

FLOW INJECTION TECHNIQUES FOR THE DETERMINATION OF TRACE ELEMENTS IN SEA WATER

*Yury A. Zolotov, Lilliya K. Shpigun, and Irina Ya. Kolotyorkina
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy
of Sciences, Leninsky Prospect 31, Moscow 117907, RUSSIA*

The content and distribution of trace components in the marine environment is of interest from many points of view. In particular, concentration profiles of some elements in sea water and in interstitial waters of sea-bottom sediments are found to be caused by the important processes operating within the ocean.

After a sea water sample has been taken, it remains to be biologically active system because of bacteria and plankton continue working on take up and excrete material. Thus, much analytical work must be performed immediately after sampling. In this connection, analytical methods that are rapid, less prone to contamination and more sensitive are required. Obviously, automatic chemical analysis can be vital for many marine hydrochemical studies, because analytical results may be available within a short period of time.

Flow Injection Analysis (FIA) is known to be one of the most promising analytical methodologies for automation of routine wet chemical procedures and for near-real time process monitoring [1]. It allows high sample throughputs and provides good reproducibility of the measurements. It was recognised that FIA offers many advantages for marine chemical research [2 - 6].

Our interest was focused on the design of flow injection (FI) techniques, available for shipboard determining trace amounts of transition metals and micronutrients owing to speed of analysis, *on-line* sample pre-treatment and reliable analytical characteristics. In order to provide the full potential of FIA methodology for detection low, sometimes extremely low, concentration of elements in sea water, however, very sensitive and selective analytical reactions or high-performance flow-through detectors are required. It can be achieved in different ways, but the use of simple and inexpensive spectrophotometric and electrochemical detectors is the most convenient. For this reason, we developed the FI methods based on the following principles [7 - 12]: 1) catalytic effects of metal ions in homogeneous oxidation reactions of some organic compounds; 2) combination of *in-valve* sorption or gas-diffusion preconcentration and separation of an analyte followed by potentiometric or spectrophotometric detection of its concentration in the eluate zone; 3) use of *in-valve* electrochemical sensor unit containing a chemically modified carbon composite electrode (CCE).

A summary of the FI techniques developed for determining Mn (II), Fe (III), Co (II),

Zn (II) and Ag (I) at natural levels in sea water is presented in Table I. It should be mentioned that all these metals, especially Mn (II) and Fe (III), were known to be very important from the geochemical point of view because hydrothermal activity can be recognised by indicating their anomalous concentration in deep sea water [13 - 15].

Table 1. Features of FI systems proposed for determining some transition metals in sea water

Species	Detection type	<i>In-valve</i> Innovertor	Range of conc./ nM	LOD / nM	RSD / %	Sampling rate/ h ⁻¹
Mn(II)	Spectrophot.det. based on catalytic reaction N,N-diethyl-aniline-KIO ₄	Column with <i>DETATA</i> - sorbent	0.2 - 300	0.04	5 - 8	4 - 12
Fe(III)	Reversed FI spectrophot. det. based on catalytic reaction N,N-dialkyl-p-phenylendiamine - H ₂ O ₂	-	2 - 1000	0.5	2 - 8	60
Co(II)	Spectrophot.det. based on catalytic reaction N,N-diethyl-p-phenylendiamine - Tiron - H ₂ O ₂	-	0.2 - 50.0	0.02	3 - 9	50
Zn(II)	Spectrophot.det. based on complex formation with Xylenol Orange	Column with Dowex 1-X8 resin	5 - 300	0.8	3 - 6	3 - 10
Ag(I)	Anodic stripping voltammetry on thiocrown modified CCE	Electrochemical sensor unit	0.1 - 10.0	0.05	4 - 10	2 - 6

The schematic diagram of the FI catalytic system proposed for shipboard determining ultralow concentration of dissolved cobalt in sea water is shown in Fig. 1. It was based on the catalytic effect of cobalt (II) in the co-oxidation of N,N'-diethyl-p-phenylendiamine and tiron by hydrogen peroxide [10]. The catalytic activity of cobalt (II) was found to be significantly enhanced by the presence of sea water conservative macrocomponents, especially by calcium ions, improving the sensitivity of cobalt determination in sea water. The comparatively weak basic medium (pH 8.7 - 9.0) of the reaction and its relative

freedom from co-existing ions allowed the direct analysis of sea water to be effectively conducted without any preliminary steps.

