphomolybdate. But most conventional solid electrodes are not satisfactory with continuous analyser because of surface contamination. Recently we developed a new "polished electrode", the surface of which is continuously renewed by polishing with a magnetic stirrer bar coated with silicon carbide. Fig. 4 shows current-voltage curves of silicomolybdate and phosphomolybdate obtained with the polished glassy carbon electrode. Curve 1, 0.05 M sodium molybdate and 0.5 N sulphuric acid, shows the increase of the cathodic current below +0.3 V possibly because of the reduction of reagent molybdate. In the contrast, curve 2 in the same figure, 10⁻⁵ M phosphate converted to phosphomolybdate, give a well-defined cathodic wave with distinct plateau

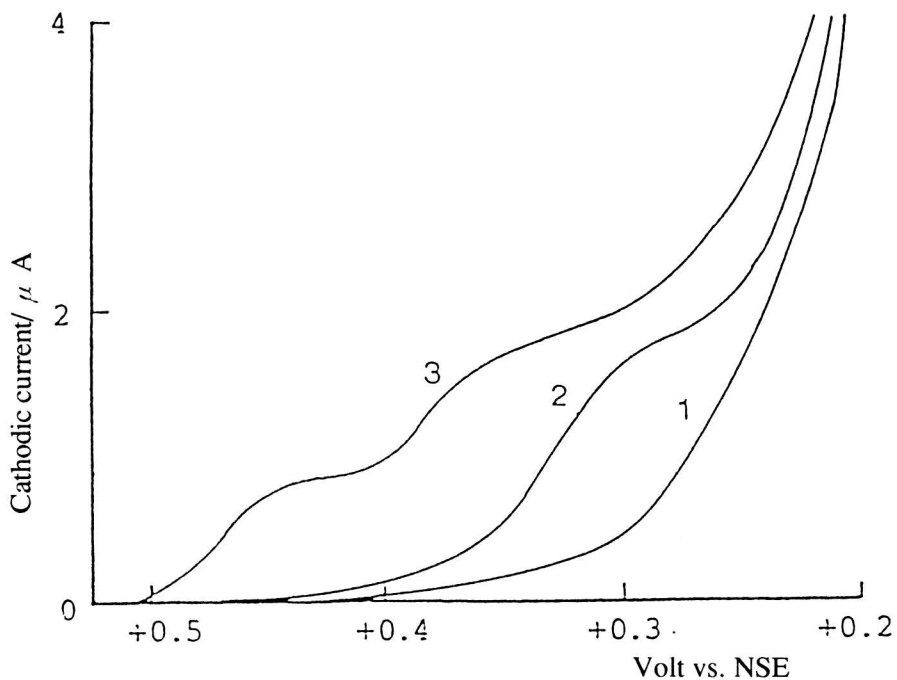
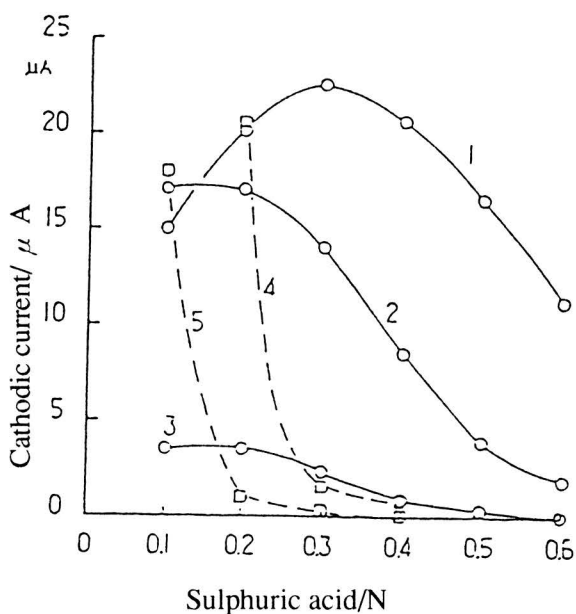


Fig.4 Current-voltage cures of phosphomolybdate and silicomolybdate obtained with polished glassy carbon electrode at a scan-rate of 1 mV/sec.
 Curve 1, the reacting reagent imposed of 0.5 N H₂SO₄ and 0.05 M Mo(VI).
 Curve 2, 10⁻⁵ M phosphate with the reagent. Curve 3, 10⁻⁵ M silicate reacted with the reagent.



Curve No.	PO ₄ ³⁻ (mM)	SiO ₄ ²⁻ (mM)	Mo(VI) (mM)
1	0.2	---	10
2	0.2	---	5
3	0.2	---	2
4	---	0.2	10
5	---	0.2	5

Fig.5 Formation curves for phosphomolybdate and silicomolybdate as a function of acidity under various molybdate concentrations measured by the polished glassy carbon electrode at a potential of +0.25V.

