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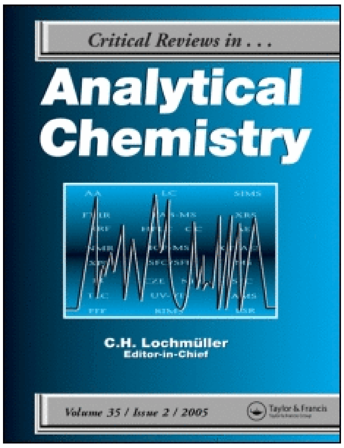

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J. Atienza[a]; M. A. Herrero[a]; A. Maquieira[a]; R. Puchades[a]
[a] Department of Chemistry, Polytechnic University of Valencia, Valencia, Spain

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Flow Injection Analysis of Seawater: Anionic and Organic Species

J. Atienza, M. A. Herrero, A. Maquieira, and R. Puchades
Department of Chemistry, Polytechnic University of Valencia, Camino de Vera, 14,
460 22-Valencia, Spain

ABSTRACT: Methodology for the analysis of compounds in seawater has developed rapidly during recent years, together with a markedly increased interest in chemical data to characterize the marine environment. Flow injection analysis (FIA) can play a significant role in laboratory automation for many traditional wet chemical methods, and can serve as the basis for new methods which have no conventional analog. The FIA technique permits the analysis of a great number of samples, rapidly and reliably. This review discusses the present status and potential applications of FIA in the determination of anions and organic species in seawater analysis.

KEY WORDS: seawater, flow injection analysis, anions, organic species.

I. INTRODUCTION

Land-derived pollution in coastal regions, semienclosed seas, and the open ocean is an area in which chemical analysis plays a fundamental role, and in which the number of analyses has increased considerably during the last 10 to 15 years.

Much of the analytical work must be performed immediately after the samples have been taken.[1] This is due not only to the fact that a prolonged storage time can change the composition of the sample, but also because in many instances the analysis results provide guidance for further sampling and for subsequent investigations.

Many of these problems can be alleviated by the application of automated methods to the analysis of seawater samples. The benefits of automating analyses of seawater samples have been recognized and utilized for several decades. Automatic analyzers allow samples to be processed rapidly and efficiently, and generally with better precision and accuracy than is attainable with most manual methods.[2]

Automated analysis has included nondestructive optic methods which have been used for the detection of oil byproducts in the open oceans to estimate the degree of oil pollution. These systems operate from airplanes and are controlled by computer. An economical technique developed for the automated analysis of seawater nutrients has been segmented continuous flow analysis (SFA), applications of which were summarized previously by Whitledge et al.[3] More recently, commercial instruments have also been developed and employed for this purpose.[4-6] However, since its first report in the mid-1970s, flow injection analysis (FIA) has, to a great extent, replaced many air-segmented continuous-flow methods for the determination of a variety of analytes in environmental samples.[7]

Nonsegmented continuous-flow analysis, developed by Ruzicka and Hansen, is similar to segmented systems in many ways. Small quantities of sample are transported through a narrow-bore tube via a peristaltic pump. Along the way, the sample is mixed with reagents to yield a reaction product which is monitored by means of a flow-through detector.[8]

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There are, however, some significant differences. In FIA, bubbles are not used to separate the samples. Instead, the samples are injected into a continuously flowing nonsegmented carrier by an injection valve. Sample integrity is maintained by performing sample injections at sufficiently long intervals to allow for adequate washing between samples. Due to the high level of reproducibility (associated with the elimination of air bubbles, the injection of a reproducible sample volume, and the maintenance of constant liquid flow-rates), an exact timing of the analytical reaction from injection to detection is possible. The absence of air bubbles in a flow-injection apparatus permits the analysis to be carried out at the high pressures of the deep sea[9] (>1000 bar), and avoids the difficulties associated with the use of devices such as reducing columns.

The potential uses of FIA systems for the determination of several analytes in water laboratories are illustrated by the work of Lázaro et al.[10] and van Staden,[11] although its application to the determination of some analytes in seawater has not yet been accomplished. Anderson[12] was the first to report on the use of FIA for the analysis of seawater micronutrients.

Flow injection techniques offer many advantages for the analysis of constituents of seawater, especially for shipboard use and continuous monitoring,[13] and recent commercial instruments for this purpose have become available.[14,15]

A summary and discussion of FIA applications for the determination of anions and organic species in seawater samples follows.

II. ANIONIC SPECIES

A number of methods have been adapted to FIA for the determination of anionic species in seawater. Examples and different features of these methods are presented in Table 1.

A. Nitrates and Nitrites

Nitrogen is an essential element for life, but nitrogen as nitrite or nitrate can be potentially hazardous to health at high concentrations because they can be transformed into other products, some of which (e.g., nitrosamines) can be toxic or carcinogenic.