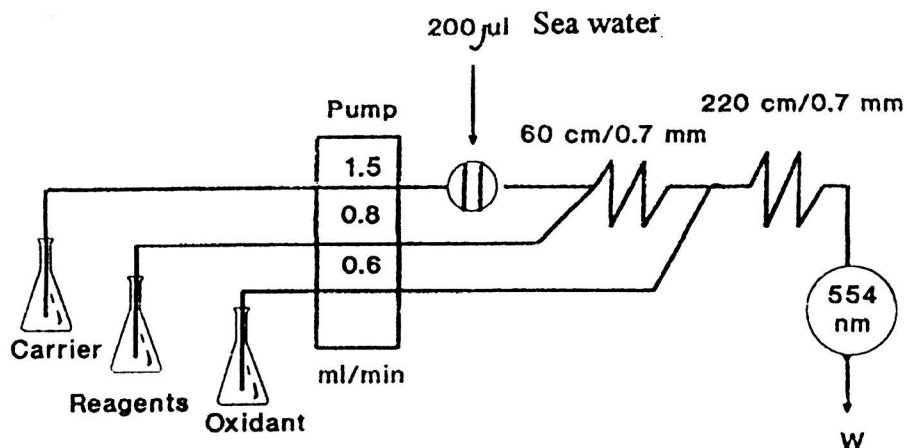


Fig. 1 Schematic diagram of the FI manifold used for determining cobalt in sea water

Analysis of North Atlantic Surface Sea Water (NASS-2) and Coastal Atlantic Sea Water (CASS-2) standards gave cobalt concentrations within the accepted ranges, conforming the accuracy of the proposed technique (Table 2). For comparison, some samples of artificial hydrothermal solutions were also analysed by the new FI method and by ICP-MS. The results are also shown in Table 2 and indicate that there were no significant differences among the values obtained by both methods.

Table 2. Results of the determining cobalt (II) in sea water samples ($P = 0.95$)

Sample	Found Co/ ng l ⁻¹				
	n	FI method	RSD / %	ICP-MC method	Certified values
NASS-2*	4	3.1 ± 0.5	10.4	-	4 ± 1
CASS-2*	14	27.1 ± 0.4	2.8	-	25 ± 6
Artificial hydrothermal solutions	5	160 ± 7	3.4	151 ± 5	-
	9	200 ± 5	2.7	210 ± 6	-
	5	175 ± 5	2.5	165 ± 5	-

(*National Research Council, Canada)

Figure 2 illustrates the FI system used for the determination of zinc in sea water. As can be seen, it includes a mini column containing a sorbing resin for *in-valve* preconcentration of zinc from acidified samples. The spectrophotometric quantification of zinc in the eluate zone was based on the reaction of zinc with triphenylmethane reagent Xylenol Orange.

