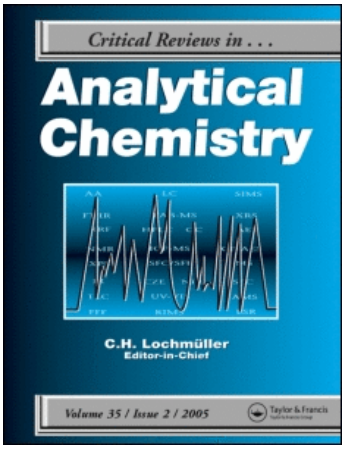

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Flow Injection Methods of Analysis for Waters. I. Inorganic Species

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ABSTRACT: A comprehensive, critical, and an updated review of the applications of flow-injection analysis (FIA) techniques for the analysis of inorganic cations and anions in several types of water samples except marine waters is presented. The preconcentration of metals in water samples and automaton of FIA systems for monitoring water quality are also discussed. The review is documented with 280 references.

Key Words: flow-injection analysis, water analysis, analysis of inorganic cations and anions, preconcentration of metals.

I. INTRODUCTION

The designation of flow-injection analysis (FIA) was proposed in 1975 by Ruzicka and Hansen.[1,2] The inclusion of the term "injection" in the name of this technique is due to the fact that at the beginning of the former technique a syringe was used to inject a sample through a septum into a reagent flow. Nowadays rotation valves are mainly used for this purpose. "Versatile" is the word that best describes flow-injection analysis. FIA may be defined as the sequential insertion of discrete sample solution into an unsegmented continuously flowing stream with subsequent detection of the analyte. The simplest flow analyzer consists of a pump, which is used to propel the carrier stream through a narrow tube, an injection valve, a microreactor in which the sample zone disperses and reacts with the components of the carrier stream, forming a species that is sensed by a flow-through detector and recorded. In the case of the FIA technique the physical equilibrium (flow homogenization) is never reached at the moment of detection. Moreover, it is not necessary for the chemical equilibrium to be obtained at the moment of detection. The concept of FIA depends on a combination of three factors: reproducible sample injection volumes, controllable sample dispersion, and reproducible timing of the injected sample through the flow system. Except for detector warm-up, the system is ready for instant operation as soon as the sample is introduced. To date, FIA offers several advantages in terms of: considerable decrease in sample (normally using 10 to 50 μL) and reagent consumption, high sample throughput (50 to 300 samples per hour) reduced residence times (readout time is about 3 to 40 s), shorter reaction times (3 to 60 s), easy switching from one analysis to another (manifolds are easily assembled and/or exchanged), reproducibility (usually less than 2% RSD), reliability, low carry over, high degree of flexibility, and ease of automation.

Perhaps the major advantage of the FIA technique is the great reproducibility in the results obtained by this technique that can be set up without excessive difficulties and at a very low cost of investment and maintenance. These advantages have led to an extraordinary development of FIA, not comparable to that of any other

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technique. However, although several methods that allow the simultaneous determination of different parameters have been developed, the FIA technique is basically monoparametric. In any case, FIA is one of the most preferred techniques in the determination of a parameter in a set of a large number of samples.

Industrial, clinical, research-oriented, environmental, and biotechnological applications of FIA have been described in over 10,000 papers and numerous books.[1-9] Furthermore, two databases are available on the Internet[10-11] and the topic is discussed at numerous meetings, where "Flow Analysis" is the most recognized international venue.

Sequential injection analysis (SIA) has been proposed by Ruzicka and Marshall.[12] It consists in a conceptually simple technique and was initially proposed as an alternative to FIA. The only bibliographical review on SIA of which we are aware has been published recently.[13] Among the advantages of SIA is the fact that the manifold is more simple and universal than that of FIA. Moreover, the consumption of samples and reagents is much smaller in SIA compared with FIA. SIA presents a series of disadvantages against FIA, the analysis frequency (which is slower) being the most important. Another disadvantage of SIA is the almost compulsory control of the whole system by a computer that imposes the performance of the instruction sequence in a well-defined period of time. However, SIA possesses the great advantage of the capacity to operate in a multiparametric way, which is of special interest when considering the design of environmental monitors.

Multicommutation flow analysis is a novel approach.[14-18] It can be implemented by using discrete commutation devices, such as three-way solenoid valves. The approach has been used to perform binary sampling,[14,15] making feasible the reduction of reagent consumption, sequential determination,[15,16] and the sequential management of incompatible reagents in a single line manifold. This technique has been proposed to also significantly widen the determination ranges.[17-18]

FIA methods of analysis could be very useful for water analysis. The collection of water samples from a stream, river, lake, or effluent provides the largest potential source of error in the chemical analysis of water. Continuous sampling would be required to obtain really representative measurements. In most cases, the cost of equipment and the amount of labor involved make this impossible. Ideally, the chemical composition of water should be measured *in situ*, thereby being subject to fewer external influences. Although there are electrochemical methods that can be used for certain parameters, for example, pH, conductivity, oxygen, selective ion electrode do not cover at all the range of analysis required. One possibility is the use of field application of flow-injection analysis that are now available. Very good results are also obtained by using the flow-injection analysis applications developed for use inside a laboratory. The application of FIA to water analysis has been reviewed by several authors.[19-28]

Valcarcel and co-workers present[27] the results of an interesting method for assessment of analytical quality in water analysis by flow-injection analysis. They evaluated a number of 225 papers regarding accuracy, applicability, precision, selectivity, sensitivity, determination range, and sample throughput. These parameters that define analytical quality were used to construct graduated quality scales that were employed to evaluate the usefulness of the applications. They concluded that:

- In literature a large number of papers regarding FIA for water analysis were published, confirming the potential of this technique for performing routine analysis in an automated and simple way;
- The overall quality of the application was quite acceptable, yet ca. 40% of them had a "percent quality" below 50%;
- Many of the surveyed applications were concerned with inorganic analysis and photometric detection;
- It is expected that there would be a much greater implementation of these procedures in control laboratories in the near future;
- Trends in the field should be focused on organic analysis especially for monitoring one or two compounds in water analysis.

This article selectively reviews the FIA applications for the determination of inorganic species

(cations and anions) in water samples of all kinds except marine waters. In a second article we intend to present a review regarding FIA methods for the determination of organic species in the same type of waters.

We will also present some of the recent papers regarding the preconcentration of metals from waters for FIA and also some papers regarding automatic FIA equipment for water analysis. Furthermore, the most important flow-injection methods of analysis for cations and anions in waters will be presented to render the review comprehensive (see Tables 1 and 2).

II. PRECONCENTRATION METHODS FOR THE DETERMINATION OF METALS IN WATERS BY USING FIA

Hashemi and Olin investigated the equilibrium and kinetic properties of an iminodiacetic-based chelating ion exchanger with a cross-linked agarose as support.[29] The adsorbent capacity of the medium showed fast adsorption and desorbtion of Cu(II), Cd(II), Ni(II), and Ca(II) ions, both in the batch and column mode. It was found to be about 50 times faster than Chelex-100 in the accumulation of these metal ions. Preconcentration by an FIA system connected to a ICP-AES instrument makes simultaneous measurement of ultratrace concentrations of a number of metal ions. Signal enhancement factors up to 1300 were obtained. The studied method of analysis was applied for tap water analysis.

A comparison of chelating resins for the preconcentration of Cu(II), Zn(II), Cd(II), Mn(II) and Ni(II) for flow-injection analysis flame photometry was presented.[30] An evaluation of controlled-pore glass immobilized iminodiacetate as a reagent for automated *on-line* matrix separation for inductively coupled plasma mass spectrometry is described.[31] The range of elements found to be retained by the column included transition metal cations, uranium, and lead. These could be eluted using nitric acid 0.5 mol L^{-1}. The method gave acceptable reproducibility with precision at the 5 ng mL^{-1} level of < 5%.

The work of Kenaway and Hafez[32] described a method for preconcentration and multielement determination in different water samples using cellulose-sodium sulfide and/or a thiourea system with atomic absorption spectrometry. The method is simple and easily applicable for the microdetermination of nine heavy metals, namely, Cd(II), Cr(III), Cu(II), Fe(III), Ni(II), Pb(II), Zn(II), Sn(IV), and VO(II).

Mentasti[33] reported an *on-line* flow injection analysis system for the determination of metal traces based on the utilization of a macrocolumn packed with XAD-2 resin that retains the analytes in the form of metal complexes. Very low detection limits can be reached.

A method for the determination of Cu, As, Se, Cd, In, Hg, Tl, Pb, and Bi in waters and biological materials by inductively coupled plasma mass spectrometry, after *on-line* separation is described.[34] The analyte preconcentration is accomplished by retention of the analytes complexed with the ammonium salt of *o,o*-diethyldithiophosphoric acid in a nitric acid solution on C-18 immobilized on silica in a minicolumn. Methanol is used as eluent. The an enrichment factors were in the range from 5 to 61, depending on the analyte.

III. AUTOMATIC FIA SYSTEMS FOR WATER QUALITY MONITORING

An automatic device for *on-line* residual water quality monitoring is described by Dressler et al.[34] It monitored sulfate, phosphate, and iron. A central control station links to the monitoring instruments via a mobile radio set for control of the instrument operation and data acquisition and evaluation.

FIA was also applied for monitoring river quality.[35,36] The parameters that can be determined are nitrite, nitrate, ammonia, phosphate, silica, arsenic, and mercury.

The development of an automated *on-line* analysis system using flow injection ultrasound filtration and charge-coupled device (CCD) detection was reported for environmental, bioprecess control, and clinical analysis.[37]

A continuous *in situ* cyanide monitoring using a highly sensitive and selective FIA system was also reported.[38] This system is based on the use of a gas-diffusion membrane. The detection limit is very low (0.4 ng mL^{-1} CN^{-}).

