Flow-injection analysis of substances in water. Part 2. Cations. A critical review

JF van Staden
Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa.

Abstract

For effective control of water quality, a routine water laboratory should be geared to analyse large numbers of samples rapidly and reliably, making use of proven methods of analysis. A critical review of the present status of flow-injection analysis (FIA) of cations in water is given, highlighting the possibilities of FIA methods in this area, such as methods for the determination of ammonium, calcium, magnesium, potassium, sodium, iron, copper, aluminium, lead, chromium, zinc, cadmium, nickel, cobalt, manganese and molybdenum.

Introduction

The first paper (Van Staden, 1987) in this series presented a critical review of flow-injection analysis (FIA) applications for the determination of anions in water samples. A short introduction to the basic characteristics of FIA was also given (Van Staden, 1987). The early history of the concept of flow-injection analysis has been thoroughly reviewed by Stewart (1981) and Mottola (1981). The basic theoretical background related to this technique has been discussed in detail by Ruzicka and Hansen (1980, 1981), Reijn *et al.* (1980), Vanderslice *et al.* (1981), Painton and Mottola (1981), Valcarcel and Luque de Castro (1987) and Van Staden (1989). The advantages of this technique have been discussed in detail in comprehensive reviews presented by Ruzicka and Hansen (1980, 1981), Betteridge (1978), Ranger (1981), Valcarcel and Luque de Castro (1987), Van Staden (1981) and by Van Staden (1989). Among the advantages are flexibility, reliability and reproducibility as well as ease of automation and high sample throughput. The beauty of FIA is that it can be interfaced with almost any detector (spectrophotometry, AA, ICP etc.) and that, in the case of cations, it can in fact serve as an automated manipulator for tedious manual procedures resulting in simple combined systems with a relatively high sample throughput. In this paper a critical review of the potential use of different FIA systems for cations in water laboratories is illustrated.

Ammonium ion

Several procedures have been proposed for the determination of the ammonium ion (ammonia) in water (Table 1) by using the FIA concept. The three spectrophotometric methods that appear to be used almost universally are the indophenol blue method (Berthelot reaction), the gas diffusion/acid-base indicator procedure and the use of Nessler's reagent. The ammonium ion has also been determined by fluorimetry and a modification of the Shinn reaction where the ammonium ion is first oxidised to nitrite before diazotation and coupling.

The Nessler reaction has been adapted successfully to flow-injection analysis for the turbidimetric determination of ammonia in natural water samples by Krug *et al.* (1979). Ammonia reacts with Nessler's reagent consisting of mercury (II) iodide and potassium iodide in alkaline solution to form a deep brown to chocolate colloidal precipitate suspension which is measured at 410 nm. In the optimised procedure aliquots of 30 $\mu\ell$ are injected into an alkaline carrier stream before the addition of Nessler's reagent. The method is suitable for the determination of ammonia in water samples in the range 0,5 to 6 mg/ℓ at a sampling rate of 120/h. Bergamin *et al.* (1980) improved the method to the μg/ℓ level employing the merging zones approach with electronically operated proportional injector to minimise the amount of Nessler's reagent used and to avoid base-line drift. Ammonium ions are preconcentrated in an ion-exchange column incorporated as part of the sample loop in the loading position. The preconcentrated sample is flushed into the conduits of the FIA system in the injected position. A LED sensor is used as detector allowing the entire process to be followed colorimetrically. The procedure is characterised by a precision of about 2%, a sampling rate of about 40/h, a reagent consumption of 40 $\mu\ell$ per sample and is almost free of interferences. Recoveries between 95 to 105% are obtained for the analysis of rain-water samples with ammonium contents of less than 200 μg/ℓ.

Oshima (1981) applied the indophenol blue method for the determination of ammonium in environmental water. Aliquots of 785 $\mu\ell$ were injected into a water carrier stream before sequential addition of the alkaline phenol and hypochlorite reagents. Reaction development took place in a reaction coil at 80°C before measurement at 635 nm. A sampling rate of 100/h was achieved and the method was suitable in the range 0 to 400 μg/ℓ at a precision of 6,2%. Krug *et al.* (1983) used a modified Berthelot reaction for the determination of ammonium in natural waters. The authors employed a zone-trapping technique where the main portion of the reacting sample zone is retained at a temperature of 38°C until about 80% of the reaction is complete without significant loss in sampling frequency. Merging zones and the application of an injector-commutator formed part of the procedure. A precision of 0,5% was obtained for a working range of 50 to 500 μg/ℓ at a sample frequency of 90 to 100/h. A spectrophotometric indophenol blue determination of ammonium in rain water has also been proposed by Slanina *et al.* (1980) using a computer-controlled multichannel continuous flow system. Water samples from a single sample were channelled via three sampling valves for the simultaneous determination of ammonium, nitrate and chloride. With 150 $\mu\ell$ samples the FIA system covered a working range of 0,2 to 20 mg/ℓ at a sampling rate of 18 to 35/h. The precision was 3%.