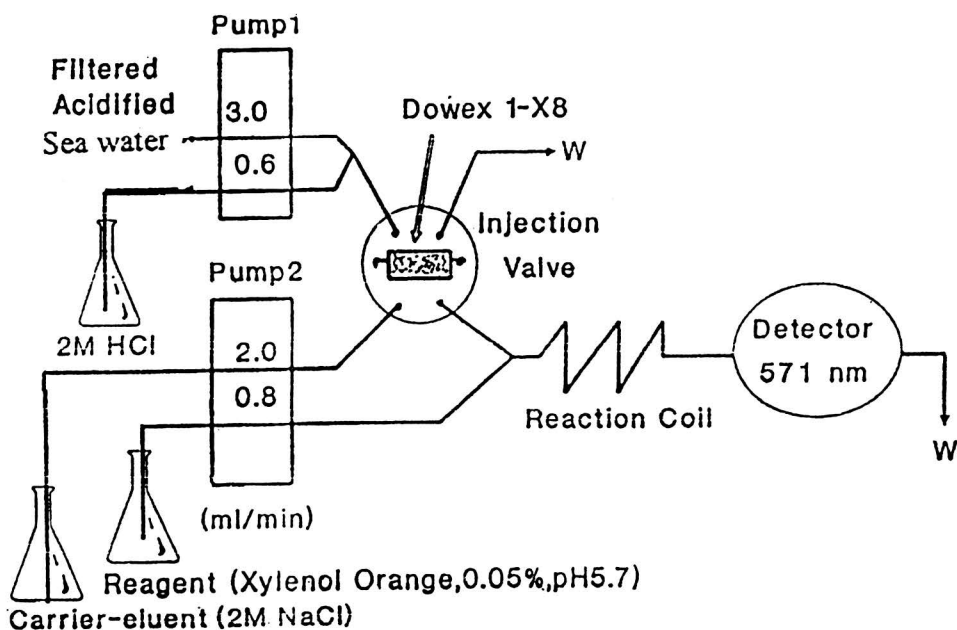


Fig. 2 Schematic diagram of the FI manifold used for determining zinc in sea water

The best selectivity enhancement was achieved by using a strongly basic anion-exchanger Dowex 1-X8 [11]. It was explained by the differences in the stability of the chloro complexes of zinc and of other metals as well as in its preferential distribution coefficient for zinc in relation to potential interfering metals. This procedure also improved the sensitivity of analysis because the eluent solution (2M NaCl) was compatible with the optimal reaction conditions required for the detection of zinc (pH 5.7). The load time could be varied to concentrate lower or higher expected metal concentration. The accuracy of the method was verified by recovering added amounts of zinc in the artificial sea water samples and by the analysis of CASS-2 standard reference sea waters (Table 3). To demonstrate the applicability of the proposed method to sea water analysis, some Black Sea water samples were also analysed for zinc. The recovery of zinc which was added to the sea water samples at concentrations of 10~150nM was 96% - 106%, indicating no significant interference.

Table 3. Recovery test analysis of sea water samples for zinc (n = 6, P = 0.95)

Sample	Concentration of Zn/ nM		RSD / %	R / %
	Added	Found		
Artificial Sea water (S=34 ‰)	10	15 ± 1	6.3	106
	30	31 ± 2	5.9	105
	75	73 ± 4	4.2	96
	150	153 ± 5	3.3	102
Black Sea water (S=16 ‰)	0	12 ± 1	7.8	-
	20	33 ± 2	5.7	105
	40	52 ± 2	3.6	100
CASS-2	30 ± 2	29 ± 2	6.0	97

A novel FI technique with *in-valve* electrochemical sensor configuration for determining silver by differential-pulse anodic stripping voltammetry was developed. In order to obtain a method for ultratrace silver determination in sea water which would be easier to use on board ship, a flow-through electrochemical cell containing a macrocycle modified silica carrier-carbon composite electrode was fabricated and incorporated into a manifold instead of the sampling loop, as it is shown in Fig. 3. The binding of silver by covalently immobilised dibenzo-18-tetrathiacrown-6 was established to be very effective for preconcentration of silver from flowing solution [16].

Silver was selectively collected on the electrode surface at a constant potential -of 0.3 V. At the adsorptive collection time of 30 min, the electrode shows an oxidation current response proportional to the silver concentration in the range from 0.1 to 1.0 nM. Table 4 shows the data of the recovery experiments obtained for standard solutions prepared with the acidified Ag-free sea water, indicating good accuracy and reproducibility of the results obtained (Table 4). It was stated that the developed FI sensor system can detect lower than 0.1 nM of silver.