TABLE 1
Cationic Species Determined Using FIA Procedures

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
NH_3/NH_4^+	Natural water		2 μg L^{-1}		15-20	On-line preconcetration micro-distillation, pH electrode.			42
NH_3, NH_4^+	River water	0-10 ppm 0-1.0 ppm	0.01 ppm	0.51-0.83	30	Gas-permeation system, spectrophotometric determination.			43
NH_3/NH_4^+	Water	4-24 ppm		0.6-1.2	30	Spectrophotometric determination with indophenol.		Generation of indophenol with NH_4^+ and NaClO in alkaline medium.	44
NH_4^+, NO_3^-	Rain water	1-5 mg L^{-1}		2.3		Fluorimetric with o-phtalaldehyde.		NH_4^+ and NO_3^- are reduced to ammonia using Dervada's alloy.	45
NH_3, NO_2^-, NO_3^-	Water		1x10^{-8} M		20	Chemiluminescence with ClO^- for NH_3 and ozone for NO.		NO_2^- , NO_3^- are reduced to NO using I^- and Ti^{3+}. Volatile compounds transformed into NO by combustion at 600 °C.	46
NH_4^+	Rain water	2-40 μM		1.1-2.3		Gas-diffusion amperometric.		Glassy carbon electrode electrodeposited with a film of $Cu_3(Fe(CN)_6)_2$ coated with Nafion film.	47
NH_4^+	Water		0.091 mg L^{-1}	R> 0.9970	30	Spectrophotometric using Berthollet's reaction.		Neutralization reaction as heat-source.	48
NH_4^+	Lake water	0.2-12 mM				Reverse flow injection spectrophotometric determination.		NH_4^+ oxidation to NO_2^- by ClO^- and KBr.	49
NH_4^+	Natural water	10-1000 μg mL^{-1}	5 μg mL^{-1}	1.02	60	NH_3 diffusion through a semi-permeable membrane into an acceptor solution of Bromcresol violet, Bromthymol blue and Cresol red and spectrophotometric detection.		Analytical system used – Lachat QuikChem Model 8000.	50
NH_4^+	River water	3.5-172 mg L^{-1}	0.03 mg L^{-1}		30	NH_3 diffusion into a Cresol red reagent stream and spectrophotometric detection.		Sequential determination of CO_3^{2-}.	51
NH_4^+	River water	0.1-10 mM	0.05 mM	1.03		Alumina pH-ISFET incorporated in a gas-diffusion flow-injection system.			52
Na^+, K^+, Ca^{2+}, Mg^{2+}	water			3		Capillary electrophoresis system.		Hydrodynamic injection.	53
Na^+, K^+	River , tap water	<0.5 mM <0.1 mM			12	Separation on silica gel column and extraction with spectrophotometric detection.		Li-acetate and benzo-18-crown-6 as eluent.	54

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Na^+, K^+	River, tap water	<0.5 mM <80 μM			12	Separation on a cation-exchanger column and solvent extraction with spectrophotometric detection.			55
Ca^{2+}, Cl^-	Natural water	$5x10^{-5}$-10^{-3} M $2x10^{-4}$-$2x10^{-2}$ M		1.9-0.6 1.8-1.2	40	Bipotentiometric determination system for simultaneous determination.		Two different ISEs placed in series.	56
Ca^{2+}	Drinking water	10^{-4}-10^{-2} M		0.5-0.8		Optimized differential potentiometric system using modified simplex method.		Substantial increase in sensitivity from 28 to 50 mV/decade.	57
Ca^{2+}, Mg^{2+}	Mineral water			2.6 1.6		Spectrophotometric determination using multivariate calibration methods based on reaction of analytes with Methylthymol blue.		Results agreed with those of complexometry and ICP-AES.	58
Ca^{2+}	Natural water	0.5-10 mM	0.01 mM	1-4		Photo-cured coated-wire ISE for Ca^{2+} and potentiometric detection.		Ca-IES = a polymer mixture applied onto Ag electrodes incorporated in a flow-through cell and exposed to UV irradiation.	59
Ca^{2+}, Mg^{2+}	River water	<80 mg L^{-1} <15 mg L^{-1}			160	Spectrophotometric determination based on Ca^{2+} reaction with o-cresolphtalein complexon an oxine as reagents and Mg^{2+} reaction with EGTA and o-cresolphtalein complexon.		FIA-system containing an Injector-commutator.	60
Ca^{2+}, Mg^{2+}	Drinking Water	2-40 mg L^{-1} 1-20 mg L^{-1}		2 4	60	SIA-system in conjunction with multicomponent technique using 4-(2-pyridylazo)-resorcinol and sectrophotometric detection.		Results comparable with those of batch and FI analysis.	61
Ca^{2+}, NO_3^-	Waters	Response slope: 31.3 mV/decade 53.4 mV/decade	 $10^{-4.75}$ M $10^{-4.3}$ M	1	145	Tubular potentiometric electrodes for Ca^{2+} and NO_3^-.		Simultaneous determination of Ca^{2+} and NO_3^-.	62
Ca^{2+}, Mg^{2+}	Natural, potable water	1-10 mg L^{-1} 1-20 mg L^{-1}			70	Spectrophotometric determination based on Ca^{2+} and Mg^{2+} reaction with 4-(2-pyridylazo)-resorcinol .	Zn^{2+} and Cu^{2+} interfere.	Simultaneous determination of Ca^{2+} and Mg^{2+}. FIA-system contained a photodiode detector and controlled by an IBM PC using DARRAY and MULTIC programs.	63
Ca^{2+}, Mg^{2+}	River water	<30 μg mL^{-1}			15	Simultaneous injection of two sample plugs and one plug mixed with a masking agent (EGTA) plug to complex Ca^{2+}. Spectrophotometric determination using 3,3'-bis-[N,N-bis-(carboxymethyl)-aminometyl]-o-cresolphtalein.	Citrate, phosphate and oxalate interfere at ~0.5 mg mL^{-1}.	One pick corresponds to Mg^{2+} and the other to Mg^{2+} + Ca^{2+}, Ca^{2+} determined by difference.	64

TABLE 1 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Ca^{2+}	River Water	<0.1 mM	0.2 μM	1		Spectrophotometric determination based on Ca reaction with propyl orange – LiOH.		Results agreed with those by EDTA titration.	65
Mg^{2+}	Tap and drinking water	$1x10^{-5}$-$2x10^{-3}$ M	$1x10^{-6}$ M	0.4		Fluorimetric with 8-hydroxyquinoline-5-sulfonic acid.		Addition of EGTA get peak of Ca to disappear completely.	66
Mg^{2+}	Tap water	2 μM-0.12 mM		0.26-0.65	80	Spectrophotometric determination using Xylylazo violet.	M^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+} interfere at >1μM	Reagent stream containing Triton and tetraborate buffer (pH=9.2).	67
Mg^{2+}	Natural waters	0.027-1.8 mg kg^{-1}	5.5 μg kg^{-1}	0.7		Amperometric detection in a wall-jet cell with a glassy carbon electrode of Mg^{2+}-complex with Eriochrome black T.		Results compared with those obtained by AAS.	68
Al^{3+}, Cd^{2+}, Mg^{2+}, Pb^{2+}, Zn^{2+}	Tap water	0.1-10 μM			60 s/peak	Fluorescent detection in a pH gradient system of metal chelates (with 8-hydroxyquinoline-5-sulfonic acid) formed in a glass beds column.		Results compared with those obtained by AAS.	69
Cu^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Mn^{2+}, $V^{4+,5+}$	Natural water	10^{-11}, 10^{-7} M				Kinetic-catalytic spectrophotometric methods based on ion catalytic effect on different color forming-reactions.			70
Cu^{2+}, As^{3+}, Se^{4+},Cd^{2+}, In^{3+},Hg^{2+}, Tl^{+}, Pb^{2+}, Bi^{3+}	Water, riverine water		0.43 ng L^{-1} (Bi) – 33 ng L^{-1} (Cu)		21	On-line separation, preconcentration and ICP-MS determination.		Retention of analytes-ammonium salt of O,O-diethyldithiophosphoric acid complexes on C-18 immobilized on silica in a microcolumn. Elution with methanol. Enrichment factor 5-61.	71
Cu^{2+}	Tap water	0.025-200 ppb	0.008 ppb	2.3		On-line system with fluorimetric detection based on ascorbic acid and o-phenylenediamine reaction.	V^{5+}, Cr^{3+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Cd^{2+}, La^{3+}, Y^{3+}, Tl^{+}	Adsorbtion of Cu^{2+} as hydroxide or colloid on Teflon tub walls. Elution with HNO_3 solution.	72
Cu^{2+}	Water		$1x10^{-7}$ M $1x10^{-8}$ M			Microelectrodes as detectors of sizes 5 and 25 μm radii.		Oxidation of Cu-diethyldithiocarbamate at Pt-electrodes which fit a wall-jet cell	73
Fe^{3+}, Cu^{2+}, Pb^{2+}, Mn^{2+}	Drinking and environ-mental water		7.5 mg L^{-1} 1.6 mg L^{-1} 3.3 mg L^{-1} 2.1 mg L^{-1}			FAAS with reverse-FI extraction system.		Ammonium pyrrolidinyl dithiocarbamate and diethyldithiocarbamate as chelating agent and isobuthyl methy ketone as eluent.	74

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Cu^{2+}	Natural mineral water	1-65 μg mL^{-1}	0.6-1.5 μg mL^{-1}	1.1	15-30	AAS with on-line preconcentration on microcolumn of Dowex 50W-X8.		Enrichment factor: 25-60.	75
Cu^{2+}	Drinking water		0.2 μg L^{-1}	1.7-3.6	46	On-line adsorption preconcentration FAAS system.	50 μg Fe^{3+} L^{-1} eliminated with ascorbic acid.	Adsorbtion of Cu-diehyldithiocarbamate chelate on PTFE knotted reactor walls. Elution with isobuthyl methyl ketone.	76
Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}	River water		17 ng L^{-1} 24 ng L^{-1} 56 ng L^{-1} 19 ng L^{-1} 23 ng L^{-1}	4.4-7.7		Preconcentration on Metpac CC-1 column, macroporous poly(styren-divinylbenzene) resin covalently bonded with iminodiacetic acid functional groups. ICP-MS detector operated in a peak-jumping mode.	Ca^{2+}, K^{+}, Mg^{2+}, Na^{+} interferences studied.	Elution with HNO_3.	77
Cu^{2+}, Zn^{2+}	Tap water	2.6-25 ng mL^{-1} 1.2-25 ng mL^{-1}	0.8 ng mL^{-1} 0.35 ng mL^{-1}		14	Preconcentration on Chelex 100 and photometric determination with Zincon based on stability variation of complexes with pH.		Cu^{2+} determined from signal obtained at pH=5 and Zn^{2+} determined by subtracting Cu^{2+} contribution from signal obtained at pH=9.	78
Cu^{2+}, Cd^{2+}, Ni^{2+}	Tap water	45-350 ng mL^{-1} 15-120 ng mL^{-1} 90-700 ng mL^{-1}	5 ng mL^{-1} 2 ng mL^{-1} 10 ng mL^{-1}	1.3-2.4		Chelating ion-exchangers based on cross-linked agarose for fast adsorption and desorption af metals and ICP- IBMK detection.		Elution with HCl.	79
Cu^{2+}	Fresh water		0.56 μg L^{-1}	0.09		Anodic stripping voltammetric determination using a glassy carbon disk working elecrode in a Perpex wall-jet flow cell.		Stripping rate: -400mV - +400 mV.	80
Cu^{2+}	Boiler feed water	5-100 μg L^{-1}	0.25 μg L^{-1}	0.81-0.86		Spectrophotometric determination based on catalytic effect of Cu^{2+} on oxidation of hydroquinone by H_2O_2.			81
Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}	Fresh waters	<15 μg L^{-1} <100 μg L^{-1} <15 μg L^{-1} <5 μg L^{-1}			30 min/cycle	Square-wave anodic stripping voltammetric determination using a wall-jet flow cell with a glassy carbon electrode.		Ag/AgCl-KCl as reference electrode and Pt as counter electrode	82
Cu^{2+}, Cd^{2+}, Pb^{2+}	Drinking water	Low μg L^{-1} levels		0.38-0.76		Anodic differential pulse stripping voltammetric determination using of hemispherical or disc Pt/Hg electrodes.			83
Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}	Tap, rain water		0.05 ng mL^{-1} 0.08 ng mL^{-1} 0.6 ng mL^{-1} 0.1 ng mL^{-1}	3-5	20	Preconcentration on carboymethalylated poly(ethylimine)-poly(methylenepolyphenylene) isocyanate column and ICP AES detection		Elution with HNO_3	84