Nitrites and nitrates have successfully been determined employing FIA and modifications of the Shinn reaction.[16] In the determination of nitrates, the nitrate is first reduced to nitrite with copperized cadmium. In the Shinn reaction, the nitrite ion is diazotized with sulfanilamide, and the resultant product coupled with *N*-(1-naphthyl)ethylenediammonium dichloride to form a highly colored azo dye which is measured at 520 nm. The Shinn modification for nitrites gives excellent results when used with FIA. Anderson[12] adapted this reaction to the simultaneous determination of nitrates and nitrites in sea-, tap-, and wastewater using a manifold with two sub-plugs. Nitrate is reduced to nitrite by a copperized cadmium column placed along one of the channels; both nitrite and nitrate are determined in this channel, whereas only nitrite is analyzed in the other one as an azo dye. The method is highly sensitive, precise, relatively free from interferences, and demonstrates the potential of FIA for marine research. In the analysis of seawater, the only significant interference arises from the turbidity caused by particles in the sample. A previous filtration of the sample is therefore necessary. However, the sampling rate obtained is rather low (30 samples per hour) and two detectors are necessary.

Giné et al.[17] combined the merging zone principle with the Shinn reaction for the simultaneous determination of nitrate and nitrite by using a special injector-commutator operating in two positions. In one position, the sample is carried out through a copper-cadmium reductor column and the azo-dye signal corresponds to nitrate plus nitrite; in the other position, the sample is injected again but the column is bypassed, and the signal only corresponds to nitrite. A single detector is used in this configuration, and the sampling rate can be increased to 90 samples per hour.

By using reverse-flow injection analysis (rFIA), Johnson and Petty[18] simultaneously determined nitrate and nitrite in seawater. The determination was carried out using a cadmium-reducing column and a light-emitting diode (LED) detector. The rFIA method allows for about 75 determinations per hour, a rate 2.5 times greater than that obtained by Anderson using FIA. The

TABLE 1
Features of FIA Determinations of Anions in Seawater

Species	Detection	Reaction	V_i	d.l.	rsd (%)	Linear range	Sampling frequency (h^{-1})	Instrumental innovations	Other features	Ref.
Nitrates Nitrites	Phot	DF	200 μl	0.1 μ*M* 0.05 μ*M*	1	1–25 μ*M*	30	Reducing column	SD Multi-detection Sample splitting	12
Nitrates Nitrites	Phot	DF	75 μl 15 μl		1.5 0.5	1–5 μg/ml 0.1–0.5 μg/ml	90	Reducing column Injector-commutator	SD Merging zones	17
Nitrates Nitrites	Phot	DF	20 μl	0.01 μ*M*	1	6.2–2480 mg/l 4.6–1840 mg/l	75	Reducing column	rFIA SD	18
Nitrates	Fluor	DF		10^{-9} *M*	0.4	0–3 10^{-7} *M* 0–5 10^{-5} *M*	45			19
Nitrates	Fluor	DF	160 μl	10^{-8} *M*	0.8	>2 10^{-4} *M*	30	Reducing column		20
Nitrites	Phot	DF			1–2	0–4 μ*M*			Kinetic	23
Sulfates	Turb	P	200 μl				40–160 μg/ml	Self-cleaning	pH gradient' Single line	24
Sulfates	Phot	CF	200 μl	Few mg/l			15–20		Ion-exchange column	26
	Turb	P	200 μl	0.45 ppm		1–100 mg/l				26
Sulfide	Phot	DF		1.2 μ*M* 0.12 μ*M*	<1					27
Silicate Sulfide	Phot	CF.RO CF		0.1 μ*M*	1	800 μ*M* 300 μ*M*		Submersible SCANNER Det. *in situ*	Continuous sample introduction SD silicate and sulfide	9
Phosphate	Phot	CF.RO	20 μl	0.05 μ*M*	1.5	10^{-8}–4. 10^{-6} *M*	90		rFIA	31
Phosphate	*Fluor*	CF	*160 μl*			*<45 ppm P*	20		Fluorescence quenching Rodamine G	32
Phosphate	Phot	Ion pair	7 ml	0.02 μg/l			20	Gel-packed detector	Solid-phase absorptio-*metry*	33
Phosphorus	Phot	Ion pair	0.15–15 ml	2 ng/l	0.3 6	0–500 ng/ml 10–50 ng/ml	15	On-line digestion		34
DOP DRP	Phot	CF	100 μl 600 μl	0.01 mg/l	0.96	0.1–4 mg/l <6.1 mg/l	72 50	Photochemical digestion		35
Silicate	Phot	CF			0.5	0.02–1.00 μg/ml	40			37
Silicate	Phot	RO DF	20 μl	0.5 μ*M* 0.1 μ*M*	>0.6 >0.1	1–5mg/l	80 50		rFIA Continous-stream sample	28
Silicate	Phot	RO			0.25	30–60 μg/l SiO_2	120		Synthetic water	38
Chloride	Phot	CF	0.1–1.0 ml		<1.5	0.2–15.0 m*M*	300		Single-line carrier stream Splitting of the sample	39
Chloride			30 μl			5–75 ppm	120			40
Hypochlo-ride	Phot	RO (D) CF.RO	60 μl	1.4 0.8		3.2–37.3 μg/ml 0.2–18.1 μg/ml	160 288		Single-line carrier stream SD of ClO^- and NH_4^+	42
Iodide	CL		300 μl	0.1 ng	2	0.25 μg/ml 0.0005–0.25 μg/l	600			43
Bromide	Phot		200 μl	90 μ/l	>1		120			46
Bromide	Phot	Phenol red		2 μ*M*			80	Two-channel valve		47
Bromide Iodide	Phot	RO		15 n*M*		1–15 n*M*	60		Ion-exchange column	48
Bromide	Phot	C, RO		10 μg/l	1.4	10–600 μg/l	45		Catalytic	49