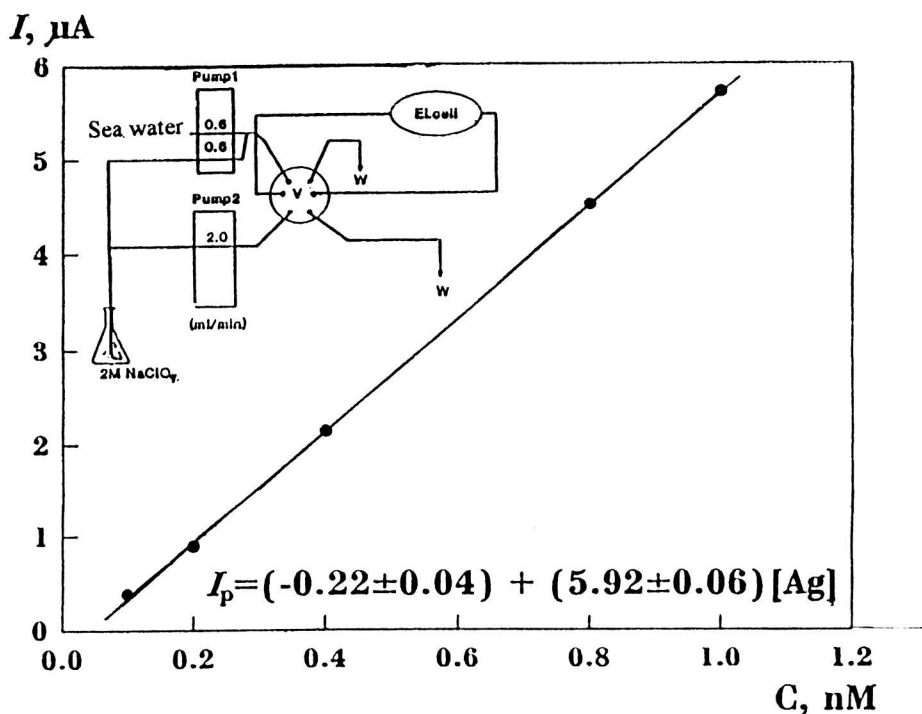


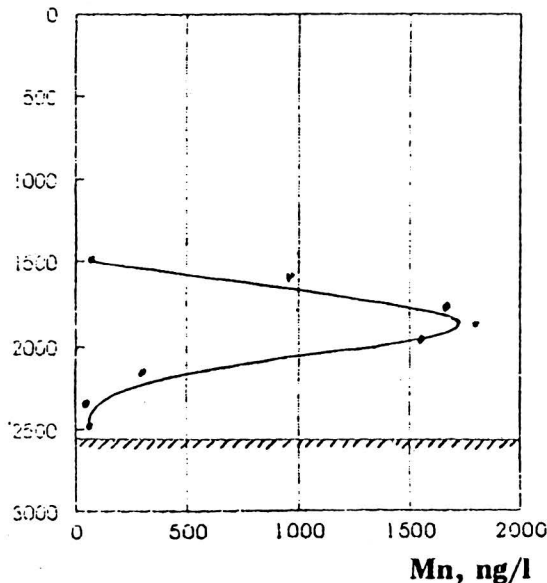
Fig. 3 Schematic diagram of the FI sensor system for ultra-trace determination of silver

Table 4. Recovery of silver from sea water (n = 6, P = 0.95)

Concentration of silver/ nM		RSD / %	R / %
Added	found		
0.10	0.11 ± 0.01	9.4	110
0.20	0.19 ± 0.02	7.1	95
0.40	0.41 ± 0.02	4.7	103
0.80	0.80 ± 0.03	3.5	100
1.00	1.00 ± 0.04	3.7	100

The proposed FI techniques were successfully applied to individual determination of dissolved metals in sea water samples collected from at and above the hydrothermal vents in the *Manus* Basin in Pacific Ocean. Vertical profiles of dissolved manganese concentration in sea water obtained at the stations are presented in Fig. 4. These data give evidence of the existence of active hydrothermal springs in this region.

Depth, m



Depth, m

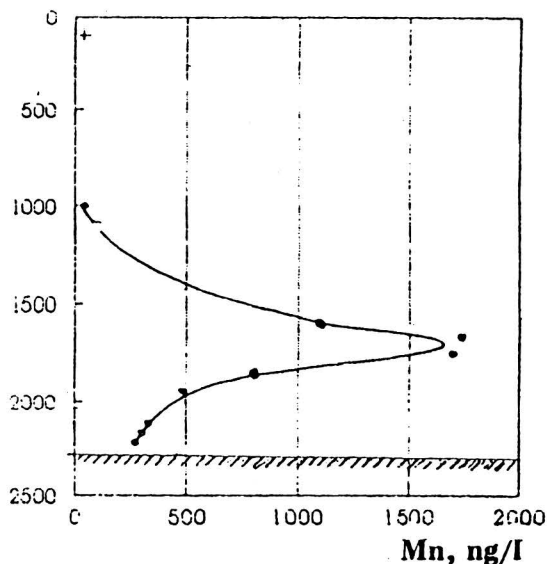


Fig. 4 Selected manganese profiles in the deep sea water columns of the Manus Basin

Several sensitive techniques for determining important micronutrients and sulphur forms in deep sea water and interstitial water of bottom sediments were also developed.