TABLE 1 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Cu^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}	Water	2-200 ng mL^{-1}	2-6.6 ng mL^{-1} 24.4 ng mL^{-1} (Pb^{2+})	1.6-5.1		Two injection valves in series, loop1 containing HNO_3 and loop 2 containing Chelex 100 column. Metals eluted onto an HPLC column of Ultrabase C18. Post-column derivatization with 4-(2-pyridylazo)-resorcinol monosodium salt and spectrophotometric detection.		Elution with tartric acid and sodium octanesulfonate.	85
Cu^{2+}	Under-ground water	0.1-10 ng mL^{-1}	0.08 ng mL^{-1}			Spectrophotometric determination of trace amount of Cu^{2+} by ion-exchanger phase absorptiometry with 4,7-diphenyl-2,9-dimethyl- 1,10 phenantroline disulfonate.		Flow-through absorptiometric detector containing QAE Sephadex A-25. Elution with HNO_3.	86
Cu^{2+}	Natural water	2 ppb				Preconcentration on Amberlite XAD-2 modified with catechol violet, 4-(2-pyridylazo)-resorcinol or Eriochrome blue black R and AAS detection.		Elution with HNO_3	87
Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}		17 ng L^{-1} 0.8 ng L^{-1} 6.5 ng L^{-1} 36 ng L^{-1}				On-line separation and preconcentration and ETAAS determination.	Interferences eliminated by diethyldithy-carbamate-C18 reversed-phase system		88
Cu^{2+}	Tap water	0.025-200 ppb	0.008 ppb	2.3		On-line adsorption preconcentration on walls of Teflon tubes and fluorimetric detection with ascorbic acid and o-phenylenediamine.	V^{5+}, Cr^{6+}, Fe^{3+}, Hg^{2+}, La^{3+}, Mn^{2+}, Cd^{2+}, Y^{3+}, Tl^{+}	Treatment of Teflon tubes with NaOH enchanced adsorption of Cu^{2+}.	89
Al^{3+}	Drinking water	0.05-0.80 mg L^{-1}				Photometric determination as triphenylmethane and azo-dye complexes.		Two systems: FIA and CFA.	90
Al^{3+}	Potable, fresh, river waters	50ng L^{-1}-3μg L^{-1}	15-40 ng L^{-1}	4		On-line preconcentration and ETAAS detection.		Preconcentration materials: 8-quinolinol immobilized on controlled pore glass and Amberlite XAD-2. Recovery: 100-115 %.	91
Al^{3+}	Drinking water	3-600 ng mL^{-1}	2.25 ng mL^{-1}	3.55		Fluorimetric using salicylaldehyde carbohydrazone.		Salicylaldehyde carbohydrazone in presence of Triton X-100 and K^{+} hydrogenphthalate-hydrochloric acid buffer.	92
Al^{3+}, Fe^{3+}	Potable, treated waters	0-1000 μg L^{-1}	13 μg L^{-1} 11 μg L^{-1}			Spectrophotometric using pyrocatechol violet for Al^{3+} and ferene S for Fe^{3+}.		Solid-state light emitting diode, photodiode through detector. Precision>98 %.	93

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Al^{3+}	Lake waters	<37 μM	3.7 nM	0.8		Fluorescent detection of Lumogallion complex.	Not interfere: citric acid, fulvic acid and Fe^{3+}.	Determination of trace levels of all aluminum forms excepting polymers. Masking agents not required.	94
Al^{3+}	Tap water	200-500 μg L^{-1}	2μg L^{-1}			Isolation and preconcentration of fast-reactive Al on Amberlite XAD column using as reagent oxine and ICP AES detection.		Stream of reagent merged with carrier stream before passing reaction coil and column.	95
Al^{3+}	Tap water	<1000 μg L^{-1}	0.15 μg L^{-1}	2.6, 2.2		Kinetic fluorimetric determination based on Eriochrome red B method.	Procedure more tolerant for Fe^{3+}. Interferences of cations and anions listed.	Reaction taking place at 80 °C and then cooled to 4 °C.	96
Fast reactive aluminum	Potable waters		10 μg L^{-1} 1.8 μg L^{-1}*	8 8*		Buffered sample mixed with 8-hydroxyquinoline and passed through Amberlite XAD-2 column.		Comparison between ICP AES and ICP MS* detectors.	97
Aluminum speciation	Bottled, tap, spring, well, river waters	10-200 ng mL^{-1}	3 ng mL^{-1}			Al^{3+}- salicylaldehide picolinyl-hydrazone complex retained on a layer of Sep-Pak C18 in flow cell for fluorescence measurements.		Non-labile monomeric Al determined by passing carrier stream through a Amberlite IR-120 column to retain cationic and anionic species.	98
Al^{3+}	Potable waters	<500 nM	3.7 nM	0.9-1.5		On-line preconcentration on a column of salicyli-deneamino-2-thiophenol immobilized on glass beads followed by eluate reaction with pyrocatechol violet at 40 °C and spectrophotometric detection.		Elution with HNO_3.	99
Al^{3+}	Water	20-300 μg L^{-1} 200-1000 μg L^{-1}				Bran-Luebbe TrAAcs 800 analyser for total monomeric Al determination with pyrocatechol violet.		Two separate manifolds designed.	100
Aluminum speciation	Natural waters	1-10000 μg L^{-1}		1.4		Separation on Amberlite IR-120 column and reaction with 8-hydroxyquinoline-5-sulfonic acid and 1,10-phenantroline using fluorescent detection.		Carrier stream either passed through column (non-labile monomeric aluminum) or diverted past column (total monomeric aluminum).	101
Aluminum speciation	Tap waters	10-80 μg L^{-1} 80-1000 μg L^{-1}	5 μg L^{-1}	0.65-1.8	40-50	Spectrophotometric determination based on pyrocatechol violet chelation-ion-exchange method	Fe^{3+}		102
Al^{3+}	Natural water	0.07-6.45 μg mL^{-1}	75 ng mL^{-1}	1.1		Samples injected via a loop into SCX preparative and eluated directly into nebulizer of flame AAS			103

TABLE 1 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Al^{3+}	Tap, mineral waters	<1μg mL^{-1}	0.35 ng mL^{-1} 0.4 ng mL^{-1}*			Fluorimetric determination based on Eriochrome red B method.		Carrier: 1,10-phenantroline and hydroxylammonium chloride. Two buffers: hexamine, sodium-acetate.	104
Al^{3+}	Tap waters	1-50 ng mL^{-1}	0.03 ppb	3		Fluorimetric determination based on formation of Al^{3+}- 5,7-dibromquinolin-8-ol complex.	Separation of interferents through a chelating column.	FIA method was more selective than batch method.	105
Al^{3+}	River waters		18 ppb	1.8		Malcome-Lawers and Pasquini flow analyser combined with Chrome azurol-hexadecylpyridinium chloride-ethanol.	Interferences discussed.		106
Residual aluminum	Potable, treated waters	<1000 μg L^{-1}	45 μg L^{-1}	1.2-12.1	48/day	Spectrophotometric determination based on pyrocatechol violet method.	Fe^{3+}	Portable, automated, FI-based solid-state device.	107
Fe^{2+}, Mn^{2+}	Under-ground waters	<1x10^{-4} μg mL^{-1} (Fe(II)) <1x10^{-4} μg mL^{-1} (Mn(II))	3x10^{-6} μg mL^{-1} (Fe^{2+}) 5x10^{-6} μg mL^{-1} (Mn^{2+})			r-FIA and chemiluminescence detection based on metal-catalyzed light emission from luminol oxidation by KIO_4.		Determination of total dissolved Fe^{3+} and Mn^{2+}.	108
Iron	Rain water		8 ppb		90	Spectrophotometric based on color reaction of Fe^{3+} with thiocyanate ions.	Not interfere: cations and anions tested.	Color reaction occurs in presence of cationic surfactant.	109
Iron	Drinking water	0.01-700 ppm	0.002 ppm		90	Spectrophotometric based on color complex Fe^{3+}-SCN–cetylpyridinium chloride-2,2'-bipyridine			110
Fe^{3+}	Tap, river water	10-200 ng mL^{-1}	4.3 ng mL^{-1}	1-3		Integratrated retention/photometric detection based on Fe^{3+}-ferrozine reaction.		Fe^{3+}-ferrozine retention in flow cell packed with an anion exchange support. Elution with sodium peroxide.	111
Fe^{3+}, I^-	Natural waters	0.06-0.4 μg mL^{-1} 0.6-3.0 μg mL^{-1}	0.02 μg mL^{-1} 0.2 μg mL^{-1}	2-5		Spectrophotometric determination based on catalytic reactions between Fe^{3+}-metol-H_2O_2 and I^--Ce^{4+}-As^{3+}.	Hg^{2+}		112
Fe^{3+}	Natural waters	5-20 mg L^{-1}			110	SIA system with colorimetric detection based on Fe^{3+}-thiocyanate reaction		Optimization and modeling of SIA technique by natural computation technique.	113
Fe^{2+}, Fe^{3+}	Natural waters	80-50 ng L^{-1}	80 ng L^{-1}			Spectrophotometric detection of Fe^{3+}-SCN^- complex retained in a flow cell packed with Dowex-1.		Carrier stream splitted in two fractions. Oxidation of Fe^{2+} to Fe^{3+} in a column of DEAE Sephadex saturated with Folin-Ciocalteu's reagent.	114