TABLE 1 (continued)
Features of FIA Determinations of Anions in Seawater

Species	Detection	Reaction	V_i	d.l.	rsd (%)	Linear range	Sampling frequency (h^{-1})	Instrumental innovations	Other features	Ref.
H_2O_2	Phot		840 µl	12 n*M*				New injection device Automatic control of the volume	rFIA	52
Alkalinity	Pot	NCR			>1		>30	Capillary glass electrode	0.3-ml mixing chamber	62
pH	Phot	DF				1.5–2.0 pH units		Immobilized reagent	Fiber-optic pH sensor	63
COD	Amp	RO	40 µl		1.4		20	PTFE reaction tube		65
Dissolved oxygen	Amp	RO	40 µl	5 µg/l		<30 mg/l		PTFE reaction tube	Standard addition method	65

Note: Phot, photometry; Fluor, fluorimetry; Turb, turbidimetry; Amp, Amperometry; DF, dyeformation; P, precipitation; CF, complex formation; RO, redox; NCR, nonchemical reaction; SD, simultaneous determination; CL, Chemiluminescence.

sample inlet of the FIA apparatus was connected directly to the seawater effluent from the pump, with no filtration at any point.

A more sensitive and precise FIA method for nitrite determination was reported by Motomizu et al.[19] The replacement of *N*-(1-naphthyl) ethylenediamine (NED) by a noncarcinogenic product, α-naphthylamine 7-sulfonic acid, results in an azoic acid derivative which forms a fluorescent salt in alkaline medium. By increasing the sensitivity of the fluorimeter, the detection limit could be lowered to 1×10^{-9} *M*. The effect of several ions and compounds were examined. Only NaCl concentrations over 0.2 *M* lowered the reproducibility. For this reason, seawater was diluted to the same volume with distilled water. This procedure was used by Motomizu et al.[20] for the determination of nitrate after its reduction to nitrite in a copperized cadmium column. The results obtained by this method were found to be in good agreement with those obtained using ion chromatography (IC).

Burke et al.[21] compared IC, SFA, and FIA for the determination of nitrate, and determined key methodological characteristics of each method (precision, accuracy, detection limit, and analysis rate). They concluded that the analytical characteristics of the colorimetric methods (SFA and FIA) were similar to those of the chromatographic method (IC), but that the former has a higher analysis rate.

Colorimetric determinations of nitrate were also accomplished using a *submersible* chemical analyzer.[22] The relative standard deviation of analysis performed *in situ* at depths to nearly 2000 m was 0.79%, and the nitrate concentrations were found to be in good agreement with data collected using a conventional method. This system can be easily extended to most other colorimetric analyses.

Finally, the kinetics of reaction for the formation of pink azo dye in the determination of nitrites in seawater were studied by Pai et al.,[23] who employed NED and examined the effect of acidity, NED concentration, and temperature on the rate of color development. Using a stopped-flow technique, 90% color development could be attained in 10 to 15 s (conditions: acidity, 67.0 m*M*; 4.2 m*M* sulfanilamide; and 4.29 *M* NED).

B. Sulfates

Several methods have been adapted to FIA for the determination of sulfate in water. Spectrophotometric methods include methylthymol blue (MTB), the dimethylsulfonazo-III-(sulfonazo-III) procedure, and the barium sulfate turbidimetric method.

A modified method for the turbidimetric determination of sulfate was proposed by Baban et al.[24] This work was based on the method described by Krug et al.[25] for the determination of sulfate based on measurements of the turbidity of barium sulfate. A problem with the original method was the formation of a precipitate resulting from the injection of the sample, which caused a low precision and formed a block in the tubing. This problem was overcome by using a solution containing barium with an excess of alkaline EDTA solution as the carrier stream and acidification of the injected sample to pH 1.5. During mixing, precipitation occurred, but the precipitate was redissolved by the action of the carrier. EDTA was also found to be useful for reducing interferences from metal ions. By using pH gradients and alkaline EDTA, a sufficiently stable barium sulfate suspension is obtained, which obviates the use of protective colloids such as a polyvinyl alcohol or thymol gelatin. The precision of this improved method ranges between 1 and 2%. The effects of some interferences were also studied. Only high concentrations of nitrate caused a serious interference. The procedure was applied to the analysis of seawater, and compared well with a gravimetric method.