Table 5 shows performance data of FI systems for determining dissolved ortho-phosphates and silicates by using two different types of detection. The both methods were based on the well-known complexation reaction of these components with acidic ammonium molybdate reagent. The reaction was carried out by using *in-valve* reactor unit. Then, the molybdophosphate or molybdosilicate anions formed in the injector manifold were injected into the carrier stream. In case of amperometric detection, a current signal was measured that caused by reduction of heteropolymolybdates at the carbon electrode at zero potential.

The data obtained by this simple and sensitive method in analysis of the artificial sea water samples containing ortho-phosphate and silicate ions are given in Table 6.

Figure. 5 shows the schematic diagram of the FI system with *in-valve* gas-diffusion configuration and intermitted pumping. It should be mentioned that utilisation of Gas Diffusion Flow Injection Analysis has been demonstrated as an effective technique to increase selectivity and sensitivity for an analytical method [17]. In the present case, the system allowed the satisfactory determining sulphide and ammonium ions in sea water at a very low level ($< 1\mu\text{M}$).

Table 7 demonstrates the features of these systems with using spectrophotometric detection and potentiometric detection by membrane ion-selective electrodes (ISEs).

Table 5. Features of the proposed FI systems for determining ortho-phosphate and silicate in sea water by using two different types of detection

Element determined	Type of FI system	Linear conc. range / μM	LOD / μM	Sampling rate /h ⁻¹
Ortho-phosphates	Reversed FI system based on spectrophotometric detection	1 - 20	0.2	60 - 70
	FI system based on amperometric detection at a carbon electrode	0.1 - 10	0.05	60
Silicates	Reversed FI system based on spectrophotometric detection	5 - 120	3.0	90
	FI system based on amperometric detection at a carbon electrode	1 - 50	0.3	60

Table 6. Analysis of sea water samples for silicates and phosphates * (n = 10, P = 0.95)

Amount taken/ μM		Amount found/ μM	
Silicate	Phosphate	Silicate	Phosphate
0.0	0.00	6.4 \pm 0.1	0.12 \pm 0.01
5.0	0.10	11.4 \pm 0.1	0.21 \pm 0.02
10.0	0.20	16.5 \pm 0.1	0.33 \pm 0.02
25.0	0.30	31.3 \pm 0.2	0.40 \pm 0.03
40.0	0.40	46.5 \pm 0.3	0.51 \pm 0.04

(* Sample volume 300 ml)

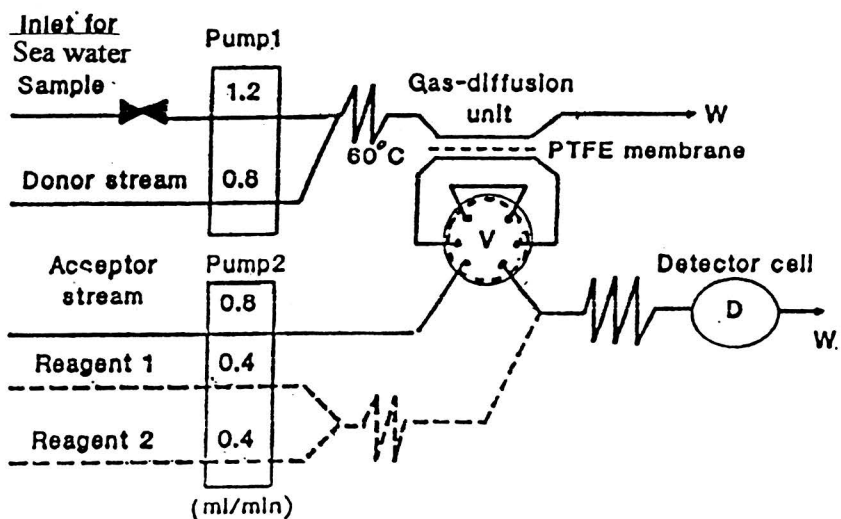


Fig. 5 Schematic diagram of the FI system with *in-valve* gas-diffusion configuration used for determination of trace sulphide and ammonium ions.