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Fe^{3+}, Al^{3+}	Tap water	0-0.8 mg L^{-1} 0-0.4 mg L^{-1}		1-3.1	90	Stopped-flow injection technique based on spectrophotometeric detection of analytes with cethylpyridinium bromide and Chrome Azurol S.	Ni^{2+}, F^-	Simultaneous determination of Al^{3+} and Fe^{3+}.	115
Iron	River water	10-200 ng mL^{-1}	4.3 ng mL^{-1}	1.3-2.9		Integrated retention/spectrophotometric detection method based on temporary immobilization of complex Fe^{3+}-ferrozine.	Tolerance levels for 11 foreign ions.	Reduction at Fe^{3+} with I^-. Fe^{2+}-I^- complex adsorbed on Dowex 1-X1 packed in flow cell of photometric detector.	116
Fe^{3+}, Co^{2+}	Water	0.15-5 μg mL^{-1} 1.2-25 μg mL^{-1}	0.045 μg mL^{-1} 0.33 μg mL^{-1}			Derivative spectrophotometric determination based on Fe^{3+}, Co^{2+}-ferrozine complexes using stopped-flow technique.			117
Fe^{3+}, Al^{3+}	Natural waters	<2 mg L^{-1}	0.06 mg L^{-1}	5-12	85	Fe^{3+}-1,10-o-phenantroline/I^- and Al^{3+}-oxine complexes extracted in chloroform and passed to diode array detector.		Results analyzed by partial least squares to separate Al^{3+}, Fe^{2+} and Fe^{3+}.	118
Fe^{3+}	Tap water	3-300* ng mL^{-1} 20-900 ng mL^{-1}	3* ng mL^{-1} 20 ng mL^{-1}	3* 4.5		Flow cell filled with entrapped pyoverdin in sol-gel glass and fluorescent detection.		Decrease in fluorescence measured. Two systems optimized: continuous-flow* and FIA.	119
Fe^{2+}	Drinking water	4-40 ng mL^{-1}	1.92 ng mL^{-1}	2.5		First-derivative stop-flow method based on treating of sample with triethylenetetramine, tetramethyl-p-phenilenediamine and H_2O_2 and spectrophotometric detection.	Five-fold of Cu^{2+} did not interfere.		120
Fe^{2+}, Co^{2+}	Tap water	0.1-2.5 ppm 0.1-3 ppm		4.2 3.2		FIA merging zone method with spectrophotometric detection using H_2O_2 and F^- and 5-(3,5-dibromo-2-pyridylazo)-2,4-diaminotoluene as reagents.	Relatively free of interferences		121
Fe^{3+}	Waters	3.5-150 ng mL^{-1}	2 ng mL^{-1}			Spectrophotometric method based on catalytic effect of Fe^{3+}-EDTA complex on oxidation of hydryoylamine by dissolved oxygen.	Co^{2+}, Cr^{3+}, Cu^{2+}	FIA-system controlled by a PC which allowed automatic sample injection, continuous acquisition and processing data. Hewlett-Packard 8453 diode-array spectrometer used.	122
Cr^{3+}, Cr^{6+}	Mineral, tap and distilled water	0.1-1.0 μg mL^{-1} 0.1-10 μg mL^{-1}		0.1-2	30	Selective oxidation of 2-(α-pyridyl)-thioquinaldinamide by Cr^{6+} yielding a intensely fluorescent product.		On-line oxidation of Cr^{3+} to Cr^{6+} with sodium metaperiodate. Simultaneous determination.	123

TABLE 1 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Cr^{6+}	Waters		0.54 ng mL^{-1}	2.8		On-line preconcentration combined with FAAS.		Cr^{3+}-pyrrolidinedithio-carbamate complexes sorption on polyether-ether-ketone loop. Hydraulic high-pressure. Nebulization sample introduction.	124
Cr^{3+}, Cr^{6+}	River waters	10-150 μg L^{-1}	3.2 μg L^{-1} 2.9 μg L^{-1}	2.7 2.9		On-line preconcentration and FAAS detection		Cr^{3+} and Cr^{6+} preconcentration and separation by sorption on activated alumina microcolumn. Elution with HNO_3 for Cr^{3+} and NH_3 for Cr^{6+}. Enrichment factor: 27, 41.	125
Cr^{3+}, Cr^{6+}	Under-ground water	0.06 μg L^{-1} – 5 mg L^{-1}				Separation and GFAAS determination.		Analytes separation using cation and anion exchangers	126
Cr^{3+}	Tap, river waters	0.5-7.5 μg mL^{-1}	0.5 ng mL^{-1} 250 ng mL^{-1}	3-10		Preconcentration in a flow-through electrochemical cell containing alumina with electrodes off-circuit and AAS detection.		Elution with HCl. Reduction of Cr^{6+} to Cr^{3+} by applying a constant current of –5 to –10 mA. Two injected sample volumes employed.	127
Cr^{3+}, Total chromium	Tap, mineral , river waters	<140 μg mL^{-1}	0.2 μg mL^{-1}	1.2-5.9 1.2-5.7		Preconcentration on poly-(aminophosphonic acid) and flame AAS detection.		Elution with HCl.	128
Cr^{6+}	River water	<0.8 mg L^{-1}	0.005 mg L^{-1}		120	Spectrophotometric method based on sampling passing through a PTFE column packed with 1,5-diphenylcarbazide and silica.			129
Cr^{6+}	Potable water	10-50 μg L^{-1} 2-10 μg L^{-1} 1-5μg L^{-1}	3 g L^{-1} 0.3 g L^{-1} 0.2 g L^{-1}	0.6-4.7		On-line preconcentration on activated alumina and spectrophotometric detection using 1.5-diphenycarbazide as reagent.		Elution with NH_4OH. Various injected sample volumes.	130
Cr^{3+}, Cr^{6+} speciation	Fresh waters	<500 μ g L^{-1}	0.05 μg L^{-1} 0.1 μg L^{-1}	4.3 2.7		Chemiluminescent determination based on analyte-luminol-SO_2-H_2O_2 complex.			131
Cr^{3+}, Cr^{6+}	Water	1-10μg L^{-1}	0.78 μg L^{-1} 1.4 μg L^{-1}			On-line preconcentration on Cellex P and CellexT columns connected in series and FAAS detection.		Elution from Cellex P with HCl and from Cellex T with NaOH.	132
Cr3+	Water	0.01-6 ppb	0.01 ppb	2.5	70	Chemiluminescent method based on measurement of light emitted from Cr^{3+}-catalysed oxidation of luminol by H_2O_2.	EDTA reduced interferences.		133

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Cr^{3+}, Cr^{6+}	Natural waters	10-200 μg L^{-1}	1.0 μg L^{-1} 0.8 μg L^{-1}			On-line preconcentration on a column packed with acid-activated Al_2O_3 and FAAS detection.	No serious interference.	Elution with Clark-Lubs buffer.	134
Cr^{6+}	Natural waters	Trace amounts		2.4		Selective spectrophotometric determination using a column of ZrO_2 coated on a silica gel surface and 1,5-diphenylcarbazide.	SO_3^{2-}, PO_4^{3-}	Elution in reverse flow with tris-(hydryoxylmethyl)-methylamine.	135
Cr^{6+}, total chromium	Natural waters		16 ng L^{-1} 18 ng L^{-1}	10		Differential determination of Cr^{3+} using sodium-diethyldithiocarbamate as complexing agent applied to a column of Rp-C18 and GFAAS detection.		Oxidation of Cr^{3+} to Cr^{6+} by peroxydisulfate. Elution with methanol.	136
Zn^{2+}	Natural water		0.85 μg L^{-1}	6.0	17	On-line preconcentration and FAAS detection.		Zn^{2+}-thiocyanate complex sorption onto polyurethane foam minicolumn placed in four-way valve loop. Elution with HNO_3	137
Zn^{2+}	Drinking mineral water		5.0 ng mL^{-1}	1.5	120	On-line preconcentration and FAAS detection.		Retention on ion exchange minicolumn under acidic condition.	138
Zn^{2+}	Drinking waters	10-1000 ng mL^{-1}	5 ng mL^{-1}	1.8		Fluorimetric method based on Zn^{2+}-salicylaldehyde-thiocarbohydrazone complex.		Reaction occurs in presence of Triton X-100 and sodium acetate-acetic acid buffer.	139
Zn^{2+}	Natural waters	<50 ng mL^{-1}	14 pg mL^{-1}	1.4		Addition of ^{67}Zn and loading on a column of SO_3H-quinolin-8-ol carboxy-methylcellulose and isotope dilution ICP MS.		$^{66}Zn/^{67}Zn$ isotope ratio calculated from peak areas.	140
Zn^{2+}	Tap water	0.072-0.05 mg L^{-1}	0.036 mg L^{-1}			Spectrophotometric determination using 2-hydroxy-3-[(4-phenylazophenyl)-triazeno]-5-sulfobenzoic acid as reagent.	Al^{3+}, Cd^{2+}, Fe^{3+} Hg^{2+} masked.	Ethanolic reagent solution containing emulsifier OP.	141
Zn^{2+}	Tap water	<2.5 μg mL^{-1}		0.8		Kinetic spectrophotometric method based on Zn^{2+}-meso-tetra-(4-sulphenil)-porphyrin complex using imidazole as catalyst.	Tolerance levels of 17 foreign ions	Results agreed with those obtained by ICP AES.	142
Zn^{2+}	Tap, well water	<1 μg mL^{-1}	3 ng mL^{-1}		40	Selective fuorimetric method using 5,7-dibromo-8-quininol as reagent	Ni^{2+}, Mn^{2+}, EDTA interfere.		143
Zn^{2+}	Potable water	10-600 μg L^{-1}	3 μg L^{-1}	1.8	180	Fluorescent method using 5,7-dichloro-2-methylquinolin-8-ol in ethanol as reagent.	Masking agent		144
Cd^{2+}	River water		12 pCd			Potentiometric determination with Cd^{2+}-ISE.	Fe^{3+}, Cu^{2+}, Pb^{2+} eliminated.		145