In other work, Marsden and Tyson[26] designed a manifold for the determination of sulfate in water and high-ionic-strength solutions. For this purpose, two methods were chosen: a spectrophotometric method using the MTB-barium complex and a turbidimetric method employing barium chloride in alkaline EDTA. The same manifold is used in both methods, but in the MTB method, an ion-exchange minicolumn placed within the loop of the injection valve was used to remove potential interferences. In the spectrophotometric method, the decrease in the absorbance of the Ba-MTB complex may be monitored at 608 nm. In alkaline solution, the absorbance of free MTB does not interfere. Preconcentration of sulfate on an alumina column may extend the detection limit to sub-ppm levels. In the last method, the reagent (barium chloride solution) contains a small amount of polyvinyl alcohol as antiflocculating surfactant. The increase in turbidity at 410 nm was monitored. Comparing the two methods investigated, the turbidimetric method seems best suited for the determination of low levels of sulfate in high-ionic-strength media.

C. Sulfide

The determination of sulfide in waters or industrial waste samples by FIA using spectrophotometric or ion-selective electrode detection is widely reported in the literature, but its application to seawater analysis is sparse. The colorimetric determination of hydrogen sulfide in seawater by the methylene blue method was automated by FIA in the work reported by Sakamoto-Arnold et al.[27] Sulfide standards were calibrated by colorimetric measurement of the excess of I_3^- after reacting $S^=$ with iodine. Low- and high-sensitivity flow-injection analysis manifolds for 200 and 75 μM-H_2S gave detection limits of 1.2 and 0.12 μM, respectively.

An instrument based on a modified flow-injection system developed by Johnson et al.[9] can perform *in situ* analysis in the ocean. This submersible chemical analyzer (SCANNER) consists of a multichannel peristaltic pump, solid-state colorimeters, manifold tubing, valves, and an electronic module. The SCANNER has successfully been tested for its use in sulfide and silicate determinations up to depths of 2500 m in the ocean. Sulfide is measured with a methylene blue technique and silicate by a molybdenum blue method adapted to FIA by Sakamoto-Arnold et al.[27] and Thomsen et al.,[28] respectively. The dynamic range of these determinations extends to 300 μM for sulfide and to 800 μM for silicate. Nitrate, nitrite, phosphate, and hydrogen peroxide have also been determined photometrically in seawater with the SCANNER system. This instrument also has sensors for measuring dissolved oxygen, temperature, and pressure.

D. Phosphate

Phosphorus occurs in natural waters in both particulate and dissolved forms, and the dissolved fraction can consist of compounds such as orthophosphates, inositol phosphates, nucleic acids, sugar phosphates, and condensed phosphates.[29] In aquatic systems, phosphorus has been shown to be a limiting nutrient for algal and macrophyte growth, but the bioavailability of the various phosphorus species is still poorly understood.

A variety of flow-injection methods are available for' the determination of phosphate in water. Among them, flow-injection colorimetry is the best known and is most often used.[30]

FIA colorimetric determination of phosphate is based on the complexation of orthophosphate with acidic molybdate. The two most commonly used colorimetric methods available for phosphate determination are yellow-colored vanadomolybdate for relatively high phosphate concentrations and the molybdenum blue procedure for rather low phosphate concentrations. The phosphorus concentration in water is <20 ng/ml; consequently, the detection limit required for analysis is <10 ng/ml of phosphorus. Johnson and Petty[31] described a high-sensitivity rFIA method for the determination of dissolved phosphate in water and seawater using the colorimetric phosphomolybdate reduction method. A discussion of the length of coils, flow rates, and residence time has been reported. Standards for use in seawater should be prepared in artificial seawater or in seawater with a low phosphate content. The authors indicated that the determination of phosphate by rFIA is about five times more sensitive than its determination by FIA, and an analysis rate of 90 samples per hour can be analyzed.

The molybdophosphate formed from phosphate and molybdate in HCl solution decreases the fluorescence of Rhodamine G. This principle was used by Motomizu et al.[32] to determine phosphorus in seawater using FIA.

In another study, the ion associate formed by the reaction of molybdophosphate with malachite green was adsorbed on Sephadex LH-20. Direct *in situ* absorptiometric measurements of this ion associate in the gel phase were carried out after either batch or on-line concentration of the species. Yoshimura et al.[33] developed a simple and sensitive method for measuring trace amounts of phosphate using either batch or flow techniques. In spite of the fact that sensitivity was lower for the flow technique than for the batch procedure, phosphate could still be determined at nanogram per liter levels or lower by flow injection using the described gel-packed detector, and the interference from silicic acid was found to be negligible.

Several methods have been reported for the determination of total phosphorus; however, they typically require a preliminary digestion step outside the flow injection system and consume a great deal of time. A rapid determination of total phosphorus would make it possible to operate the process of dephosphorization at much less cost, by reducing the resultant sludges. The proposed method[34] is based on peroxidisulfate digestion (which can effectively be carried out in a heated capillary tube containing a platinum wire) and subsequent spectrophotometric measurement of phosphate in an acidified solution of ammonium molybdate containing malachite green. Applications to seawaters and industrial wastewaters mixed with seawater are discussed. The authors indicate that platinum is a very effective catalyst for converting various forms of phosphorus into orthophosphate, with a better recovery than the conventional sulfuric acid/nitric acid digestion procedure. A study of the design and performance of the capillary digestor was also reported. The "color fading" of malachite green caused by Cl^- present in seawater was resolved by introducing a reducing agent (sodium thiosulfate) into the system just after the digestor. The values obtained by the official method are compared with those provided by the proposed method.

