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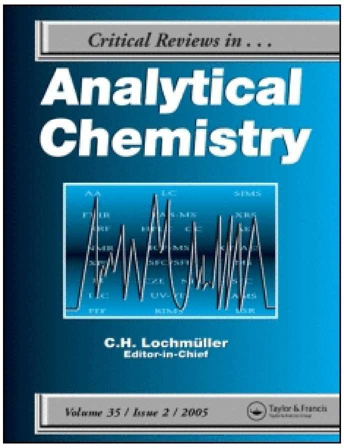

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
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Flow Injection Analysis of Seawater. Part II. Cationic Species

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To cite this Article Atienza, J. , Herrero, M. A. , Maquieira, A. and Puchades, R.(1992) 'Flow Injection Analysis of Seawater. Part II. Cationic Species', Critical Reviews in Analytical Chemistry, 23: 1, 1 — 14

To link to this Article: DOI: 10.1080/10408349208051645

URL: http://dx.doi.org/10.1080/10408349208051645

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Critical Reviews in Analytical Chemistry, 23(1):1–14 (1992)

Flow Injection Analysis of Seawater. Part II. Cationic Species

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ABSTRACT: The demand for fast techniques in the control of environmental pollution is rising at an ever-increasing rate. Flow injection analysis (FIA) can provide a simple, handy, and versatile tool to determine metal cations in seawater. Furthermore, the use of FIA techniques coupled with on-line sample preconcentration and matrix modification has recently attracted considerable research effort in attempts to control interference effects. Since the analytes reported in this paper are metal cations, the most common active agents used for sample preconcentration are chelating resins of different types. The combination of FIA with detection techniques, such as atomic spectroscopy (AS), for the determination of cationic species in the general context of seawater analysis is reviewed.

KEY WORDS: seawater, flow injection analysis, cations.

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I. INTRODUCTION

With an increasing sense of environmental awareness and the accompanying recognition of the need for its protection, seawater contamination has been the focus of numerous research studies.[1]

The rapid rate with which water pollution control activities have grown has intensified the need for an efficient procedure that would reduce the time necessary for determination of species causing seawater pollution.[2]

The determination of cationic species in seawater is difficult (especially for trace elements) due to various factors, the most important of which are very low element concentrations, high salt content of the matrix, and contamination or loss of elements from samples during sampling, preservation, and pretreatment.[3] The first two factors are dictated by the seawater medium and cannot be totally controlled, although their effects can be minimized,[4,5] but any loss or contamination during pretreatment is determined by the care taken in sample handling and by the analytical method chosen.

Although many detection techniques have been used for the determination of trace metals in seawater,[6] atomic spectroscopic (AS) techniques should be included among the most important for the direct assay of cationic species.[7] All of these methods require sample preconcentration prior to the measurement step.

In spite of the great improvement in intensity and selectivity of modern analytical detection systems, conventional separation techniques such as precipitation, distillation, liquid-liquid extraction, ion exchange, and dialysis are frequently used to overcome interferences from matrix elements as well as to improve detection limits through the preconcentration of the analyte.[8,9] Manually operated separation and preconcentration procedures are usually tedious and involve large samples, time, and reagent consumption; they are also susceptible to contamination.

The existence of such time-consuming manual operations has led a number of researchers to

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examine various approaches for automating the sample handling in AS.[10] An early approach utilized segmented continuous flow (SCF) analysis, but the required air segmentation of SCF can result in an air noise signal from the analyte.[11] Commercial Autoanalyzer systems are also widely used for the determination of micronutrient elements in seawater, and the instruments can be operated at sea without problems.[12] One advantage of automated analysis is that chemical reactions take place in closed systems and sample manipulation is minimal. This greatly reduces the risk of sample contamination. Another advantage is that reaction conditions can be closely controlled and repeated.

Since its introduction, interest has been sustained in the application of flow injection analysis (FIA) techniques to the development of automated, on-line sample pretreatment procedures.[13,14] Benefits are associated with flow injection separation: preconcentration techniques include high efficiency, simple on-line operation, low sample reagent consumption, relatively simple and compact hardware, and freedom from contamination. Flow injection techniques have much to offer in improving the efficiency and in the automation of different separation and preconcentration processes.[15] Pretreatment steps performed using FIA are rapid; pretreatment and analysis, including chemical conversions, generally require <1 min. Most FIA preconcentration methods are based on the use of a microcolumn, which can significantly reduce analyte volume. The use of ion-exchange columns for trace preconcentration and interference removal is one of the most widely used on-line techniques in FIA systems.[16]

The growing interest in the use of FIA techniques in conjunction with AS was demonstrated in several reviews[17–19] and in a recent book.[20] Since the appearance of the first paper, which described the use of an in-line column of solid reagent for the determination of some trace elements in seawater using a two-step procedure wherein the metal removal step was followed by elution with an acid carrier stream,[21] a considerable increase has been observed in method development in this area.[8,22] Examples include the combination of FIA with atomic absorption spectroscopy (AAS) for efficient sample introduction involving merging zones and the direct aspiration of samples; the application of flow injection systems with on-line ion-exchange preconcentration and flame atomic absorption spectroscopy (FAAS); the determination of several elements by hydride generation AAS (HG-AAS); standard addition using an inductively coupled plasma (ICP-AAS) system; and others.[23,24]

This article intends to outline these applications and to provide a general overview of the determination of cationic species by FIA, and is the final installment of an examination by Atienza et al.[25] to illustrate the potential of FIA in seawater analysis.

II. CATIONIC SPECIES

In spite of the fact that trace elements such as As, Se, B, etc. can be found as anions in seawater, they have been included in this review because most of the analytical procedures shown here exhibit speciation (i.e., they are directly analyzed).

A summary of FIA methods proposed for the determination of cationic species in seawater is given in Table 1.