TABLE 1 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Cd^{2+}, Pb^{2+}, Cu^{2+}	Water		0.3 μg L^{-1} 3 μg L^{-1} 0.2 μg L^{-1}	1.4 1.0 1.3	120	On-line preconcentration and flame AAS detection.		Me-diethylammonium-diethyldithiocarbamate complexes sorption onto a microcolumn of bonded silica with octadecyl functional groups.	146
Cd^{2+}	River water	0.05-2 μg L^{-1} 2-4 μg L^{-1}	0.028 μg L^{-1} 0.83 μg L^{-1}			On-line preconcentration on Bio-Rad AG1-X8 resin of Cd^{2+}-I^- complex, reaction with Cadion and spectrophotometric detection.		Elution with HNO_3.	147
Mn^{2+}	Waters	5-200 ng mL^{-1}	1 ng mL^{-1}		45	Binary fluorescent complex using 8-hydroxyquinoline-5-sulfate aluminium as kinetic fluorescent indicator in Mn-H_2QS-$NaIO_4$		Fiber optic was coupled to FIA system	148
Mn^{2+}	Natural waters	1-5 ng mL^{-1}	0.56 ng L^{-1}	1.78		Spectrophotometric determination based on Mn^{2+} oxidation using a solid-state PbO_2 reactor to form permanganate.		PbO_2 embedded in silica gel beads.	149
Mn^{2+}	Potable water	0-100 ppb	4.5 ppb	4.9-5.3		Chemiluminescence method based on reaction between Mn^{2+}-7,7,8,8-tetracyanoquinodimethane-di-dodecyl-di-methylammonium bromide-Eosine Y.	Interference of Fe^{3+} masked.	Carrier stream containing injected sample merged with reagent stream in spiral flow cell.	150
Mn^{2+}	Surface water	0.5-5 μg mL^{-1}	0.076 μg mL^{-1}			On-line solvent extraction of Mn^{2+}-ammonium pyrrolidine-dithiocarbamate in isobutyl ketone and AAS detection.			151
Mn^{2+}	Tap, river, lake water	0.05-1.0 ng mL^{-1}	10 pg mL^{-1}	1.5	25	Spectrophotometric determination of Mn^{2+}-H_2O_2-N,N-dimethyl-p-phenylenediamine-tiron-cysteine-phenylendiamine-triethylentetramine-NH_3 complex.	Foreign ions interfere.	Reaction taking place in a reactor at 35 °C.	152
Mn^{2+}	Natural waters	<640 nM			40	Catalytic kinetic spectrophotometric determination of Mn^{2+}-H_2O_2-tiron-1,10-phenanthroline complex using stopped-flow and gradient calibration.			153
Ni^{2+}	Drinking river water	Sub-ppb concn. level	50ng L^{-1}			Ni^{2+} tetracarbonyl generation in-situ trapping GFAAS.	Heavy metals.		154
Ni^{2+}, Cr^{3+}	Natural waters	Below μg L^{-1}				Two on-line preconcentration computer-assisted methodologies and ICP-AES detection.		Iminodiacetic acid-ethyl-cellulose as ion-exchanger. Recovery range 97-102 %.	155
Ni^{2+}	Waters		0.18 μg L^{-1} 0.01 μg L^{-1}			On-line preconcentration of Ni^{2+} by carbonyl vaporization with FIA and continuous-flow system and GFAAS detection.		Results obtained agreed with certified values for Ni^{2+}.	156

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Ni^{2+}	Waters	1-100 μg L^{-1}	1 μg L^{-1}	2.2	120	Microwave-induced plasma optical emission spectrometic method based on conversion of Ni to Ni^{2+}-tetracarbonyl by $NaBH_4$.			157
Pb^{2+}	Waters	At ppb concn. level	1 ppb	5.2		Stopped-flow FIA kinetic method based on resurin reduction to resorufin by Pb^{2+} ions.	Interferences removed by extraction.		158
Pb^{2+}	Tap water	<15 μg L^{-1}	4.2 μg L^{-1}			Spectrophotometric determination of Pb^{2+}-5,10,15,20-tetra(4-N-sulfoethylpyridinium)-porphyrin using merging zones.	Al^{3+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+} eliminated by adding acetyl-acetonate to reagent.	Recovery range: 98-108 %	159
Pb^{2+}, Cd^{2+}, Ni^{2+}	Natural waters		3.2 μg L^{-1} 0.23 μg L^{-1} 20 μg L^{-1}	4.2 4.2 3	65	On-line co-precipitation-preconcentration with Cu^{2+}-DDTC and collected on inner wall, dissolution in IBMK and flame AAS detection.			160
Pb^{2+}, Cd^{2+}, Mn^{2+}	River water	<300 ng mL^{-1} <150ng mL^{-1} <150 ng mL^{-1}	4.8 ng mL^{-1} 1.9 mg mL^{-1} 1.5 ng mL^{-1}	3.2 2.1 2.5		Ion-chromatographic method with post derivatization and spectrophotometric detection using 2-(5-nitro-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)-phenol – 2-(cyclohexylamino)-ethanesulfonic acid – NaOH as reagents.		Simultaneous determination.	161
Pb^{2+}, Cd^{2+}	Natural, potable water	Trace amounts	9 ng L^{-1} 7 ng L^{-1}			Preconcentration on AGMP-1, BioRad column and GFAAS detection using a modifier of $NH_4H_2PO_4/MgNO_3$	Interferences and Tiron purity studied.	Sample, Tiron solution and ammonium borate buffer loaded into preconcentration manifold	162
Pb^{2+}	Potable, river water		A: 9 μg mL^{-1} B: 5 μg mL^{-1} C: 18 μg mL^{-1}	A: 3 B: 2.5 C: 4		Three acid/oxidant systems used to generate PbH_2 and flame AAS detection. A: HNO_3/H_2O_2, B: lactic acid/$K_2Cr_2O_7$, C: HNO_3/ammonium persulfate and $NaBH_4$	As^{3+}, Sb^{3+}, Hg^{2+}, Cu^{2+}, Ni^{2+} tabulated.	Results agreed with those obtained by GFAAS	163
Pb^{2+}, Al^{3+}, Cd^{2+}, Mg^{2+}, Zn^{2+}	Tap water	0.1-10 μM			60	pH-gradient FIA method with fluorescence detection using different buffer systems and 8-hydroxyquinoline-5-sulfonic acid as reagent.		Results comparable to those obtained by AAS.	164

TABLE 1 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Pb^{2+}	Natural waters		0.17 μg L^{-1}	5.9		Preconcentration on different cellulose sorbents with phosphoric acid and carboxymethyl groups, C18 sorbent non-modified with pyrocatechol violet or 8-quinolinol, chelating sorbents modified with pyrocatechol violet and several cation-exchange resins and FAAS determination.		Elution from Cellex P with HNO_3 and ethanol allowed differentiation between tetra-alkyllead, other organo-lead species and inorganic Pb^{2+}.	165
Pb^{2+}, Cd^{2+}	River water	20-250 nM 2-50 nM	4.9 nM 1 nM			Adsorptive stripping voltammetric determination using a homemade detector based on PARC model 310 polarographic detector.			166
Pb^{2+}	water	<1000 ppb	2.7 ppb	1.7-6 5.3-10.6		Potentiometric-stripping and square-wave anodic-stripping-voltammetric methods.		Mercury film deposited on electrode incorporated in a wall-jet flow-cell.	167
Pb^{2+}	Tap, ground, river water	10-100 ng mL^{-1}	10 ng mL^{-1} 6 ng mL^{-1} 4 ng mL^{-1}	6-12		On-line preconcentration on silicagel coated with chloroformic extract of ion pair formed from Aliquat 336 and nitroso-R-salt in a glass column and flame AAS detection.	Ni^{2+}, F^-	Elution with HCl.	168
Pb^{2+}	Potable waters	2.5-100 μg L^{-1}	0.7 μg L^{-1}	2.3-4.9		On-line preconcentration on PTFE micro-column of fibrous alumina and flame AAS detection		Elution of HNO_3	169
Pb^{2+}	Drinking water	0.3-10 μM	10 nM			Dithizone immobilized on XAD-4 resin studied as sensing element of optical sensor.		Measurements expressed as reflectance of Pb^{2+} complex minus that of immobilized dithizone alone.	170
Pb^{2+}	River water	At ng L^{-1} levels	3 ng L^{-1}	1.9		On-line sorbent-extraction preconcentration of Pb^{2+}-di-ethyl-di-thyocarbamate complex on conical C18-bonded silica column and GFAAS detection.		Results agreed with certified values.	171
Hg^{2+}	Drinking water	2-20 μg L^{-1}		1.4	7	Inhibition of urease reactor by Hg^{2+} and potentiometric detection of released ammonia.		Integration of urease reactor into a gas-diffusion unit. pH electrode	172
Hg^{2+}	Natural water		5.3 ng L^{-1}	5	6	CVAAS method based on amalgamation of stripped reduced metal from a gas-liquid unit on a Au wire column and heating Au wire automatically to release amalgamated Hg.		N_2 as carrier. An external nichrome wire coil for heating.	173
Organo-mercury and Hg^{2+}	Waters		200 pg/100μL 2 pg/100μL		17	Atomic fluorescence spectrometry method based on on-line oxidation of organo-Hg species to Hg^{2+} followed by reduction to Hg^0.		$SnCl_2$ as reducing agent.	174