Ultraviolet (UV) photooxidation can also be used to destroy organic matter, and this has been applied to the determination of dissolved organic phosphorus (DOP). A simple Teflon photoreactor with a low-pressure mercury lamp was used by Mckelvie et al.[35] in an FI manifold to perform in-line UV photooxidation of DOP. This method provided good sensitivity and precision. Four different photoreactors were tested, but the Teflon photoreactor was chosen because it was found to be robust and inexpensive, required no special fabrication, and was suitable for field applications. The results showed a good correlation with those obtained using batch acid persulfate digestion, but the recoveries of the FI method are higher.

E. Silicate

Silicon is an essential and, in some cases, growth-limiting micronutrient for marine organisms that form a siliceous test.[36] It is important to monitor dissolved silicon because of its influence on plankton growth and its use as a trace measure of water mass movement.

The FIA spectrophotometric determination of silicate, similar to the approach used for phosphate, is based on the formation of a yellow molybdosilicic acid complex or its reduced heteropoly-blue complex form. Both methods were used by Yokoyama et al.[37] — the yellow method in the concentration range of 2 to 100 mg/l (SiO_2) at a rate of 60 samples per hour (precision, 1.7%), and the blue method in the concentration range of 0.02 to 1.0 mg/l (SiO_2) at a rate of 40 samples per hour (precision, 0.5%). Ascorbic acid was used as reductor, and oxalic acid was used to remove phosphate interference.

Thomsen et al.[28] developed an rFIA procedure for the determination of silicate in seawater by the molybdenum blue method, using stannous chloride or ascorbic acid as reductor. The reaction kinetics with stannous chloride were found to be much faster than with ascorbic acid. In addition, analysis with stannous chloride was more sensitive, having a detection limit of 0.5 μM compared to 1.0 μM when ascorbic acid is used for 80 determinations per hour. A detection limit of 0.1 μM could be obtained when the sample rate was decreased to 50 per hour. This methodology has been applied using the SCANNER instrument, as described above.[9]

Linares et al.[38] designed a robust FIA procedure for the spectrofluorimetric determination of dissolved silicate in synthetic water samples containing various amounts of common cations and anions, appropriate to several types of waters such as seawaters. Their method was based on the oxidation of thiamine to fluorescent thiochrome by molybdosilicate. The effect of different interferences such as Co (II), Fe (II), Fe (III), and Cu (II) was eliminated by introducing an additional channel containing EDTA to be mixed with the molybdate stream prior to the injection valve. The method is suitable for analysis at a rate of up to 120 samples per hour with a precision of 0.25%.

F. Halides

Although the number of FIA systems for chloride determination in waters is high (using not only spectrophotometric detection, but also electrochemical detection or turbidimetric procedures), application to seawater is very poor.

One of the most frequently used methods for the determination of chloride in water systems is by spectrophotometric measure at 480 nm of the color of an iron (III) thiocyanate complex. The popularity of this method is enhanced by the simplicity of the reaction and the ease of its incorporation into a simple FIA manifold system. The intensity of the red-colored complex is directly proportional to the amount of chloride present.

Ruzicka et al.[39] described a simple single-line manifold for the low-level determination of chloride between 7 and 177 mg/l at a rate of 300 samples per hour using the above-mentioned spectrophotometric procedure. They also extended the concentration range to 532 mg/l by stream splitting, and applied this to seawater samples. A single sample is split, channeled through two different reaction lines with different line lengths and tube inside diameters, rejoined, and transported into a single detector. The splitting of the sample gives expansion of the analytical range without loss of reproducibility.

The same manifold was used by Hansen and Ruzicka[40] for chloride determination in seawater, with a sampling rate of 120 samples per hour in the range of 5 to 75 ppm. The samples were prediluted 500-fold in order to accommodate the analytical readouts. Predilution can be avoided by using an automatic prevalve dilution technique.[41]

Two spectrophotometric methods for the determination of residual chlorine (hypochlorite) in seawater have been reported by van Staden[41] using a simple flow-injection apparatus. The first method was based on decolorization of methyl-orange in a pH 2 buffer solution; the second method was based on the formation of a yellow complex with *O*-tolidine. The proposed methods are straightforward and provide a high sampling rate (>200 samples per hour). The levels below which most of the common cations and anions do not interfere in either method were also reported.

Another procedure was developed[42] for the determination of chlorine in the presence of ammonium ions, using *O*-tolidine and a merged stream of sodium arsenite solution (OTA). The OTA method involves the determination of total chlorine, followed by a separate determination of free chlorine. It involves the application of the standard addition method to each sample.