A. Ammonia

Ammonia is an important micronutrient in the estuaries and oceans of the world. It is the primary excretory product of marine organisms. However, biological and oceanographic studies that require accurate measurement of ammonia are difficult due to its low concentrations in coastal and oceanic waters. Several flow injection methods have been used for the determination of micromolar levels of ammonium ions. The commonly used methods based on the Nessler and Berthelot reaction do not possess adequate detection limits for seawater analysis. Leggett et al.[26] proposed a method for simultaneous determination of ammonium and hypochlorite ions using *o*-toluidine and a merged stream of a sodium arsenite solution. Růžička and Hansen[27] described an improved FIA method for ammonia determination using a gas-permeable membrane. Advantages of gas-diffusion techniques include

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TABLE 1
Features of FIA Determinations of Cationic Species in Seawater

Species	Detection	Reaction	V_i	Detection limit	rsd (%)	Linear range	Sampling frequency (h^{-1})	Instrumental innovations	Other features	Ref.
NH_4^+	Phot.	o-Toluidine		0.5 μg l^{-1}					S.D. NH_4^+, ClO^-	26
NH_4^+	Phot.	Nessler	260 μl	0.5 μ*M*	<2	0.1–10.0 μ*M*	60		Phenol red Gas diffusion	28
NH_4^+	Phot.	Indophenol	200 μl	1 μ*M*		50–500 μ*M*			Gas diffusion	29
	Phot.	Bromocresol purple	480 μl	0.01 μ*M*	<2	1–25 μ*M*			Gas diffusion	
	Cond.	N.C.R.		50 μ*M*		>50 μ*M*			Gas diffusion	
	Pot.	N.C.R.	500 μl	<10^{-7} *M*		10^{-6}–10^{-4} *M*		ISE, ion-exchange column in sample loop		
Ca^{2+}	Phot.	C.F.			0.57	0–10 ppm	180	Merging zones Proportional injector	Good tolerance to Mg^{2+} and heavy metals	32
Ca^{2+}, Mg^{2+}	Phot.	C.F		0.02 mg l^{-1}	3.7, 3.2	0–2 mg l^{-1}	200		S.D.; pH = 7.0	33
Ca^{2+}	Phot.	C.F.		0.1 mg l^{-1}	2.3	0.2–2.0 mg l^{-1}	250		pH = 2.2	
Ca^{2+}	ICP-AES	N.C.R.					60	Sampling zone	Computer controlled S.D. Ca, Mg, Al, Fe, P, Si	35
As^{3+}	HG-AAS		1 ml	0.07 ng ml^{-1}	2.5		150	Gas-liquid separator		37
As^{3+}	HG-AAS			0.15 μg l^{-1}				Gas-liquid separator		38
Sb^{3+}				0.24 μg l^{-1}						
Au^+	ICP-MS	C.F.		10 fmol				Radiotracer	Anion-exchange	53
Au^+	ICP-MS	C.F.	120 μl	1 fmol	15			Radiotracer	Anion-exchange	54
B	Phot.	C.F.	35 μl		0.9	0.02–0.50 μg ml^{-1}	70		nFIA	39
			135 μl		1.1	0.05–0.50 μg ml^{-1}	50		rFIA	
B	Phot.	C.F.		5 μg l^{-1}	<10	0–200 μg l^{-1}	20		Ion exchange	40
				1 μg l^{-1}	<5		10		Computer controlled	
Co^{2+}	C.L.	R.O.	3 ml	8 p*M*	5		8		Immobilized chelating agent	46
Co^{2+}	Phot.	R.O./C.		0.005 ng ml^{-1}		0–0.088 ng ml^{-1}	2		Ion-exchange S.A.M.	47
Cu^{2+}	AAS	N.C.R.	10 ml	0.0015 μg ml^{-1}			15		Immobilized chelating agent	49
Cu^{2+}	C.L.	C.	20 μl	0.1 ng	2.2	0.1–10.0 ng	200	Cyclic flow system New C.L. system		50
Cu^{2+}	Phot.			0.7 μg l^{-1}		>50 μg l^{-1}				51
Cu^{2+}	Pot.	R.O./C.			<5	0.5–250 ng ml^{-1}	40	ISE	Chelating column	52
Cr(VI)	Phot.	R.O.	30 μl	<1		0.1–200.0 ppm	120		Detectors in series	41
Cr(III)	AAS	N.C.R.				1–50 ppm				
Cr(VI)	Phot.	C.F.	4.4 cm^3	0.5 ng	4.3			Resin-filled flow cell	Ion exchanger Phase absorptiometry	43
Cr(III)	AAS	N.C.R.	20 μl	0.1 μg ml^{-1}	1.3	20–100 μg ml^{-1}			Chelating column New resin	44
Fe	Phot.	R.O.	100 μl	0.4 ng ml^{-1}	0.6	10–100 ng ml^{-1}	30			56
Fr(II) Fe(III)	C.L.	R.O.		0.45 n*M*	2–5	<2.5 n*M*	12	Ion-exchange column in flow cell	Microprocessor-controlled injector valve	59
Mn(II)	Phot.	R.O./C.			19	0.02–10.00 ng ml^{-1}	25		Commercial FIA system	64
Mo(VI)	Phot.	R.O./C.	200 μl	0.7 mg l^{-1}	<1	1–100 μg l^{-1}	90		Good tolerance to V, W	68
Mo(VI)	Stripping current electrode	R.O.	5 ml			0–20 μg l^{-1}		Constant current reduction	Computer controlled	70
Mo(VI)	Phot.	C.F.		15 ng			4	Ion-exchange column in flow cell	Ion exchanger Phase absorptiometry	71
Mo(VI)	ICP-AES	N.C.R.		0.2 ng ml^{-1}	<5	10–1000 ng ml^{-1}			Ion exchange	72
Pb^{2+}	AAS	N.C.R.	1 ml			10–500 ppb	30–60	Automation; two valves in series or two synchronized pumps	Ion-exchange column with counter current elution	21
Cd^{2+}						1–100 ppb				
Zn^{2+}						1–100 ppb				
Pb^{2+}	Phot.	C.F.	12 ml	0.01 μg l^{-1}	12	0.7–100.0 μg l^{-1}		Ion-exchange column in sample loop		60