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Hg^{2+}	Tap water	0.5-100 μg L^{-1}	0.25 ng mL^{-1}	1.9		Potentiometric stripping method using a thin Au layer of recordable compact disks		Low cost of this new source of electrodes (CDtrodes)	175
Hg^{2+}	Drinking water		8 ng L^{-1} 1.0 ng L^{-1}			Hg-specific detector used for automated analysis of water for Hg^{2+}-ultratrace concns.		Improving detection limit coupling FIA system with an amalgamation unit.	176
Total mercury	Drinking water		0.035 ng L^{-1}	1.1	5 min for 3 detns	On-line microwave digestion coupled to dedicated CVAAS mercury system.			177
Hg^{2+}	Drinking waters		10 ng L^{-1}		120	Dedicated flow injection system for Hg^{2+} using CVAAS as detection.		20-fold improving Hg^{2+} detection limit.	178
Hg^{2+}	Potable water	2-10 μg L^{-1}		1.4	7	Potentiometric measurements based on inhibition of an urease reactor immobilized on polyacrylamide gel by Hg^{2+}.		Ingold LOT 453 S-7 pH electrode.	179
Hg^{2+}	Drinking, rain water	20ng-40 μg L^{-1} 1-200* ng L^{-1}	5 ng L^{-1} 0.3 ng L^{-1}*		90-91	HGAAS determination with high-intensity radiation source. Preconcentration by amalgamation*.			180
Hg^{2+}	Potable waters	0.035-50 ng mL^{-1}	0.035 ng mL^{-1}	1-2		On-line microwave digestion coupled with Perkin-Elmer Flow Injection Mercury System.			181
Hg^{2+}	Potable water	0.2-10 mg L^{-1}	10 ng L^{-1}			HGAAS determination based on reduction with $SnCl_2$			182
Hg^{2+}, Al^{3+}	Tap water	0-75 ng mL^{-1} 0-64 ng mL^{-1}	0.5 ng mL^{-1} 1 ng mL^{-1}	3.52-5.2 3.2-4.89		Stopped-flow injection kinetic spectrophotometric multicomponent determination based on catalytic effect on ligand substitution reaction between hexacyanoferrate(II) and α,α'-bipyridyl.			183
Co^{2+}	Un-polluted natural waters		2-3ng L^{-1}			Tandem on-line preconcentration and gas phase chelates generated by merging-zones with ETAAS detection.		Amberlite IR-120 as ion-exchanger. Volatile Co-chelates are decomposed on pre-heated graphite platform	184
Co^{2+}	Natural waters	0.2-1 ng mL^{-1}	4 pg mL^{-1}	2.1	120	Trace chemiluminescent detection of Co^{2+}-di-brom alizarin violet-H_2O_2-hexadecyltrimethylammonium bromide complex.	Effect of 20 cations and anions investigated.	Results agreed with those obtained by GFAAS	185
Co^{2+}, Mn^{2+}	Natural waters	0.01-12 ng mL^{-1} 0.06-7 ng mL^{-1}	0.01 ng mL^{-1} 0.02 ng mL^{-1}	4.3 2.1		Chemiluminescent determination of Co^{2+} and Mn^{2+}-KIO_4-luminol complex.	Sodium citrate used as masking agent for foreign ions	Simultaneous determination of Co^{2+} and Mn^{2+}.	186
Vanadium	Natural waters		0.5 ng mL^{-1}	1.5	15	Spectrophotometric method based on vanadium catalytic action on a new indicator reaction: Victoria blue B and $KBrO_3$.		Citric acid as activator.	187

TABLE 1 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
$V^{4+,5+}$	Natural fresh, tap waters	0-8 μg L^{-1}	4 ng L^{-1}		30	Spectrophotometric method using V-catalysed oxidation of o-phenylenediamine with BrO_3^-	Tolerable humic acid <3000 μg/L	Gallic acid as activator.	188
V^{5+}	River water		2pg/200 μL	1.1	40	Spectrophotometric method using gallocyanine oxidation by bromate in presence of vanadium as catalyst .		Decrease in absorbance is measured.	189
$Se^{4+,6+}$	Natural water		49 ng L^{-1} 0.8 μg mL^{-1}			Preconcentration and successive gradient elution for differentiate the species and GFAAS determination.		Alumina microcolum. Elution with different concns. and volumes of NH_3	190
$Se^{4+,6+}$	Tap, surface waters	10 ng mL^{-1} - 2.2 μg mL^{-1} 0.1-2.4 μg mL^{-1}		0.1-2	25	Fluorimetric method based on selective oxidation of 2-(α-pyridyl)-thioquinaldinamide by Se^{4+}.		On-line Se^{6+} reducing to Se^{4+} in a reduction coil installed in photoreactor	191
Se^{4+}	River, lake, tap water	0.12-80 μg mL^{-1}	0.12 μg mL^{-1}	0.2-0.6		On-line retention of Se^{4+} and tetrahydroborate on Amberlite IRA-410 followed by HGAAS determination.		Elution with H_2O and removing SeH_4 with an Ar stream.	192
As^{5+}, Ge^{4+}, P^{5+}, Si^{4+} as heteropoly acids	Waters	10-1000 μg L^{-1} 50-25000 μg L^{-1} 1-1000 μg L^{-1} 50-10000 μg L^{-1}	10 μg L^{-1} 50 μg L^{-1} 1μg L^{-1} 10 μg L^{-1}			Luminol chemiluminescence with hetoropoly acids after separation by ion-chromatoghraphy.		Post-column detection system involved formation of heteropoly acids in H_2SO_4 before CL reaction.	193
$As^{3+,5+}$	Dinking water		37 ng L^{-1} (As(III)) 33 ng L^{-1} (As(V)) 111ng L^{-1}* (As(III))	1.1 1.3 0.7*	180	On-line reduction of As^{5+} to As^{3+} by ascorbic acid and KI in heated, thermostated bath for total-As determination using HGAAS. Selective A^{3+} determination without heating.*		Heating combined sample and reducing agent by flowing throught a knotted reactor immersed in a thermostated oil bath. As^{5+} not convert to As^{3+} without heating.*	194
As^{5+}	Drinking water					Microbial oxidation of As^{3+} to As^{5+}.			195
$As^{3+,5+}$	Drinking water	0.75 ng mL^{-1}				AsH_3 formation and HGAAS detection.		As^{5+} to As^{3+} reduction not required if AsH_3 is generated in conc. HCl.	196
As^{3+}	Rain water	1 ng mL^{-1}				Chemiluminescent determination of As^{3+} as AsH_3 mixed with O_3.		Results slightly higher than those obtained by FIA-AAS	197
As^{3+}, As^{5+}	Tap, ground, mineral, artificial waters	20-150 ng mL^{-1} 15-140ng mL^{-1}*	4.5 ng mL^{-1} 15* ng mL^{-1}	2.2 2.3*		As reduced to AsH_3 by $NaBH_4$ followed by total As* determination by AAS and similar As^{3+} determination using citric acid.		A^{5+} calculated by difference	198

Note: FIA — flow injection analysis; FI — flow injection; AAS — atomic absorption spectrometry; FAAS — flame absorption spectrometry; CVAAS — cold vapor atomic absorption spectrometry; HGAAS — mercury atomic absorption spectrometry; ICP — inductive coupled plasma; MS — mass spectrometry; ISE — ion selective electrode; ETAAS — electrotermic atomic absorption spectrometry; GFAAS — graphite furnace atomic absorption spectrometry; IBMK— iso-buthyl-methyl ketone; AES – atomic emission spectrometry; Concn. – concentration; Detn. - determination.

TABLE 2
Anionic Species Determined Using FIA Procedures

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
SO_3^{2-}	Tap water	0.01-5 mg L^{-1}	0.01mg L^{-1}	5	500	Wet-chemiluminescence produced by auto-oxidation of sulfite in presence of Rhodamine 6G immobilized on cation exchange column	Interfering ions eliminated by upstream cation exchanger	Rhodamine 6G immobilized electrostatically. Tween 80 surfactant enchanges CL	199
SO_4^{2-}	Rain waters	0.1-7 mg L^{-1}	0.1 mg L^{-1}	1.8	12	Spectrophotometric method using Ba-dimethylsulfonazo-III complex		Results agree with those obtained by ion-chromatography	200
SO_4^{2-}	Ground, drinking waters	50-200 mg L^{-1}		1.2-1.3		Indirect titration (Gran's plot method) and Ba-ISE as sensor.		Sample passed through ion-exchange column, mixed with Li-acetate and injected in $BaCl_2$ stream	201
SO_4^{2-}	Natural waters	10-20 mg L^{-1}	0.5 mg L^{-1}	<2		Spectrophotometric method based on SO_4^{2-} ability to catalyze Methylene blue and Zr-aquocomplexes reaction and preconcentration.	PO_4^{3-}, F^- retained by resin	Ag 1-X8 anionic resin used for preconcentration. Results agree with those of turbidimetric method	202
SO_4^{2-}	Tap water	20-2000 mg L^{-1} 20-1000 mg L^{-1}*	26 mg L^{-1}	4		A growing liquid drop as windowless optical detection cell used for SO_4^{2-} spectrophotometric determination with Ba^{2+} performed with a blue ligth-emmiting diode and a plastic optical fiber.		Peak observed over several drops (3,5 and 4*). Liquid drop served also as reactor cell. Results confirmed by ion chromatography.	203
SO_4^{2-}	Fresh waters	2-20 μg mL^{-1}	0.3 μg mL^{-1}		35	Turbidimetric determination using as reagent $Pb(NO_3)_2$ and poly-(vinyl alcohol)	Cl^- interference eliminated (>55 °C)	Precipitation coil maintained at 61 °C	204
SO_4^{2-}	Well, rain water	0.5-5 ppm		0.75		Indirect spectrophotometric method based on sample passing through a Dowex 50W-X4 column followed by a $BaCrO_4$ powder column. Corresponding $BaCrO_4$ conc. to analyte conc. monitored.	Cations and anions Interferences eliminated		205
SO_4^{2-}	Natural water	25-1000 μg mL^{-1}	25 μg mL^{-1}	1.5		In-line preconcentration on Bio-Rad AGI-X8 resin column in injector sample loop and spectrophotometric detection using methyl thymol blue as reagent	Tolerance limit for PO_4^{3-} of 1-5 mg/L	Elution with NaCl solution stream	206
SO_4^{2-}	Natural water	50-10000 mg L^{-1}		1.7		Indirect determination by direct measurement of Pb with a coated tubular Pb-selective electrode using $Pb(ClO_4)_2$ as reagent			207