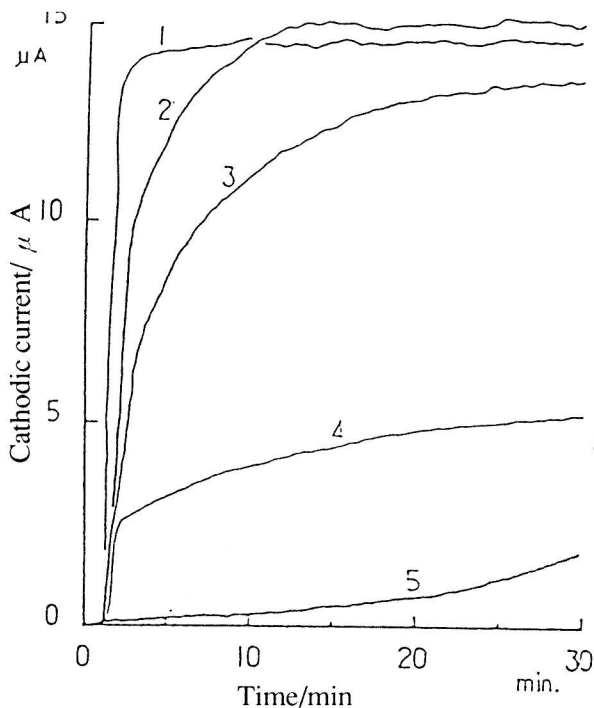


Fig. 6 Reaction time needed for phosphomolybdate and silicomolybdate phosphomolybdate and formation in 5×10^{-3} M Mo(VI) and 0.3 N H_2SO_4 containing; Curve 1: 15% v/v ethanol and 2×10^{-4} M phosphate at $20^\circ C$; Curve 2: 2×10^{-4} M phosphate and at $60^\circ C$; Curve 3: 2×10^{-4} M phosphate and $40^\circ C$; Curve 4: 2×10^{-4} M phosphate and at $20^\circ C$; Curve 5: 2×10^{-4} M silicate at $60^\circ C$.

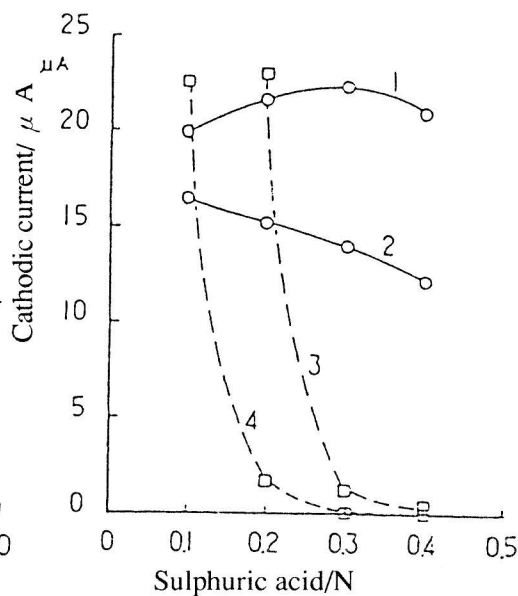


Fig. 7 Formation curves for silicomolybdate as a function of acidity in aqueous solution contains 15% CV (V) ethanol and (Curve 1) 10^{-2} M Mo (VI) and 2×10^{-4} M phosphate; (Curve 2) 5×10^{-3} M Mo (VI) and 2×10^{-4} M phosphate; (Curve 3) 10^{-2} M Mo (VI) and 2×10^{-4} M silicate; (Curve 1) 5×10^{-3} M Mo (VI) and 2×10^{-4} M silicate.

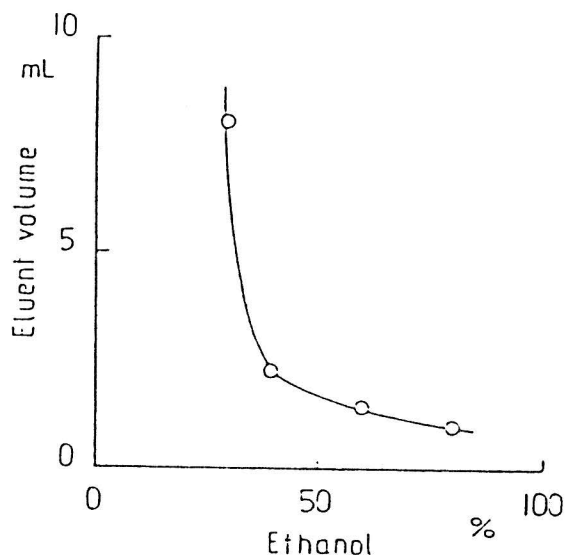


Fig. 8 Elution curve of phosphomolybdate on the column as a function of ethanol concentrations in the eluent. Acidity of the eluent; 0.3 N H_2SO_4 .