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TABLE 1 (continued)
Features of FIA Determinations of Cationic Species in Seawater

Species	Detection	Reaction	V$_i$	Detection limit	rsd (%)	Linear range	Sampling frequency (h^{-1})	Instrumental innovations	Other features	Ref.
Mn^{2+}	Phot.	R.O./C.		20 μg	<20	0.02–1.00 μg l^{-1}	40		Stopped flow	
Cu^{2+}	Pot.		500 μl	0.5 μg l^{-1}	5	0.5–1000.0 μg l^{-1}	50	ISE	Ion exchange	
Pb^{2+}				8.10^{-10} *M*		0.36–0.70 ppb				
Cd^{2+}	Anodic stripping voltammetry			7.5, 10^{-10} M	<5	0.18–0.29 ppb	6	Electrochemical flow cell for oxygen removal		61
Cu^{2+}				1.2, 10^{-9} *M*		0.15–0.37 ppb				
Pb^{2+}	Phot.	C.F.	600 μl	25 μg l^{-1}		50–200 μg l^{-1}	45		Liquid-liquid extraction	62
	Phot.	C.F.		5 μg l^{-1}	9		36		Liquid-liquid extraction and ion exchange	62
Se	HG-AAS			0.002 μg l^{-1}	1		50	Automated multifunctional valve	Ion exchange gas-liquid separator	73
Bi				0.001 μg l^{-1}	1.1					
Cu^{2+}	AAS	N.C.R.		0.07 μg l^{-1}	1.2–3.2	5–20 μg l^{-1}	60	Two-layer valve with 8 channels	Dual column ion exchange	36
Zn^{2+}				0.03 μg l^{-1}		5–20 μg l^{-1}				
Pb^{2+}				0.5 μg l^{-1}		25–100 μg l^{-1}				
Cd^{2+}				0.05 μg l^{-1}		2.5–10.0 μg l^{-1}				
Ni^{2+}	AAS	N.C.R.			1.5–4.1	100–400 μg l^{-1}	40	Multifunctional rotary valve	Ion exchange	74
Cu^{2+}						25–100 μg l^{-1}				
Pb^{2+}						100–500 μg l^{-1}				
Cd^{2+}						25–100 μg l^{-1}				
Mn^{2+}	ICP-MS	N.C.R.	100 μl						Chelating column Isotope dilution technique S.A.M.	75
Mo^{2+}										
Cd^{2+}										
U										
Cd^{2+}	GF-AAS	C.F.	23 μl	0.5 μg l^{-1}	1.9	25–200 μg l^{-1}, except for Co^{2+}	30	Pulse dampers Two extraction steps		76
Co^{2+}				2.0 μg l^{-1}						
Cu^{2+}				2.4 μg l^{-1}	1.9					
Fe^{2+}				4.4 μg l^{-1}	1.7					
Ni^{2+}				5.0 μg l^{-1}	1.5					
Pb^{2+}				3.3 μg l^{-1}	2.7					
Co^{2+}	GF-AAS	C.F.					30			77
Cu^{2+}										
Ni^{2+}										
Pb^{2+}										
Cd^{2+}										
Fe^{2+}										
Ni^{2+}	Cathodic stripping chronopot.	C.F.		0.1 n*M*			30	Automated analyzer	Ion exchange	78
Co^{2+}				0.1 n*M*						
Cu^{2+}				1.8 n*M*						
U				1.6 n*M*						

Note: Phot. = Photometry; Cond. = conductimetry; Pot. = potentiometry; ICP-AES = inductively coupled plasma atomic emission spectrometry; AAS = atomic absorption spectrometry; HG-AAS = hydride generation atomic absorption spectrometry; ICP-MS = inductively coupled plasma mass spectrometry; N.C.R. = nonchemical reaction; C.F. = complex formation; R.O. = redox; C. = catalysis; C.L. = chemiluminescence; S.D. = simultaneous determination; and S.A.M. = standard addition method.

high selectivity, ease of automation, and promising detection limits. In this method, the sample is injected into a carrier stream and merged with an alkaline solution. The ammonia formed diffuses across a hydrophobic membrane and reacts with an acid-base indicator in an acceptor stream. Willason and Johnson[28] modified this method for its use in seawater. Phenol red was used as the indicator. The detector incorporated a light-emitting diode (LED) photometer, which measures the change in light transmittance of the acceptor stream produced by the ammonia. The magnitude of the color change is proportional to the concentration of ammonia in the seawater sample. Sodium citrate, which is added to the sodium hydroxide solution, acts as a chelating agent for Mg^{2+} and Ca^{2+}, thereby reducing precipitate formation in the FIA manifold. Detection limits of the reported method have improved from 30 to 62% via the use of long pathlength cells. The

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authors have also adapted this FIA method for use in a submersible chemical analyzer (SCANNER). The concentration of ammonia in seawater can be determined *in situ.*

Low levels of ammonium ion in seawater were determined by Schulze et al.[29] using different approaches. Ammonia determinations, with and without gas diffusion, were compared. The effects of operating parameters on ammonia concentration using a gas-diffusion unit in combination with several detection methods were studied. By using spectrophotometric detection and bromocresol purple as an indicator, a detection limit of 2×10^{-7} mol l^{-1} was achieved. Better detection limits were reported using potentiometric detection with a liquid-membrane ammonium-sensitive electrode. On the other hand, conductivity detection does not appear to be suitable for the determination of low ammonium ion levels. Finally, the effect of on-line preconcentration was also studied. For this purpose, an ion-exchange microcolumn and a gas-diffusion unit are placed in the injection loop of the valve. Both preconcentration methods are satisfactory, and the final choice depends on particular analytical requirements.

Urea was shown to contribute a significant fraction of the total nitrogen utilized by phytoplankton in coastal and oceanic environments. However, accurate and precise measurements are required to determine urea uptake and excretion rates. Currently, two techniques for measuring the concentration of dissolved urea in seawater are in use. A Technicon Autoanalyzer was used by Harrison et al.[30] for the determination of ammonium ion generated by the urease method. Urea determination in seawater using a Technicon Autoanalyzer was also reported by Price and Harrison[31] using the diacetyl monoxime procedure. The results are compared with those obtained by the urease method. The former method is generally recommended due to its freedom from interferences.