TABLE 2 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
SO_4^{2-}	Well, tap, bottled waters	2-30 μg mL^{-1} 30-150 μg mL^{-1} 1.5-150 μg mL^{-1}*		3.5 2.3*	30 12*	Normal and open-closed* FIA configurations and spectrophotometric detection using biacetyl mono-oxime nicotinoylhydrazone-Zr^{4+}-HCl as mixture reagent	PO_4^{3-}; MoO_4^{2-}; F^-; Fe^{3+} interfere in eqimolecular concn.	Sample plug could be recirculated through flow cell in open-closed system	208
SO_4^{2-}	Rain water	4-100 ppm			60	Spectrophotometric determination using a barium chloranilate reaction column incorporated in FIA system		Results agrred well with those obtained by standard manual method	209
SO_3^{2-}	Water	<440 μg/200 μL	0.8 μg/200 μL	1.02-0.76	40	SO_2 resulted from SO_3^{2-} and H_2SO_4 reaction, separated from liquid stream using a gas-liquid separator and measured with a UV-VIS spectrophotometer	Relatively free from interferences		210
SO_3^{2-}	Water	0.25-20 mg L^{-1}				Gas-diffusion separation of free and formaldehyde-bound SO_3^{2-} using 4,4'-dithiopyridine as colorimetric reagent	NO_2^-; S^{2-}; CN^-	Method used for SO_2 determination in air	211
S^{2-}	Waters	0.75-15 mg L^{-1}	0.08 mg L^{-1}			Fluorescent method based on Methylene blue production by oxidative coupling of S^{2-} with N,N-dimethyl-p- phenylenediamine in presence of Fe		Diode laser as excitation source and photodiode as detector	212
S^{2-}	Natural waters	0.25-25 μg mL^{-1}	0.25 μg mL^{-1}	1	20	Gas-diffusion separation of H_2S formed in reaction with H_2SO_4 and spectrophotometric determination using 1,10-phenentroline and Fe^{3+} as reagent	8 foreign ions investigated		213
Cl^-	Water	<6 μg mL^{-1}				Differential electrolytic potentiometry		Computer-controlled injector	214
Cl^-	Natural, potable water		0.2 ppm	1	60	UV-spectrophotometric method based on Hg-EDTA complex absorbance measuring.		Two lines manifold	215
Cl^- and F^-	Drinking water					Potentiometric detection using two ISEs in 2 serial flow-through cells			216
Cl^-	Potable, mineral waters	10-100 μg mL^{-1} 10-500 μg mL^{-1} 20-1000 μg mL^{-1}		1.42 2,87 3.2	15	Spectrophotometric method based on $Hg(SCN)_2$-Fe^{3+}-Cl^- reaction	Relatively free of interferences	Plug-sample splitting device. Three calibrations curves.	217
Cl^-	Natural waters	0.5-10 mg L^{-1}			25	Quasi-independent determinations and performing recovery tests FIA manifold used for Cl^--mercury thiocyanate-Fe^{3+} spectrophotometric determination and AgCl turbidimetric method			218
Cl^-	Natural waters	1-135 mg L^{-1}	20μM	3-8		Potentiometric detection using an ISE with polycrystaline membranes based on AgCl and Ag_2S in conjunction with $AgCl_2$ EVL-IM3 reference electrode			219

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
ClO_2	Potable water	0-0.5 μg mL^{-1}	0.02 μg mL^{-1}		50	On-line determination using chlorophenol red and gas diffusion unit	Metal ions, ClO_2^-,ClO_3^- interferences eliminated		220
ClO_2	Waters	0.005-1.5 ppm	5 ppb	2.4		Spectrophotometric determination using a purge-trap system for analyte separation and 4-aminoantipyrine and phenol reaction	Metal ions, ClO_2^-,ClO_3^- interferences eliminated		221
ClO_3^-	Natural waters	Low μg L^{-1} levels	5 nM			Ion-chromatography followed by osmate-catalyzes postcolumn reaction of ClO_3^- with I^- and I_3^- UV-detection		Simultaneous determination of ClO_2^-, BrO_3^-, NO_2^-	222
ClO_2; ClO_3^-	Drinking water					Iodometric detection and ion-chromatography			223
ClO_2^-; ClO_3^-	Drinking water	2-150 μM 2-100 μM		0.4 1.2		Reaction with I^- at pH=2 for ClO_2^- and pH=6 for ClO_2^- and ClO_3^-			224
ClO^-	Water	5-500 μg mL^{-1}	5 μg mL^{-1}	1.0	50	Chemiluminescent determination based on indole oxidation with H_2O_2 in presence of ClO^-	Relatively free of interferences	Indole prepared in iso-propanol. Reaction occurs in alkaline medium	225
ClO^-	Tap water	$1x10^{-8}$ – $4x10^{-5}$ g mL^{-1}	$8x10^{-9}$ g mL^{-1}	5		Chemiluminescence method based on luminol immobilization followed by elution with NaOH and mixed with sample stream		Immobilization of luminol on anion exchange resin column	226
ClO^-	Tap water	0.05-0.8 mg L^{-1}		0.8-1.3	120	Spectrophotometric determination using Rhodamine 6G as reagent			227
ClO^-	Waters	<4 ppm	90 μ L^{-1}			Rhodamine 6G chemiluminescence determination and its combination with electrochemical modification in presence of charged Pt electrode to quantify a number of chlorine-containing species			228
ClO^-, chloramine	Natural, drinking water	0.1-10 mg L^{-1}	0.05 mg	2.3		Spectrophotometric determination using 2,4-dinitrophenylhydrazine as reagent	Foreign ions interference tabulated		229
Chlorine species	Natural waters	1.6-4 mg L^{-1}	0.5 mg L^{-1}			Rhodamine 6G chemiluminescence with electrochemical analyte modification at a Pb electrode	No interferences		230
Free and combined residual chlorine	Natural waters	0.05-10 μg mL^{-1}	0.03 μg mL^{-1}		110	Spectrophotometric determination using 4-nitrophenylhydrazine and N-1-naphtylethylenediamine hydrochloride. For total residual chlorine reagent contained KBr, Br produced used as oxidizing reagent	ClO_2 interfered; ClO_3^-; ClO_2^-; NO_3^- interfered up to 3μg mL^{-1}	Combined residual chorine determined by difference	231

TABLE 2 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Free and combined residual chlorine	Potable water	0.1-8 mg L^{-1}	0.07 mg L^{-1}	0.5-3		Spectrophotometric determination using N,N-diehyl-p-phenylendiamine as reagent. For total chlorine reagent contained KI.		Combined chlorine determined by difference. Results compared with colorimetric and titrimetric method.	232
Residual chlorine	Tap water	0.1-1 mg L^{-1}	0.2 mg L^{-1}	2		Potentiometric determination using Pb-ISE		Results agreed with those obtained by colorimetric conventional method of o-tolidine	233
F^-	Water					Potentiometric method and on-line sample dilution and treatment		Simultaneous determination of phenols using an amperometric detector	234
F^-	Tap water	0.04-3.0 mg L^{-1}	0.03mg L^{-1}		45	Spectrophotometric method based on F^--Alizarin complexon-La^{3+} reaction		Reagent prepared in acetone-water medium	235
F^-	Natural, borehole water	1.9-1900 mg L^{-1}		0.6	60	F^--selective membrane electrode			236
F^-			0.012 µg mL^{-1}	3.2		Ion exchange preconcentration and wall-jet ion-sensitive electrode		Sensitivity >50 times that without ion-exchange resin	237
Cl^-; Br^-; I^-; F^-	Natural waters	<100 µM <5 µM <1 µM <5 µM		1		ISEs constructed from Ag_2S-AgCl and Ag_2S-AgI combined with suppresor columns of AgCl and amalgamated lead		Simultaneous determination. Results agreed with those obtained by three reference materials	238
Br^-	Natural waters	>40 µg L^{-1}	1 µg L^{-1}	0.45-6.4	100	Spectrophotometric method based on Br^- catalytic effect on 4,4'-bi-(dimethylamino)-diphenylmethane oxidation by Chloramine T			239
BrO_3^-	Drinking water	>15 µg L^{-1}	0.28 µg L^{-1}			Fluorimetric method using an anion-exchange column for separation and stopped-flow post-column reaction based on azo-dye sulfonaphthol-azo-rezorcinol oxidation by BrO_3^-			240
I^-	Rain, surface, ground water		0.1 ng mL^{-1}		50	Spectrophotometric method based on I^- catalitic destruction of Fe(III)-SCN^--cetylpyridinium chlorine complex colour			241
NO_2^-	River water	2.0-100 ng mL^{-1}	0.6 ng mL^{-1}	1.3-2.4	30	Colorimetric method based on NO_2^- catalytic effect on oxidative coupling of N-phenylen-p-phenylenediamine with N,N-dimethylaniline		Reaction occurs in presence of BrO_3^-	242

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
NO_2^-	Natural waters	<5 mg L^{-1}	0.053 mg L^{-1}		49	NO_2^- diazotized with N-(1-naphtyl)-ethylendiammonium dichloride in SIA with spectrophotometric detection			243
NO_2^-	River water	0.5-6.6 μg/5 mL		1.13-1.55		NO_2^- reaction with p-aminoacetophenone/p-nitroaniline and coupling with 1-naphtol followed by azo-dye complexes adsorption on inactivated naphtalene packed in a column and spectrophotometric detection		Elution with ethanol	244
NO_2^-	Waters	4-48 μg mL^{-1} 0-4 μg mL^{-1}		3.63 2.33	40	Stopped-flow FIA with spectrophotometric detection of NO_2^--sulfanilic acid-α-naphtylamine complex	Relatively free of interferences	Two working variants	245
NO_2^-	Waters	8 ng mL^{-1} - 1 μg mL^{-1}	1.6 ng mL^{-1}	1.5		Chemiluminescence reation between analyte, luminol and I_2.	23 ions inferference studied		246
NO_2^-	Natural waters	0.1-4 μM		3.4		Amperometric determination based on inhibitory effect on I_2-EDTA photochemical reaction and using a Pt electrode	23 ions interference studied		247
NO_3^-	Bottled, spring waters		0.05 μg mL^{-1}	2.3-2.6	35	NO_3^- reduction on Cd-column to NO_2^- and Cd^{2+} measured by ETAAS	Na, Ca, Mg eliminated on Amberlite		248
NO_3^-	River, drinking water		2μM		60	Square-wave polarography and on-line deaeration using NO_3^--uranil ion catalytic reaction			249
NO_3^-	River, well water	0.1-190 mg mL^{-1} 0.4-30 mg mL^{-1}	50 μg L^{-1} 40 μg L^{-1}			Amperometric method using a glassy modified electrode and NO_3^- reduction on Cd-column to NO_2^-. Fibre optic sensor based on dual wavelength absorption for NO_3^-.		Comparison between two detection method	250
NO_2^- and NO_3^-	Water		0.085 μg L^{-1}	0.77 1.56	50	NO_3^- reduction on Cd-column to NO_2^- followed by spectrophotometric detection of NO_2^- -N-(1-naphtyl)-ethylendiammonium dichloride complex		Simultaneous determination of NO_2^- - NO_3^-	251
NO_2^- and NO_3^-	Water	0.010-2.50 μg mL^{-1} 0.02-3.50 μg mL^{-1}	0.001 μg mL^{-1} 0.002 μg mL^{-1}		20	Spectrophotometric method based on NO_2^- catalytic effect on gallocyanine oxidation by BrO_3^-. NO_3^- reduction on Cd/Cu-column to NO_2^-		Splitting injected sample in two segments. Simultaneous determination of NO_2^- and NO_3^-	252
NO_2^- and NO_3^-	Natural waters		0.5 μg L^{-1} 2.5 μg L^{-1}	2	30	Spectrophotometric method based on NO_2^- catalytic effect on naphtol green oxidation by BrO_3^-. NO_3^- reduction on Cd/Cu-column to NO_2^-		Double zone injection technique. Simultaneous determination of NO_2^- - NO_3^-	253