Iodine can be selectively determined by a chemiluminescent (CL) reaction.[43] The method is based on the emission generated when an iodine solution is injected into a hydrogen peroxide-sodium hypochlorite flow system. The reaction is started by injecting 300 μl of the sample into the mixed-reagent stream. This was the first time that the emission spectrum of iodine has been reported. The emission intensity was recorded as a function of time at 556 nm. The effect of some ions commonly found with iodine was studied. It was observed that 50-fold w/w amounts of Ca^{2+}, Fe^{2+}, Cr^{3+}, Mn^{2+}, Br^-, Cl^-, and CN^- did not have any significant effect on the determination of 100 ng of iodine, whereas Sb^{3+}, $S_2O_3^{2-}$, and NO_2^- suppressed the emission intensity 18, 30, and 37%, respectively. The flow system used provides a simple and rapid manifold means of monitoring the chemiluminescent reaction, and should be applicable to the determination of iodine in seawater with a precision of about 2% at nanogram levels.

Wang and Zheng[44] determined iodine by a redox reaction with Ce(IV) + As(III) and photometric detection. The linear range was 45 to 440 ppb I^-, and the precision (rsd) was 3.8%.

Interest in the determination of bromide has increased in a variety of fields. Bromide may occur in varying amounts in well water and ground water supplies in coastal areas as a result of seawater intrusion. Industrial discharges provide bromide in some freshwater streams. The use of bromide-containing biocides is becoming more and more important. Several methods have been developed for the determination of bromide using air-segmented flow analysis (SFA), but they lacked high detection sensitivity.

Adaptation of the chloramine T-phenol red method[45] for the determination of bromide to an automated flow-injection analyzer was described by Anagnostopoulou and Koupparis.[46] Since the reaction is fast, potential interferences from chloride and bicarbonate are totally eliminated and the other interferences, such as NH_3, are significantly reduced. The proposed automated method was optimized by a simple procedure, and was used to measure bromide in coastal seawater with recoveries as high as 99.9%.

The same FIA method was applied by Anfält and Twengstrom.[47] They used a double-loop injection technique to premix the samples before the reaction step. This feature of the system was convenient for studying interferences and as a means of spiking the samples. The chloride interference, expressed as the ratio of Cl^- to Br^- concentrations (in which the two ions contribute equally to the overall signal), was estimated to be about 3.5×10^4. The chloride content was also determined by flow-injection analysis using the standard method, after appropriate dilution. When the method was applied to water samples taken from the Baltic Sea, the ratio of Cl^- to Br^- was found to be about 600.

Carlsson et al.[48] described a flow-injection system for the determination of bromide using a modified peroxodisulfate method. If the concentration of bromide is very low (<1 μ*M*), an on-line preconcentration step employing an ion-exchange column is used. The sum of bromate and iodate produced in the oxidation was determined by treating the oxidized sample with iodide in hydrochloric acid; the iodate was separately determined by applying the reaction in acetic acid. Chloride concentrations in the range of 0 to 0.1 *M* did not affect the absorbance signal. This method offers advantages in waters containing large amounts of humic substances, but its sensitivity is not sufficient for samples with very low bromide content.

The need for methods capable of determining traces of bromide is increasing. The FIA phenol red method for the determination of bromide has not been sensitive enough to determine bromide in several waters. Kinetic methods adapted to air-segmented flow analysis provide a low limit of detection, but present serious interferences. However, the interferences can be eliminated by shortening the reaction times with a flow-injection system.

Adaptation of the pyrocathecol violet (PV)-hydrogen peroxide method for the determination of bromide to a flow-injection system was proposed by Yonehara et al.[49] An aliquot of the sample solution was injected into the water carrier and mixed with the PV-hydrochloric acid and hydrogen peroxide solution streams at the confluence points. The reaction proceeded in a 10-m-long reaction coil maintained at 37 ± 0.5°C, and the absorbance was recorded at 550 nm. The method is rapid (45 samples per hour), simple, and more reproducible (rsd of 1.4% for 0.105 mg/l Br^-) than the conventional batch method. Furthermore, this method is applicable to the analysis of seawater for traces of bromide in the presence of iodide.

G. Hydrogen Peroxide

Hydrogen peroxide is produced in oceanic and fresh waters by photochemical reactions, which may involve dissolved organic compounds.[50] The concentration of H_2O_2 ranges from less than 5 n*M* in deep seawater to 300 n*M* in surface seawater; however, samples must be analyzed immediately after collection. For this, one needs a sensitive technique capable of rapidly analyzing many samples for H_2O_2 ranging from nanomolar to micromolar concentrations. The development of flow-injection analysis makes it feasible to perform a variety of chemical analysis *in situ*. Several FIA methods based on fluorimetric or spectrophotometric detection have been applied to the determination of H_2O_2 in seawater. For example, nanomolar quantities of hydrogen peroxide can be determined by fluorescence by using horseradish peroxidase to catalyze the reaction of hydrogen peroxide with leucodiacethyldichlorofluorescein.[51]

Flow injection with spectrophotometric detection is well suited for the determination of H_2O_2 concentrations over a fairly broad concentration range, and the robustness of such systems makes them well suited for field operations. However, it can be difficult to determine H_2O_2 concentrations at nanomolar levels with these systems. In particular, refractive index gradients in the sample slug, detector baseline noise, and light scattering caused by particles in the sample make it difficult to measure absorbance changes smaller than 0.001 related to the chromophore. Only a change in detector geometry or a significant rearrangement of the reaction manifold allows for the spectrophotometric determination of very low concentrations of H_2O_2.