Table 7. Features of the proposed FI systems for determining sulphide and ammonium ions in sea water by using two different types of detection ($n = 6$, $P = 0.95$)

Parameter	Sulphide	Ion	Ammonium	Ion
	Spectrophotometric detection	Potentiometric detection with S^{2-} - ISE	Spectrophotometric detection	Potentiometric detection with NH_4^+ - ISE
Donor solution	0.2 M H_2SO_4	0.5 M H_3PO_4	0.1 M NaOH	0.1 M NaOH
Acceptor solution	2.5mM - NaOH	2.5mM - NaOH	Phenol Red (pH 6.8)	0.02 M TRIS-HCl (pH 7.5)
Measuring range/ μM	1 - 20 (10 - 200)*	5 - 50 (50 - 500)*	0.5 - 10 (5 - 100)*	2 - 100 (20 - 1000)*
RSD/ %	0.4 - 1.0	0.7 - 4.0	0.5 - 2.0	0.2 - 3.0
LOD/ μM	0.25	1.0	0.07	1.0

$T_{conc.} = 10$ min, (*) without preconcentration;

The systems were used for routine determining sulphide and ammonium-nitrogen in sea water samples during two cruises of the research vessel "Academik Boris Petrov". The distribution of dissolved oxygen, pH and redox potential values, total alkalinity, phosphates, nitrates, iron and manganese in Black Sea and Kara Sea were also investigated. In particular, the vertical distribution study of dissolved hydrogen sulphide and ammonium-nitrogen concentrations in and near the oxic-anoxic interface zone (to depth as 400 m) in the Black Sea was carried out (1994 Black Sea Expedition of "Akademik Boris Petrov"). The presence of sulphide within 150 m of the surface was found. As can be seen from Fig. 6a, the overlap of the dissolved oxygen and sulphide was observed in the central part of the basin between 100 and 110 m when dissolved sulphide and oxygen coexisted at trace concentration.

The vertical profiles of dissolved manganese (II) and iron (III) as well as redox potential values obtained at this station are shown in Fig. 6b.

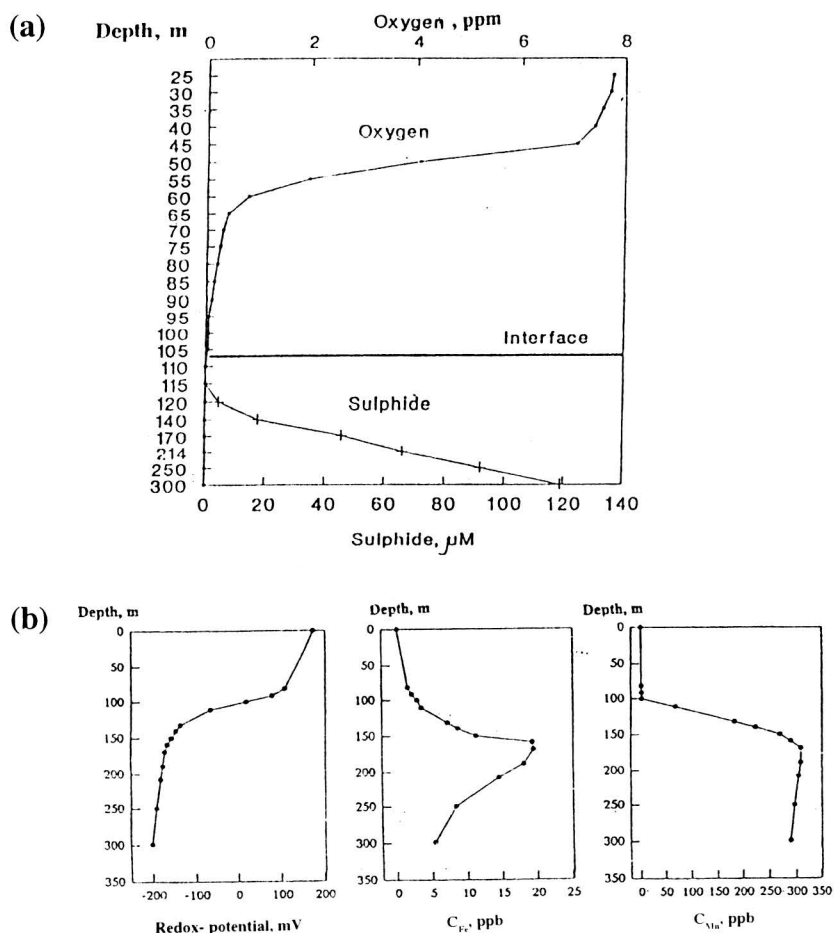


Fig.6 Vertical profiles across oxic-anoxic interface at one of the station in the central part of the Black Sea (43° 19'06"N, 31°26'069"E)

Figure 7 illustrates typical FI signals and the selected vertical profile for $\text{PO}_4\text{-P}$ obtained at one of the station in Kara Sea.