between +0.32 V to +0.28 V, the plateau current is proportional to the phosphate in the test solution. Curve 3, 10^{-5} M silicate and hence silicomolybdate, shows two distinct diffusion currents at potentials around +0.45 V and +0.35 V. In this reagent condition, the concentration of silicate can be measured without the interference of phosphate at potentials around +0.45 V, however, phosphate can not be determined in the presence of silicomolybdate. Therefore, for phosphate determination, it is important to control the formation of silicomolybdate. Fig. 5 shows the formation of phosphomolybdate and silicomolybdate as a function of acidity under various molybdate concentrations. Phosphomolybdate and silicomolybdate were investigated by polished glassy carbon electrode at a potential of +0.25 V. As shown in the figure., silicomolybdate is not formed over a acidity at 0.3 N (curve 5), therefore, appropriate conditions for measuring phosphate might be selected to the acidic concentration around 0.3-0.4 N and the molybdate concentration around 5×10^{-3} M. Fig. 6 shows the reaction time needed for phosphomolybdate and silicomolybdate formation at various conditions. The concentration of phosphomolybdate and silicomolybdate were measured by polished glassy carbon electrode. Curve 5 were obtained by the aqueous solution which contained 2×10^{-4} M silicate instead of phosphate at the reaction temperature of 60 °C. Curve 1 shows a solvent effect to the reaction time. It were obtained in the presence of 15 % ethanol under the conditions in curve 4. It is clearly seen that the formation rate of phosphomolybdate is much enhanced in the presence of ethanol. Fig. 7 shows the formation of phosphomolybdate and silicomolybdate as a function of acidity under the condition in the presence of 15 % ethanol in aqueous solutions.

The detection limit of this voltammetric method for measuring phosphate is around 1×10^{-6} M, so that it is less sensitive to apply to measure phosphate in environmental water, therefore, we developed preconcentration method for phosphomolybdate before the measurement with the polished glassy carbon electrode. As phosphomolybdate is extracted to some organic solvents, it is expected to preconcentrate on a column coated with an organic solvent. We used " Sep-Pak C18 " column (Waters Assos. Inc.) which consisted of octadecane ($C_{18}H_{38}$) coated on the porous silica gel. The sep-pak has large adsorption capacity for phosphomolybdate in aqueous solution. Fig. 8 shows the elution volume measured by flowing the various concentrations of ethanol mixture in 0.3 N sulphuric acid solution the adsorption of 15 ml of 10^{-4} M phosphomolybdate on the column. Phosphomolybdate on the column is not eluted by the solution lower 25 % v/v of ethanol concentration, and is eluted higher 40 % v/v. Curves 2,3, and 4 in Fig. 8 were obtained by measuring the aqueous solution which contained 2×10^{-4} M phosphate in 5×10^{-3} M molybdate and 0.3 N sulfuric acid at the reaction temperature of 60 °C (curve 2), 40 °C (curve 3) and 20 °C (curve 4). From these studies method above, we designed a new automatic