B. Alkaline-Earth Cations

The potential of the merging-zones approach was considered by Jacintho et al.[32] in the development of an FIA procedure for the spectrophotometric determination of Ca using glyoxal bis(2-hydroxyanil) as the color-forming reagent. Stability of the system and measurement reproducibility were verified by continuous analysis of a sample for 2 h [relative standard deviation (rsd = 0.57%)]. Magnesium caused no observable interference in the Ca measurement, even at concentrations of 200 ppm. Interference effects from elements such as Fe, Cu, Mn, and Al, were minimized through the addition of triethanolamine and potassium cyanide to the carrier system. Results obtained with the proposed system are in close agreement with those obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Yuan[33] described a flow injection method for the determination of the total concentration of Ca and Mg using a triethanolamine/hydrochloric acid buffer (pH 7.0) and chlorphosphonazo-III (CPA-III) chromogenic agent. The concentration of Ca alone is also determined using hydrochloric acid (pH 2.2) and CPA-III. In the former case, linear ranges for Ca^{2+} and Mg^{2+} are 0 to 2.00 mg l^{-1} (detection limit = 0.02 mg l^{-1}); in the latter, the linear range for Ca^{2+} is 0.20 to 2.00 mg l^{-1} (detection limit = 0.1 ng l^{-1}). Sampling throughput of 200 to 250 injections per hour are typical. In seawater, alkaline earth metal concentrations are usually about 0.02 mg l^{-1} Ba, 8.1 mg l^{-1} Sr, 400 mg l^{-1} Ca, and 1300 mg l^{-1} Mg. Therefore, for the determination of Ca^{2+} and Mg^{2+}, Sr^{2+} and Ba^{2+} interferences are generally insignificant.

Seawater analysis using ICP-AES has been achieved with the use of a resin for analyte preconcentration and separation from the saline matrix.[34] A computer-controlled flow injection-ICP system was described by Giné et al.[35] for the analysis of Ca, Mg, Al, Fe, P, and Si in water samples with a saline matrix up to 2.5% (w/v) NaCl. The sampling zone approach is used to level the sample and standard saline contents in order to compensate for matrix effects. Sample and standard salinity matching is done automatically by processing the sample Na signal from ICP with a microcomputer and adding a suitable amount of Na. Sodium standards (standard addition method) containing 800, 3500, and 10,000 mg l^{-1} were used for the analysis of water samples whose salinity varied from 100 to 10,000 mg Na l^{-1}. Accuracy of the automatic procedure was determined by comparing the generated Na solutions with ten manually prepared Na standards covering the same concentration range. After receiving a suitable amount of Na, the sample reaches the ICP and the elements are determined. The proposed method is suitable for 60 samples per hour.

III. TRACE ELEMENTS

Several elements that have high ecotoxicological significance are present in natural waters at trace levels.

Because of the low concentrations of heavy metals in seawater, sample preconcentration is almost always required. Matrix exchange is often required to avoid interferences from the sample matrix. Because the resulting sample work-up is elaborate and time consuming, efforts to develop mechanized systems have been implemented. When developing such a system, four major factors must be considered: avoidance of sample contamination, necessary preconcentration, degree of matrix separation, and sample throughput. Chelating exchangers are most commonly used in FIA-AAS because of their great selectivity toward some transition metal ions. Fang et al.[36] carried out a careful comparative study of the properties of three exchangers [Chelex-100, immobilized 8-quinolinol (8-Q), and Resin 122] and indicated that concentration efficiency varied considerably between elements as a function of the selected exchanger.

A. Arsenic

Flow injection HG-AAS is a simple, rapid, and precise method for the determination of metals. Sampling rates and detection limits of this system can be increased using a gas-liquid separator with a porous membrane. An application of this analytical technique was the determination of total inorganic As in seawater using a membrane tube gas-liquid separator.[37] Calibration curves were prepared by the addition of appropriate amounts of NaCl to adjust the ionic strength of standard solutions to that of seawater, and potassium iodide and hydrochloric acid must be added to each seawater sample prior to the measurement. Metal ions generally interfere with hydride generation. Therefore, if the hydride is rapidly separated from the solution in order to shorten the interaction period with such metals or metal borides, interferences will be minimized. A detection limit of 0.070 ng As and a throughput of 150 samples per hour were achieved using an 8 mm I.D. membrane tube.

In other work, Lu et al.[38] described an online cold trap hydride collection flow injection system for the determination of As and Sb in seawater. The system consists of a hydride generator, a nebulizer for gas-liquid separation, and a liquid nitrogen bath hydride collector. Hydrides are generated by reacting samples with sodium borohydride followed by flameless AAS determination, at 193.7 nm for As and 217.6 nm for Sb. Detection limits of 0.15 and 0.24 ng l^{-1}, respectively, were reported.

B. Boron

Boron is one of the parameters of interest in monitoring water quality. Diverse analytical procedures for the determination of B in water have been developed. Several spectrophotometric methods based on the formation of ion-association compounds were described, but a prior separation step is needed.

An FIA method based on the formation of a blue ternary complex between the anionic complex of boric acid with 2,6-dihydroxybenzoic acid and crystal violet was proposed by López-García et al.[39] The calibration graph is linear over a B concentration range of 0.02 to 0.50 $\mu g\ ml^{-1}$; the sample throughput is 70 samples per hour. Alternatively, a simple manifold based on reversed FIA (rFIA) can be used. The resultant calibration plot is linear between 0.05 and 0.50 $\mu g\ ml^{-1}$ (sampling frequency 50 samples per hour). Ions normally present in natural and seawater samples do not interfere with B determinations. With adequate sample size and reasonable B concentrations, rFIA is recommended.