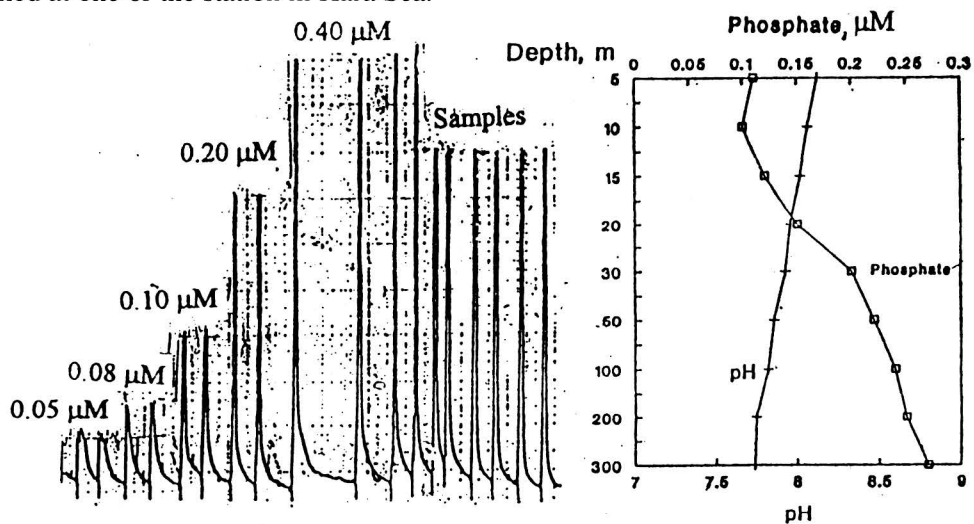


Fig. 7 Typical analytical signals and selected profile of dissolved phosphates at one of the station in KARA Sea

In conclusion, the FI techniques described here have advantages for shipboard use over conventional methods in that. They are simple and inexpensive, have increased sensitivity and selectivity caused of kinetic discrimination effects, and can provide geochemically consistent analytical results with good reproducibility and high sampling rate. These techniques are widely applicable to a variety of hydrochemical studies.

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[和文要旨]

フロー分析法による海水の微量元素の定量

クルナコフ一般化学無機化学研究所

Yu.A. ゴロトフ、L.K. シピグン、I.Ya. コロチルキーナ

海洋の本性を化学的に理解するには、分析化学を発展させることと分析機器を進歩させることが不可欠である。観測船上での測定に各種のフロー分析法を採用することを目的として、フローインジェクション分析 (FIA) 法を詳しく研究した。FIA法は丈夫であることの他にも様々な利点を持つため、海が荒れていても採水後すぐに誤差の少ない分析結果を得ることができる。そして、海水の微量元素の定量や観測においてFIA法の特性を十分に生かすには感度及び選択性の高い化学反応とフロースルー型検出器が必要である。

本研究では、海水の微量溶存成分であるMn、Fe、Co、Znを定量するためのFIA装置を開発した。微量のFeとCoの定量には、これらの金属イオンが有機物の酸化反応の触媒となることを利用して、分光光度法により検出を行うFIAを、また、MnとZnの定量用には、予備濃縮を行うために、インジェクションバルブにイオン交換樹脂を満たした微小カラムを装備したFIAを開発した。これらの方法によって、Loibe海底火山のPele噴出孔で採取した海水試料中の溶存態FeとMnの定量に成功した。山頂の熱水噴出孔及びその上方で採取した海水は、MnとFeを異常に高濃度で含んでいることがわかった。

その他、海洋深層水と海洋堆積物の間隙水に含まれている栄養塩と有害成分の重要なものを定量するためのFIAを提案する。観測船”Academician Boris Petrov”の航海において、FIAを使用し、海水中の硫化物イオンとアンモニア態窒素を自動測定した。黒海とKara海では、溶存酸素、pH、酸化還元電位、アルカリ度、リン酸、硝酸の分布の調査も行った。