A computer-assisted FIA method that permits nanomolar concentrations of H_2O_2 to be quantified by photometric detection has been reported[52] which is a modification of the photometric flow-injection method of Madsen and Kromis.[53] The method, which has a detection limit of 12 n*M* of hydrogen peroxide in seawater, is based on the formation of a colored condensation product of *N*-ethyl-*N*-(sulfopropyl)aniline (ALPS) and 4-aminoantipyrene (AAP). An LED photometer was used to measure changes in light transmission. Errors arising from decomposition of H_2O_2 were minimized by using a submersible pumping system to collect the water, and by interfacing the manifold directly to the pump effluent. A reagent injection manifold is described which allows for automatic control of the volume of reagent to be injected. This system also eliminates problems in photometric detection due to refractive index and from light scattering effects from suspended particles in the sample. Furthermore, this technique can be extended to the determination of other trace species such as phosphate, nitrate, and silicate.

H. Alkalinity

Titration alkalinity is an important parameter related to carbon dioxide chemistry in natural waters. Components of the carbon system can also be determined by FIA. The measurement of pH in the marine environment is important since this parameter is related to biological and chemical processes occurring in the sea, such as the acid-base state of seawater, which is related to the chemical equilibrium of the sea. Another phenomenon depending on the pH of seawater is the exchange of CO_2 between the atmosphere and the ocean,[54] its bioavailability, and the level of primary CO_2 production.

In practice, the pH of seawater primarily depends on the concentrations of CO_2 species. As CO_2 is removed from seawater by photosynthesis and added to seawater by respiration and remineralization, pH measurements provide valuable information on the CO_2 cycle and the greenhouse effect.[55]

The pH in seawater is approximately 8 and is ensured by buffer systems, such as CO_2–HCO_3^-–$CO_3^=$, which is the most important one. Other electrolytes such as borates, silicates, and arsenates also contribute to the pH and its stability.[56]

The rapid, accurate measurement of pH using FIA with a glass electrode has been reported by Ruzicka et al.[57,58] The pH can be measured with a precision of ±0.002 pH units (240 samples per hour). An analysis of total dissolved CO_2, using FIA which might be particularly well suited for pore water samples, has been reported for blood plasma.[59] Acid-base pseudotitrations are also possible in FIA.[58,60] Ramsing et al.[61] developed techniques for a rapid pseudotitration that could be suitable for a moderately precise determination of alkalinity.

More recently, Turner et al.[62] described a flow-injection manifold using a capillary glass electrode as the detector; in this FIA-titration system, an approach is adopted involving the measurement of peak width rather than the more common measurement of peak height. This technique can determine alkalinity in seawater at a rapid rate (>30 samples per hour), but the precision is poorer than that required for detailed studies of the CO_2 system in natural waters. The main limitation of this method is the capillary glass electrode, which is quite noisy. These problems might be overcome by alterations of the FIA manifold, or by the use of an alternative detector method such as spectrophotometry in conjunction with an indicator.[63]

Various fiber-optic pH sensors based on the use of an acid-base colorimetric or fluorescent indicator have been proposed in the last decade. Serra et al.[64] designed an inexpensive fiber-optic pH sensor applicable to marine monitoring. The colorimetric technique was chosen for its compatibility with inexpensive optoelectronic components. The characteristics of this probe, which uses phenol red adsorbed on Amberlite resin as a chemichromatic element on top of an optical fiber, are described and the effects of interfering parameters, such as a variable salinity and temperature of seawater, are assessed. More reproducible results were obtained using a single-fiber probe (working range of up to 5 pH units) than a double-fiber optic probe (working range of about 1.5 to 2 pH units).

Chemical oxygen demand (COD) is an important parameter when determining the degree of pollution in water. The standard official methods are manual and based on the titration of the sample with potassium permanganate or potassium dichromate. There are also a few reliable instrumental methods. A computer-controlled water analysis based on FIA methodology has also been introduced.[15] This robotic analyzer system (SKALAR) is capable of automating such determinations as COD, biological oxygen demand, conductivity, pH, and titration procedures. Automation of dissolved oxygen (Winkler method) using FIA based on iodometry has also been proposed by Novic et al.[65]

III. ORGANIC SPECIES

The analysis of organic pollutants in water is a subject of very large scope that can include a description of many analytical techniques. A large number of papers in this field have been published.[66]

The determination of amines and amino acids in waters has received frequent attention. Chromatographic methods used for such determinations are generally slow and tedious, and the samples must be carefully selected and prepared before being submitted for chromatographic analysis.

Different features of FIA methods for the determination of organic species in seawater are illustrated in Table 2.