An automated method for the determination of B in water samples is described by Sekerka and Lechner.[40] This method involves flow injection with on-line ion exchange preconcentration,

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and spectrophotometric detection of the azomethine-H-B complex. The method is applicable to various water samples, including seawater, and is relatively free from interferences. Detection limits of 5 μg l^{-1} at 20 samples per hour and 1 μg l^{-1} at 10 samples per hour (rsd <10%) were achieved. The method compared favorably with ICP-AES.

C. Chromium

Chromium in natural waters is present as Cr(VI) and Cr(III). The former is far more toxic than the latter. Total Cr dissolved in natural water samples is below 1 μg l^{-1}. The determination of Cr in natural waters is dependent on the preconcentration method used, changes in the oxidation state, and in losses of Cr that occur during sample storage. Therefore, a simple and rapid direct analytical method that is selective to one particular chemical species is desirable. Speciation of metals present in mixed oxidation states via the use of sequential spectrophotometric and AAS dectectors in a flow injection system was proposed by Lynch et al.[41] The method was applied to the determination of Cr(VI) and total Cr in corrosion test seawater. Chromium(VI) is measured spectrophotometrically, and the total Cr concentration is determined by AAS. The working ranges are 1 to 50 ppm of total Cr and 0.1 to 20.0 ppm of Cr(VI), with a sampling throughput of up to 120 samples per hour. The photometric determination of Cr(VI) in natural waters as 1,5-diphenylcarbazide (DCP) is well established as a standard method.[42] Yoshimura[43] applied ion-exchange phase absorptiometry with DCP as a coloring agent to the direct determination of Cr(VI) in seawater using flow analysis. Chromium(VI) detection limits as low as 0.5 ng were reported. Cations such as Ca and background electrolytes present in natural waters at high concentrations caused a change in the background attenuation. Consequently, for seawater, it is necessary to use a calibration graph prepared at similar concentrations to those in the sample solution. Without preconcentration, the proposed method is directly applicable to the analysis of samples containing Cr(VI) at <1 μg l^{-1}.

The determination of Cr(III) by flow injection AAS was reported by Shah and Devi[44] using a poly(hydroxamic acid) resin for on-line preconcentration. In this work, conditions were optimized for the enrichment of the microcolumn as well as for the chromatographic separation of Cr from binary and quaternary mixtures. By direct injection of Cr (without microcolumn) for 50 μg ml^{-1} solutions, the detection limit obtained was 0.1 μg ml^{-1} and the rsd was 1.3%. When a 4-cm long column was used, the calibration plot obtained for the preconcentration of 10 μl of 20 to 100 ng ml^{-1} Cr solutions was linear ($r = 0.994$). The method thus shows a good potential for shipboard determination of Cr(III).

D. Cobalt

Little is known of Co oceanic distribution since its very low concentrations make its determination difficult. Laboratory studies indicate that Co exists in seawater primarily as Co(II) ion and as the carbonate complex. Previous analyses of the total Co concentration in seawater have used preconcentration by solvent extraction or Chelex-100 ion exchange followed by FAAS.[45]

Sakamoto-Arnold and Johnson[46] reported an FIA method with chemiluminescence (CL) detection for the determination of picomolar levels of Co in seawater by using gallic acid/hydrogen peroxide after an in-line preconcentration/separation step in the FIA manifold to remove alkaline earth ions. Measurements that were made at sea and compared to samples analyzed by preconcentration-FAAS are also reported. The shipboard determination of Co using FIA-CL was simple and relatively fast (≈8 samples per hour).

The same column (silica-immobilized 8-Q) was used by Yamane et al.[47] for Co preconcentration in seawater. A simple and sensitive catalytic determination of Co based on the oxidation of protocatechuic acid by hydrogen peroxide in alkaline medium is used. The preconcentration/separation steps permit the attainment of better limits of detection (0.0050 ng ml^{-1}) and a greater selectivity than via direct application of the catalytic determination.

More recent methodologies based on stripping voltammetry have also been proposed for Co determination in seawater,[48] but their appli-

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cations to flow injection techniques have not yet been reported.

E. Copper

Different methods have been applied for the determination of traces of Cu in seawater using FIA. Silica-immobilized 8-Q proved to be a particularly useful material for sample preparation, matrix isolation, and preconcentration of trace metal ions. The capabilities of this material for on-line preconcentration of Cu(II) in waters using an FIA-AAS instrumental system were evaluated by Marshall and Mottola.[49] This procedure has a detection limit of 0.0015 $\mu g\ ml^{-1}$ and permits 15 samples per hour. Smaller sample sizes and high analytical throughput (200 samples per hour) can be achieved using FIA-AAS without a preconcentration step, but sensitivity and detection limits are lower.

The use of CL resulting from the β-nitrostyrene/NaOH/hexadecyltrimethylammonium bromide(CTAB)/fluorescein system for the determination of traces of Cu(II) by a flow injection method was recently reported by Yamada and Suzuki.[50] The system is fairly selective for Cu, and the reagent stream is continuously cycled. Such conditions gave a detection limit of 0.1 ng, with a sample throughput of 200 samples per hour and an rsd = 2.2% for 1 ng of Cu.

Yuan and Qu[51] described a method based on the catalytic effect of Cu(II) on the oxidation of quinol by hydrogen peroxide using spectrophotometric detection. The calibration graph was linear up to 50 $\mu g\ l^{-1}$ of Cu, and the detection limit was 0.7 $\mu g\ l^{-1}$. A potentiometric determination of Cu(II) was also reported by Shpigun et al.[52] using a Tecator FIAstar analyzer linked to a cascade-type Cu^{2+}-ion selective electrode. The sample is preconcentrated on-line using a column packed with Chelex-100. The sample throughput is 40 samples per hour and a coefficient of variation (CV) under 5.3% can be accomplished when determining 0.5 to 250.0 ng ml^{-1} of Cu in seawater.