TABLE 2 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
NO_2^- and NO_3^-	Natural waters		$1x10^{-7}$ M			NO_3^- reduction on Cd/Cu-column to NO_2^- followed by spectrophotometric detection of NO_2^--sulphanilamide-N-(1-naphtyl)-ethylendiamine complex		Splitting injected sample in two segments. Simultaneous determination of NO_2^- - NO_3^-	254
NO_2^- and NO_3^-	Natural waters		$3x10^{-8}$ M		30 10*	NO_3^- reduction in a tubing coiled on low-pressure mercury lamp followed by diazotation-coupling reaction and spectrophotometric detection		Buffered solution containing phosphate and EDTA as carrier. Splitting carrier stream after injection valve for simultaneous determination*.	255
NO_2^- and NO_3^-	Water	0.06-4 mg L^{-1}		>0.5		Spectrophotometric determination using proflavin as reagent and Cd-Cu column to reduce NO_3^- to NO_2^-	Foreign compounds interference tabulated	Reagent and sample merged into a mixing chamber.	256
NO_2^- and NO_3^-	Tap water	0.002-10 mg L^{-1}		1.2	20	Spectrophotometric detection using N-(1-naphthyl)-ethylene diammonium dichloride and sulfanilamide as reagents. NO_2^- oxidation with $K_2S_2O_8$ and NO_3^- reduction with hydrazine, $CuSO_4$ and $ZnSO_4$ to nitrogen	Little interference observed		257
NO_2^- and NO_3^-	Natural water	46-460 ng mL^{-1} 62-620 ng mL^{-1}	27 ng mL^{-1}	1.3		Spectrofluorimetric detection using phenosafranine, H_2SO_4 and $KBrO_3$ as reagent mixture. A Cu-Cd column allowed NO_3^- determination.		A selection valve permitted NO_2^- and NO_3^- simultaneous determination.	258
PO_4^{3-}	Drinking waters		0.16-0.32 μM	1.0		Chemiluminescent method based on PO_4^{3-}-pyruvate oxidase and H_2O_2 released detected by luminol, reaction catalysed by Arthromyces ramosus peroxidase		Sensor works 48 days using pyruvate oxidase immobilized on Chitoperl BCW-2601 beads. Results agree with those of Methylene blue method.	259
PO_4^{3-}	Natural, drinking waters	1-30 μg mL^{-1}		1.8	30	Spectrophotometric detection based on Methylene blue method.	Relatively free of interferences	Several mono-channel injection device that can be opened/shut simultaneously	260
PO_4^{3-}	Natural waters	0.1-2 μM	39 nM	1.41-2.62	20	Enzymatic reactor consisting of purine nucleoside phosphorylase and xanthine oxidase and chemiluminescent determination of resulted H_2O_2 with bis[2-(3,6,9-trioxadecyloxycarbonyl)-4-nitrophenyl]oxalate, Rhodamine B and Triton X-100		Enzymes immobilized on glass beads	261

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
Ortho- and pyro-phosphate	River water	5-100 ng mL^{-1}	0.3 ng mL^{-1}			Chromaton N-AW-HMDS extraction minicolumn and pos-column spectrophotometric detection based on molybdenum blue produced.		Elution with HCl	262
PO_4^{3-}	Natural waters	0.02-0.4 ppm	12 ppb	0.013-0.13 (c.v.)	55	Spectrophotometric determination using molybdate and Rhodamine B		Baseline drift corrected by polyvinyl alcohol	263
PO_4^{3-}; SiO_3^{2-}	Natural waters	0.05-2.5 ppm 0.8-15 ppm	0.05 ppm 0.8 ppm		20	Spectrophotometric determination using molybdate and Rhodamine B as regents	Interfering species discussed	Splitting of sample and molybdate mixture	264
Total-P	Natural waters	1.0-50 μg L^{-1}	0.6 μg L^{-1}	1.0		Spectrophotometric detection based on Methylene blue method using a highly sensitive detection system		Detection system composed of a thin, long, light path made of PTFE rod as absoption cell along with a GaAlAs semiconductor laser emitting as light source	265
Total-P	Natural waters	0-18 mg L^{-1}	0.15 mg L^{-1}		32 (8x4)	On-line digestion and filtration followed by molybdenum blue method		Digestion performed using UV photoreactor and thermal digestion unit connect in series	266
Total-P	Natural waters	1-50 μg L^{-1}	0.6 μg L^{-1}	1		Thin long flow-through cell in conjunction with GaAlAs semiconductor laser source and a photodiode detector. Mixture of ascorbic acid, Sb-K tartrate and ammonium molybdate used as color reagent		Results agreed with official method	267
Total-P	Natural waters	<18 mg L^{-1}	0.09 mg L^{-1}		32	Digestion in a modified domestic microwave oven and measuring of phosphomolibdenum blue product absorbance using photometer incorporating red a light-emitting diodes		Filtration on-line	268
Dissolved P	Natural waters	100-1000 μg L^{-1} 10-100 μg L^{-1}*	27 μg L^{-1} 1.1 μg L^{-1}			P-compounds oxidation by exposure to UV radiation and spectrophotometric detection using Molybdenum blue method		P-compounds exemplified by phytic acid and phosphate*	269
Dissolved P	Run off waters	0-15 mg L^{-1}	7 μg L^{-1}		40	On-line photo-oxidation with a low power UV lamp and spectrophotometric detection using Molibdenum blue method	Al^{3+}; Si^{4+}; Fe^{2+}; Fe^{3+} interference eliminated	Results agreed with those obtained by batch spectrophotometric reference method	270

TABLE 2 (continued)

Species	Sample Matrix	Determination range	LOD	RSD (%)	Sampling rate (h^{-1})	Determination method	Interferences	Other features	Ref.
CN^-	Waters		0.5 μg L^{-1}		10	Gas-diffusion separation followed by CN^- transferred reaction with o-phtalaldehye and glycine to form a highly fluorescent isoindole derivate	Tolerate 40-fold excess of sulfite	$Zn(CN)_4^{2-}$; $Cu(CN)_3^{2-}$; $Cd(CN)_4^{2-}$; $Hg(CN)_4^{2-}$; $Hg(CN)_2$; $Ag(CN)_2^-$; completely recovered and $Ni(CN)_4^{2-}$ low recovery	271
CN^-	Waters		5 μg L^{-1} 0.4 μg L^{-1} 0.25 μg L^{-1} 0.03 μg L^{-1}			Several fluorimetric reactions: fluoresceine-iodide method; Pd-HQS-Mg method; OPA method; NDA method			272
CN^-	River water	0.001-0.1 ppm 0.01-0.5 ppm		3.1		Chemiluminescent determination using uranine/di-dodecyldi-methyl ammonium bromide as reagent	Co-existing anions interference listed	Determination carried out at 5 °C	273
CN^-	River water	Over three orders of magnitude	5 pg	3.3		Chemiluminescent system CN^--fluorescein applied			274
CO_3^{2-}	Waters	<20 mM	10 μM	1	45	Gas-diffusion of CO_3^{2-} as CO_2 across PTFE gas membrane from an acid stream into a tris-(hydroxymethyl-amino)-methane and KCl followed by detection with a bulk acoustic wave impedance sensor	H_2S, SO_2; HF, HCOOH; CH_3COOH interfere	Direct determination of total inorganic CO_3^{2-} and indirect determination of total organic C content based on wet chemical oxidation of sample	275
H_2O_2	Rain water	1.0×10^{-8}-6.0×10^{-5} M	6.0×10^{-9} M	1.6-2.3		Chemiluminescent method based on sample mixture with OP and injection in acidic $KMnO_4$ stream		Improved chemiluminescence in presence of OP micellar system	276
H_2O_2	Surface, tap waters		0.2 μg L^{-1}			Fluorimetric method based on enzymic catalysed reduction of H_2O_2 in presence of p-hydroxyphenylacetic acid	O_3; Cl_2; dissolved organic matter	Comparison with two other methods	277
Dissolved O_2	Waters		0.02mg L^{-1}	1-5	60	Photometric detection of colored oxidation product between Leucomethylene blue and O_2		Reverse stopped-flow FIA system	278
Dissolved O_2	Natural waters	0.9-5.5 mg L^{-1}	0.4 mg L^{-1}	0.6-2.2		Methylene blue immobilized on Dowex 50X8-299 resin column and spectrophotometric detection		Results agreed with those obtained using an electrochemical probe	279
COD	Well, river, canal water	<100 mg L^{-1}	1.5 mg L^{-1}	2.1		Oxidation adding drop wise of $K_2Cr_2O_7$ to H_2SO_4, resulted solution passed through a reaction coil enclosed by a microwave oven then through a cooling coil followed by absorbance measurement.		Results agreed with those obtained by standard method	280

Note: FIA — flow injection analysis; FI — flow injection; AAS — atomic absorption spectrometry; FAAS — flame absorption spectrometry; CVAAS — cold vapor atomic absorption spectrometry; HGAAS — mercury atomic absorption spectrometry; ICP — inductive coupled plasma; MS — mass spectrometry; ISE — ion-selective electrode; ETAAS — electrothermal atomic absorption spectrometry; GFAAS — graphite furnace atomic absorption spectrometry; IBMK— iso-buthyl-methyl ketone; AES — atomic emission spectrometry; Concn. — concentration; Detn. — determination.

Elsholz et al.[39] reported *on-line* determination of mercury in river water at a German monitoring station. The monitor provides *on-line* mercury determination at concentration of 20 to 1000 ng Hg mL^{-1}. It used sequential injection analysis (SIA). A 5-day stand-alone operation was performed successfully.

A similar method for monitoring of total mercury in the River Elbe, including a FIA-device for *on-line* digestion, was also reported.[40]

Li and Wang[41] described automatic analytical methods for monitoring water quality at power plants with reversed flow-injection analyses. The methods are as follows: several and simultaneous determinations were used for 0.2 to 30 ppm phosphate and 0.02 to 5 ppm silicate in boiler water and ppm sulfate in feed water and natural water. The advantage and deficiencies of applying reverse FIA to *on-line* monitoring and water-quality analysis in power plants were also discussed.

IV. CONCLUSIONS

Flow-injection methods of analysis have been used widely in the analysis of environmental parameters, and especially in water analysis, to which they are particularly adapted. In the Hansen database,[11] which may be accessed through the Internet, more than 850 citations related to water analysis are found, most of which are based on the use of FIA. The potential and great capability of different FIA systems in water laboratories for cations and anions determination are demonstrated in this review. It appears that flow-injection analysis has taken a prominent place in routine water laboratories where a widespread application of FIA methodologies is possible.

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