The flow-injection technique with a carrier stream of *O*-phthalaldehyde (OPA) reagent and a fluorimeter offers a rapid and precise method for screening large numbers of samples for total primary amines. Petty et al.[67] developed an FIA procedure for the *in situ* determination of total primary amines in seawater, and its advantage over a previous segmented-flow procedure[68] is discussed. Primary amines can be determined with a detection limit of 0.01 μM and a sampling rate of 150 samples per hour. The precision is less than 2% at concentrations higher than 5.10^{-7} *M*. In addition, the simplicity and robustness of the FIA manifold make this technique well suited for shipboard or similar field-type analytical work.

The measurement of dissolved primary amines in seawater by FIA with OPA was also performed by Delmas et al.,[69] with a sampling

TABLE 2
Features of FIA Determinations of Organic Species in Seawater

Species	Detection	Reaction	V_i	d.l.	rsd (%)	Linear range	Sampling frequency (h^{-1})	Instrumental innovations	Other features	Ref.
Total primary amines	Fluor	OPA		1.10^{-8} *M*	>2	$0–10^{-6}$ *M* $0–10^{-5}$ *M*	150			67
Dissolved primary amines	Fluor	OPA		<0.1 muM	<10		100			69
Total organic carbon	CL			0.03 ppm	1.5	0.06–12 ppm			PTFE PMT as detector	70
Dissolved organic carbon	Color	RO			2	0–7 mg/l		Photochem-oxidation	Commercial continuous-flow apparatus	5
Tertiary amines	CL	RO	50 µl		<2	$0–10^{-4}$ *M*			Rodamine B as sensitizer	72
Nonionic surfactant	CL		100 µl	3 mg/l^{-1}	0.9	0–50 mg/l			Kinetic studies	73

Note: Fluor, fluorimetry; CL, chemiluminescence; Color, colorimetry; OPA, O-phtaladehyde; RO, redox; PMT, photomultiplier tube.

frequency exceeding 100 samples per hour. The procedure is very sensitive (<0.1 m*M*) and reproducible (rsd, <10% at 0.2 to 1 n*M*). Good agreement was found between the results obtained with FIA and HPLC methods for most of the samples.

A continuous-flow determination of total organic carbon in seawater using membrane separation and chemiluminescence (CL) detection has been designed in which the inorganic CO_3^{2-} produced from the oxidation of organic species by $S_2O_8^{2-}$ reacts with H_2SO_4, and the CO_2 formed is fed to a double-tube separation unit.[70] The CO_2 permeated through the microporous PTFE membrane and reacted with luminol reagent. The method has a precision of 1.5% for 4.8 ppm of total organic carbon and a detection limit of 0.03 ppm.

A commercial continuous-flow method for the determination of dissolved organic carbon (DOC) in seawater was described by Aminot and Kerouel.[5] The method is a highly improved version of the only existing commercial continuous-flow method proposed by Technicon.[71] The CO_2 resulting from the photochemical oxidation of DOC was measured colorimetrically by phenolphthalein discoloration. Concentrations of up to 10 mg/l could be measured, using a sampling rate of 20 samples per hour.

Tertiary amines are compounds that have useful industrial applications (e.g., as surfactants, corrosion inhibitors, etc.). For environmental quality (e.g., monitoring of residual surfactants in water), a sensitive method is required. Lancaster et al.[72] reported on a completely aqueous CL reaction for triethylamine, using sodium hypochlorite as oxidant and Rhodamine B as a sensitizer, and described an FIA procedure for the determination of triethylamine in water and seawater in the range of 1.10^{-5} to 1.10^{-2} *M*. The reaction is also suitable for the determination of trimethylamine and tripropylamine, but the sensitivity and limit of detection are inferior to those obtained for triethylamine (rsd, <1%). This method is specific for tertiary amines, but a quenching of the CL signal for triethylamine occurs in the presence of a tenfold excess of diethylamine or ethylamine. Finally, a flow-injection procedure for the determination of a commercially available fatty amine ethoxylate-based nonionic surfactant in seawater over the range of 0 to 50 mg/l is described by Lancaster et al.[73] The procedure is based on the same principle as reported above,[72] and a detection limit of 3 ng/l was obtained. The effect of different metallic ions on the CL emission of the surfactants was also investigated.

IV. CONCLUSIONS

Automatic analysis can be vital for many measurement programs, as analytical results may have to be available within a short period of time after sampling, and with a minimum error.

The applicability of FIA in determining the chemical quality of seawater is demonstrated. Among the advantages of this technique over existing methods are high sample throughout, very good precision, the use of relatively inexpensive equipment, and ease of automation. Furthermore, a rapid method of development is possible, and changeover from one type of determination to a different one is simple and quick.

The FIA technique is extremely versatile, and its application to seawater has been described for a wide variety of analytes. This technique also is well suited for oceanographic investigations of small- and mesoscale features in the ocean. Most of the reported methods of analysis are based on the adaptation of an existing "conventional" method to the flow-injection format.

In spite of the fact that chemical parameters such as phenols, hydrocarbons, surfactants, and other pollutants have been determined in natural waters using FIA[74-75] and new detection systems,[76,78] the complete evaluation of seawater has not yet been accomplished. It is noteworthy that the application of FIA to studies of the chemistry of the marine environment is widespread, and that its implementation in routine water laboratories continues to increase.

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