F. Gold

A variety of techniques for the preconcentration and determination of Au in natural waters were recently reported in the literature, but these do not provide appropriate detection limits for the determination of Au in open ocean waters. Falkner[53] presents an analytical technique for the determination of Au in seawater using an ion-exchange preconcentration and flow injection inductively coupled plasma-mass spectrometry (ICP-MS). The radiotracer ^{195}Au was used to monitor the recoveries in the preconcentration step (90 ± 5%). The method has a detection limit of 10 fmol for 4 l of seawater preconcentrated to 1 ml, and a relative precision of ±15% at the 100-fmol level. Although detection limits and the precision offered by ICP-MS (using a VG Plasmaquad ICP-MS) are good, the low levels of Au in seawater make it desirable to seek further improvements. With lower detection limits, less sample is required, which diminishes contamination and practical problems. Falkner and Edmond[54] have achieved a tenfold improvement in detection limits using an electrothermal vaporization (ETV) system coupled to a VG Plasmaquad ICP-MS. At the 1-fmol detection limit, seawater analysis could be carried out on samples <1 l, a volume that can readily be accommodated into routine hydrographic programs.

G. Iron

The marine biogeochemistry of Fe is complicated by its redox speciation, low solubility, and involvement in biological cycles. Many FIA determinations of Fe in natural waters are possible, but the detection limit obtained with these analyses (0.1 μM) is not adequate for measurements in open ocean waters.[55] The reaction of perbromate and iodide proceeds very slowly in alkaline, neutral, or acidic solutions, but in the presence of Fe(II), the oxidation of iodide is accelerated. At high concentrations of iodide, Fe(III) is reduced to Fe(II) and total Fe can be determined. The Fe(II)-induced perbromate-iodide reaction has the advantage of being specific for Fe and was used successfully in the spectrophotometric determination of nanogram per milliliter levels of Fe.

Yerian et al.[56] adapted this Fe determination technique to an FIA system at a level of sensitivity that would allow analysis of seawater samples. Calibration graphs are linear from 10 to 100

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mg ml^{-1} and the average sampling rate is 30 samples per hour. To minimize the refractive index and viscosity differences, a line containing Na nitrate was included in the manifold. Standard addition calibration of Fe(II) in seawater samples in order to increase the Fe concentration by 20 and 40 ng ml^{-1} indicated no significant interference from the 1:1 diluted seawater matrix. Recently, a catalytic method for the determination of ultratrace amounts of Fe(III) (capable of being adapted to FIA) was described by Hirayama and Unohara.[57] The method is based on the catalytic action of Fe(III) on the oxidation of *N*,*N*-dimethyl-*p*-phenylenediamine by hydrogen peroxide in weakly acidic media. The catalyzed reaction was monitored spectrometrically at 514 nm by the fixed time method. The Sandell's sensitivity obtained was 3.3 pg cm^{-2}, about 15,000 times higher than that of the 1,10-phenanthroline method.[58] Most metal ions did not interfere with the determination, even when present at concentrations 500 to 1000 times as much as the amount of Fe (rsd = 2.4% at 0.8 ng ml^{-1}).

Recently, a flow injection determination of Fe(II) and total dissolved Fe in seawater was developed by Elrod et al.[59] using CL detection. The Fe in the sample is concentrated with an 8-Q ion-exchange column in the sample loop. The resultant CL emission is detected from the reaction of brilliant sulfoflavin with hydrogen peroxide and Fe(II). The detection limit was 0.45 nmol l^{-1} when 4.4 ml of sample were passed through the column. An ascorbic acid solution is used to reduce Fe(III) to Fe(II), which allows total dissolved Fe to be determined. This method permits a rapid and relatively inexpensive procedure with excellent detection limits for the shipboard determination of dissolved Fe(II) and Fe(III) in seawater.

H. Lead

Lead is one of the most common environmental pollutants. It is dissipated in the atmosphere and natural waters as a result of the combustion of antiknock fuel additives, the discharge of industrial wastewaters, etc. The need for its reliable determination in environmental samples is well recognized because of its adverse toxic effects. A very interesting FIA/ion-exchange symbiosis permits the assaying for cationic species in seawater at microtrace levels, following a preconcentration period.

Olsen et al.[21] described a method for the determination of Pb in polluted seawater using FIA and FAAS. The system incorporates a Chelex-100 microcolumn for the on-line preconcentration of the sample. The preconcentration and elution step improves the detection limit for Pb by a factor of 4 (50 n*M*). Problems such as nonhomogenization between samples and reagents and time measurement were eliminated by different modifications in the manifold and with an electric timer capable of sequencing pumps for each preconcentration-elution cycle. The use of these systems allows the determination at the 10-ppb level for Pb, and the 1-ppb level for Cd and Zn. The method was applied to seawater samples with a throughput of between 30 and 60 samples per hour.

Three automated flow injection systems using spectrophotometric or potentiometric detection were proposed by Zolotov et al.[60] for the determination of Pb, Cu(II), and Mn(II) in sea- and wastewaters. The determination of Pb in the range of 0.7 to 100.0 μg l^{-1} is based on the spectrophotometric detection of the Pb(IV)/(2-pyridylazo) resorcinol complex at 525 nm after on-line preconcentration of the sample on a minicolumn filled with Chelex-100 or Dowex 1-X8 resin. When a potassium cyanide solution was used as a masking agent, the interferences caused by other metals were largely eliminated.

A potentiometric flow injection system with a Cu ion-selective electrode (ISE) is applied for the determination of 0.5 to 1000 μg l^{-1} Cu(II) after on-line preconcentration of 50 to 500 ml of sample on a Chelex-100 resin. When this FIA/Cu-ISE system is applied to seawater, the rsd obtained analysis is <5.2%. The last system utilizes the catalytic effect of Mn(II) on the oxidation of *N*,*N*-diethylaniline by potassium periodate at 30°C and is used for the spectrophotometric determination at 475 nm in the range of 0.02 to 1.00 μg l^{-1}; the system involves reagent injection and stopped flow, and Fe(III) interference was eliminated by using phosphate or citrate/phosphate buffer (pH 6.86 to 7.10).[60]

The combination of a preconcentration step with a detection system, such as anodic stripping voltammetry (ASV), may make it possible to determine trace metals in seawater on a routine basis. An essential requirement for ASV is oxygen removal down to very low levels. For ASV flow analysis, purging of solutions prior to their introduction into the flow system is not a good approach because oxygen diffuses back into the flow system, adversely affecting detection limits. Tay et al.[61] developed a simple and effective method of oxygen removal for a FI-ASV system, based on a novel flow-cell design with nitrogen purging. The method involves deposition of Hg and metals in the presence of oxygen, followed by medium exchange with nitrogen purging prior to the stripping analysis. Advantages of this simple method are demonstrated by the determination of Cu, Pb, and Cd in seawater samples. Detection limits for the metals were between 10^{-9} and 10^{-10} M for a deposition time of 3 min. The remaining features of the procedure are given in Table 1.