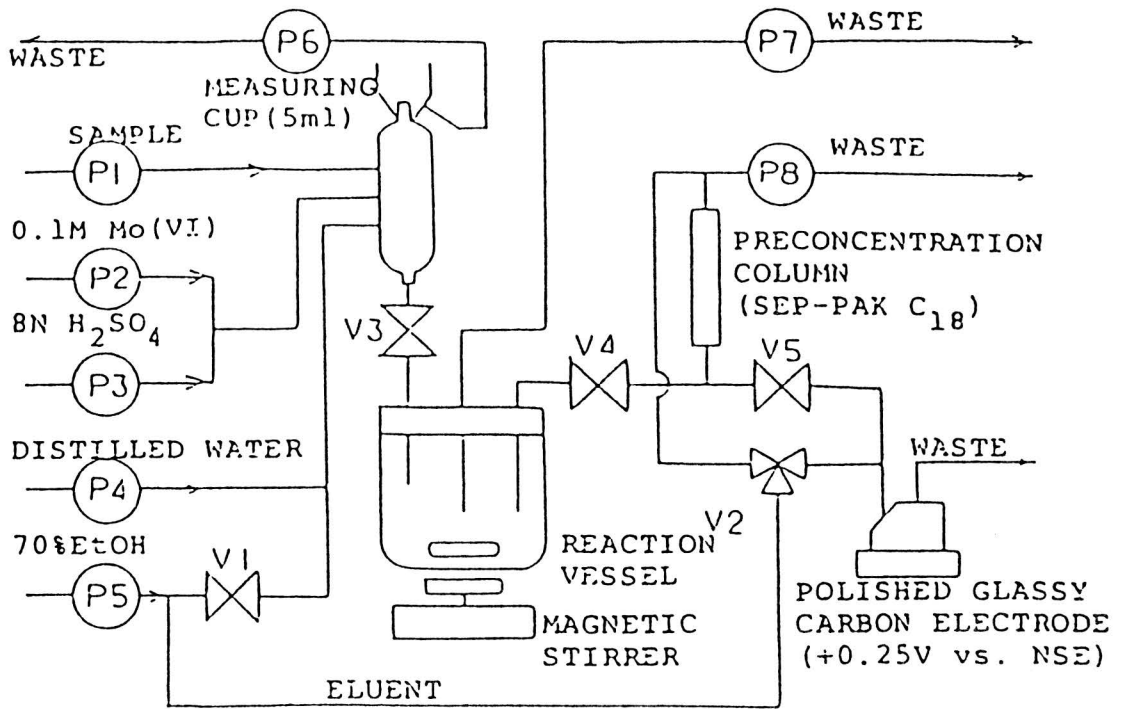


Fig.9 Flow chart of the phosphate analyser

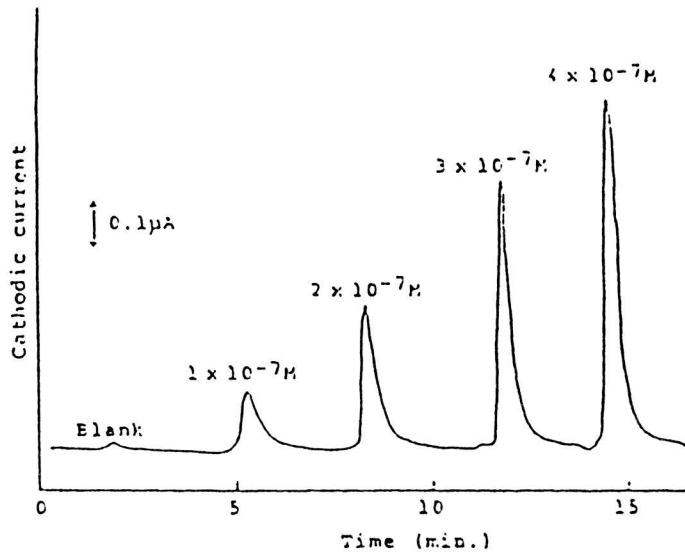


Fig.10 Recording chart for the measurement of various concentrations of phosphate

phosphate analyser based on the principle of the preconcentration and separation of phosphomolybdate and the measurement by the polished glassy carbon electrode. Fig. 9 shows the flow chart of phosphate analyser. The sample is pumped up to the measuring cup (P1). Aliquots (5-35 ml) of the sample is introduced to the reaction vessel and is mixed with the reagents. Phosphomolybdate alone is rapidly formed in the condition (5×10^{-3} M molybdate, 0.4 N sulphuric acid, 14 % ethanol). After definite reaction time (1 min), the solution in the reaction vessel (50 ml) is introduced to produced to preconcentration column (Sep-pak C18), and is washed by distilled water. The condensed phosphomolybdate on the column is eluted by the eluent (70 % ethanol /0.3 N sulphuric acid. P5 ; operation, V2 and V5 valve open) to polished glassy carbon electrode. Current-time profiles recorded for varing concentrations of phosphate in this phosphate analyser are shown in Fig. 10.

REFERENCES :

- Dickey, T.D., 1991. *Rev. Geophys.*, 29, 383.
- Kimoto, T. and Fujinaga, T., 1990. *Mar. Chem.*, 30, 179-192.
- Fujinaga, T. and Kimoto, T. *Trans. of the Research Institute of Oceanchemistry*, 1, 4 (1986)
- Hiiro, K. Nagao J. and Kimoto, T., *Environmental Conservation Engineering*, 16,671 (1987)
- Fujinaga, T. Okazasi, S. and Hori, T., *Bunseki Kagaku*, 29, 367 (1980)
- Hori, T. and Fujinaga, T., *Chem. Lett.*, 687 (1983)
- Hori, T. and Fujinaga, T., *Talanta*, 30, 925 (1983)
- Fujinaga, T. and Kimoto, T., *Talanta*, 31 720 (1984)
- Kimoto, T. and H. Hirata, *I. S. SMEC (Kyoto) abstract*, S2-11 (1986)
- Hiro, K., Nagao, J. and Kimoto, T. 1989. *In RED TIDES : BIOLOGY, ENVIRONMENTAL SCIENCE AND TOXICOLOGY*, Elsevier, Amsterdam, pp. 165-168.
- Martin, H. H., Gordon, R. M., Fitzwater, S. and Broenkow, W. W. 1989. *Deep Sea Res.* 36, 649-680.