Finally, Novikov et al.[62] describe two automatic flow injection systems for the determination of low concentrations of Pb. The method is based on the extraction of Pb with the crown ether dicyclohexyl-18-crown-6 into chloroform from an acidic medium, subsequent addition of dithizone as chromogenic reagent to the extract, and measurement of the absorbance. Using this system, Pb can be determined in the range of 50 to 2000 μg l^{-1}. Throughput is 45 samples per hour with a detection limit of 25 μg l^{-1}. In order to improve detection limits, a minicolumn containing Chelex-100 resin was introduced into the system for on-line preconcentration of Pb. With a preconcentration time of 79 s, a detection limit of 5 μg l^{-1} is achieved with an overall sampling rate of 36 samples per hour. An important advantage of this system is that the nitric acid eluent also serves as a medium for the liquid-liquid extraction, making the combination of ion-exchange minicolumn preconcentration with subsequent extraction very simple.

I. Manganese

Manganese in seawater is an indicator of submarine geothermal activity, and several colorimetric methods were reported in the literature for its determination. The leuko-malachite green method of Strickland and Parson[63] was automated using the Technicon AutoAnalyzer II by Olafsson.[12] Reaction conditions were modified and optimized. Variations in reaction conditions, namely, pH, temperature, and time, were also studied using this segmented continuous flow system. The method has a high precision (rsd = 1.3% at 0.9 μg l^{-1}), similar to what can be achieved by preconcentration and AAS procedures. A test for possible interferences from transition metals Zn, Cu, Cd, Ni, and Cr did not show interferences at the oceanic concentrations of these metals. However, Fe produces negative interferences at the concentrations found in estuaries, and the method is not suitable for such samples.

Kinetic determination of Mn(II) in seawater (0.02 to 10 ng ml^{-1}) using a Tecator FIAstar automated instrument was reported by Kolotyrkina et al.[64] The method is based on the catalytic effect of Mn on the oxidation of *N,N*-diethylaniline by potassium iodate. Using a stopped flow technique, a 25 samples per hour throughput was achieved.

J. Molybdenum

Molybdenum is a biologically essential trace element having an important role in biochemical and geochemical cycles in the oceans. Several kinetic methods for the determination of Mo based on the Mo-catalyzed oxidation of iodide by hydrogen peroxide in acidic medium to form the triiodide ion have been developed since the original proposal by Yatsimirskii and Afanas'eva;[65] however, manual procedures are tedious and difficult to control. Automation was attempted using a Technicon AutoAnalyzer.[66] Nevertheless, due to an excessive carryover in the system, the sampling rate was limited to 10 samples per hour. Using the AutoAnalyzer, Bradfield and Stickland[67] increased the sampling rate to 40 samples per hour, but the precision was inferior. By means of the FIA technique, Mo can be determined in natural waters (rivers, sea-, and domestic waters), without preconcentration, at a sampling rate of 90 samples per hour.[68] A detection limit of 0.7 μg l^{-1} and rsd values <1%

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were achieved. The procedure has good tolerance for species close to Mo, such as V and W (4- or 2-fold-tolerated amounts, respectively), 20-fold levels of Fe(II), and even higher for alkaline earth elements and common anions.

Progress in adsorptive stripping analysis has increased the number of elements that can be determined by electrochemical stripping techniques.[69] Hua et al.[70] proposed a fully automated procedure for the determination of Mo in seawater by means of constant-current reduction of the adsorbed 8-Q complex in a computerized flow potentiometric stripping analyzer. As very few easily reducible elements are capable of forming complexes with 8-Q at pK values below 3, interference problems (Cu^{2+}, Cd^{2+}, Pb^{2+}) were largely solved. Because the concentration of Mo in seawater was 10 $\mu g\ l^{-1}$, it was concluded that a linear response is achievable if the product of deposition time and Mo concentration is <400 s $\mu g\ l^{-1}$.

Recently, Yoshimura et al.[71] developed a method of ion-exchange absorptiometry combined with FIA using Tiron as a color reagent for the determination of trace amounts of Mo in natural waters. The minimum detectable amount of Mo was 15 ng; Mo in three or four seawater samples could be analyzed within 1 h.

Finally, the acidic form of alumina was used to preconcentrate Mo on-line from seawater samples prior to its determination by ICP-AES.[72] Improvement by 50-fold in detection limits was obtained when a 10-min preconcentration was used. The absorbed molybdate was eluted by the injection of 250 μl of a 2-*M* ammonia solution.

K. Selenium and Bismuth

On-line ion-exchange preconcentration was combined with flow injection HG-AAS to produce an efficient system for ultratrace analyses of hydride-forming elements.[73] Selenium and Bi were preconcentrated on a strongly basic D-201 anion exchanger and a controlled porous glass-8Q (CPG-8Q) chelating ion exchanger, respectively, by time-based sample loading, and eluted by 1 *M* hydrochloric acid directly into the HG-AAS system. Detection limits were 0.002 $\mu g\ l^{-1}$ for Se and 0.001 $\mu g\ l^{-1}$ for Bi on the basis of enrichment factors of 15 and 30, respectively, at sampling frequencies of 50 samples per hour. Precision was 1.0% rsd for Se and 1.1% for Bi at the 0.5 $\mu g\ l^{-1}$ level. Recoveries for the analytes in waters (tap, snow, sea, mineral) were in the range of 90 to 108%. Interference studies on possible interferents in the ion-exchange process and in the hydride generation reaction showed wide tolerance for concomitant ions. Interferences in the analysis of aqueous samples of environmental origin are not likely except in polluted waters having large amounts of heavy metals. The most serious potential interferent for both analytes seems to be Cu(II), which at 0.5 mg l^{-1} has shown a 50% signal depression for Se, and at 1.0 mg l^{-1} a 46% signal depression for Bi. The interference was minimized by adding 0.5% thiourea to the hydrochloric acid eluent.

L. Multielement

A flow injection system with on-line ion-exchange preconcentration on dual columns was described by Fang et al.[36] for the determination of trace amounts of heavy metals by FAAS. The degree of preconcentration ranges from 50- to 105-fold for different elements at a sampling frequency of 60 samples per hour. The detection limits for Cu, Zn, Pb, and Cd are 0.07, 0.03, 0.50, and 0.05 $\mu g\ l^{-1}$, respectively. Three types of exchangers, Chelex-100, 8-Q, and 122 resin, were compared with respect to their concentration efficiency, separation reproducibility, and freedom from interferences. For samples with high concentrations of alkaline earth metals, such as seawater, Chelex-100 resin gave the best performance. Finally, a comparison of some features of this method with graphite furnace-AAS (GF-AAS) indicated that sample throughput and precision are higher and spectral interferences lower for the FIA-AAS system.

A similar system was used by Fang et al.[74] for the determination of Ni, Cu, Pb, and Cd using a miniature column packed with 122 chelating resin with a salicylic acid functional group for preconcentration. A multifunctional rotary sampling valve, which incorporated two parallel sampling columns, allowed for sequential sampling exchange, elution, and AAS. A 20- to 28-fold

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increase in sensitivity compared to direct aspiration of the samples was obtained for these metals at a sampling rate of 40 samples per hour. Recoveries for Cd in seawater were unsatisfactory in both methods.[37,74]

Beauchemin and Berman[75] described a preliminary implementation of an on-line preconcentration technique in ICP-MS, using a miniature column packed with I-8-HOQ. This methodology improved the detection limits of several elements by a factor of 2 to 7 compared to ICP-MS alone. The system was successfully applied to the determination of Mn, Mo, Cd, and U in the reference open ocean waters NASS-2 standard, using an isotope dilution technique and the standard addition method.

More recently, a continuous flow two-step extraction system for the determination of heavy metals was reported by Bäckström and Danielsson.[76] In the first extraction step, the metals are extracted as dithiocarbamates into Freon 113, and in the second step they are stripped into a dilute aqueous Hg(II) solution. Heavy metals in aqueous samples are concentrated 50- to 100-fold and separated from the matrix using membrane-type phase separators. A new segmenter (falling drop segmenter) suitable for use in extractive sample concentration from an aqueous to an organic phase was designed in order to control the segment formation. An interface between the continuous flow of aqueous extract and a GF-AAS system has now made it possible to mechanize the system, starting with the aqueous sample and ending with the determination of heavy metals by GF-AAS. Sample throughput is 30 samples per hour, giving a sample carryover of 1.2% when concentrating the samples 50-fold. Extraction yields are in the range of 80 to 107% for Cd, Co, Cu, Fe, Ni, and Pb with detection limits <10 ng l^{-1}. The system was validated further by the determination of trace metals in a reference seawater sample.[77] The results obtained were in good agreement with values certified for Co, Cu, Ni, and Pb, but they were slightly high for Cd and Fe.

The potential of cathodic stripping chronopotentiometry for the determination of Ni, Co, Cu, and U in the presence of dissolved O was investigated by Newton and Van den Berg,[78] using an automated continuous-flow analyzer with fast data acquisition. Adsorptive collection of surface-active metal complexes on the hanging Hg drop electrode was followed by cathodic scans in which a constant current was passed through the working electrode. The detection limits were 0.1 n*M* Ni, 0.1 n*M* Co, 1.8 n*M* Cu, and 1.6 n*M* U. In the presence of dissolved oxygen, the detection limit for Ni was higher at 0.6 n*M*, and Co could not be determined because its peak was superimposed with the oxygen peak. Observed detection limits for stripping chronopotentiometry in the presence of dissolved oxygen are similar to those of fast linear-sweep voltammetry in the absence of dissolved oxygen.

IV. CONCLUSIONS

FIA has great potential as an ideal tool for the handling and pretreatment of seawater samples prior to their analysis. Sample handling may be as simple as the use of FIA for the introduction of the sample into a detector, or as complicated as the extraction of an analyte followed by back extraction prior to reaction and detection. By employing FIA methods, sample throughput can be significantly increased and, in many cases, the overall precision, compared with batch style sampling, pretreatment, and analysis schemes can also be improved. A considerable expansion has taken place in the use of flow injection techniques in combination with AS. The further combination of FIA with systems for hydride generation and cold-vapor AAS determination results in methods with ultrahigh detection limits. Simultaneous multielement analyses of trace elements are well suited to FIA-ICP. All of these methods could also be used to improve the determination of the chemical speciation of trace constituents in environmental samples.

The biggest areas of growth have taken place in the use of on-line preconcentration and matrix removal. At present, the most widely used methods of preconcentration for the determination of trace elements in seawater are retention of chelating resins and ion exchange, but the potential of the technique is far from being fully explored.

Combinations of different on-line separation techniques in series are feasible and further extend the scope of FIA methods. Miniaturization and integration of certain components of on-line separation manifolds could result in very compact and easily operated systems.

FIA provides a simple means for complete automation; the efficiency of this instrumentation currently permits analyses at a very moderate cost. The technique also offers an array of on-line methods that effectively modify difficult samples and their matrices. However, kinetic aspects, as well as the efficiency of ion-exchange columns (usually used on-line for the elimination of matrix components and detection limit enhancements) require further study.

The authors expect that new trends in FIA-AS research and instrumentation development will stimulate the use of this new approach for oceanographic research, particularly for routine analyses and speciation measurements.

ACKNOWLEDGMENTS

The authors express their gratitude for financial support to the National Science & Technology Commission (Spanish Project ALI 63390).

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