A gas diffusion/acid-base indicator procedure for the determination of ammonium in canal water was described by Van Son *et al.* (1983). Aliquots of 29 $\mu\ell$ were injected into an alkaline stream in which the ammonium ions were converted to ammonia

Received 18 October 1988

TABLE 1
AMMONIUM ION

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Natural waters	120	0,5-6,0	–	30	Nessler's reagent. Mercury (II) iodide and potassium iodide in alkaline solution Turbidimetric	Single line carrier stream and also sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Krug *et al.* (1979)
Natural waters (rain water)	40	<0,20	2	–	Nessler's reagent	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector. Merging zones and injector-commutator	Spectrophotometry	Bergamin *et al.* (1980)
Environmental waters	100	0-0,40	6,2	785	Berthelot's reaction (Indophenol blue method)	Sequential addition of reagents to a water carrier stream. Temperature of reaction coil 80°C	Spectrophotometry	Oshima (1981)
Natural waters	90-100	0,05-0,50	0,5	100	Modified Berthelot reaction	Merging zones and injector-commutator with zone-trapping. Reacting sample zone retained at 38°C	Spectrophotometry	Krug *et al.* (1983)
Canal water	100	0,017-1,70	3	29	Absorbance change of an acid-base indicator solution	Sequential addition of reagents to a reagent carrier stream and gas diffusion through a gas-permeable membrane	Spectrophotometry	Van Son *et al.* (1983)
Rain water	18-35	0,2-20	3	150	Berthelot's reaction	Sequential addition of reagents to a water carrier stream	Spectrophotometry	Slanina *et al.* (1980)
River water	40	0,03-0,15	–	40	Reaction with o-phthalaldehyde in the presence of 2-mercaptoethanol to form a fluorescence product	Sequential addition of reagents to a water carrier stream	Fluorimetry	Mikasa *et al.* (1985)
Water	25	0-5	3,8	140	Absorbance change of an acid-base indicator solution	Sequential addition of reagents to a reagent carrier stream and gas diffusion through a gas-permeable membrane	Spectrophotometry	Kuwaki *et al.* (1987)
Natural waters	40	0-0,10	1,67	2 000	Oxidation of ammonium to nitrite. Diazotation of nitrite with sulphanilamide. Coupling of product with N-(1-naphthyl)-ethylenediammonium dichloride	Merging zones	Spectrophotometry	Youxian (1987)

molecules. Ammonia diffused through a gas-permeable membrane (a piece of Teflon tape with a thickness of 45 μm) and reacted with the acidic form of bromothymol blue to change it to the basic form. The resulting absorbance change was measured spectrophotometrically at 620 nm in a flow-through cell. The response was linear between 0,017 and 1,70 mg/ℓ (17 to 1 700 μg/ℓ, which is very sensitive) with a precision of 3%. The sampling rate was 100/h. This procedure is excellent and should revolutionise the determination of ammonium at very low concentrations in most water laboratories.

A fluorimetric method for the determination of ammonia in river water was also proposed by Mikasa *et al.* (1985). Ammonia reacted with o-phthalaldehyde in the presence of 2-mercaptoethanol to form a fluorescent substance at pH 9,5. Fluorescence was measured at 486 nm. Trace amounts of ammonia (3 to 150 μg/ℓ) in river water were determined at a sampling rate of 40/h.

Youxian (1987) described a method where the ammonia was oxidised to nitrite with sodium hypobromite. The nitrite is diazotised and coupled with N-(1-naphthyl) ethylenediammonium dichloride to form a coloured product which is measured spectrophotometrically. The merging zones concept was used to produce a sampling rate of 40/h in the range 0 to 0,10 mg/ℓ with a precision of 1,67%.

Calcium

Various detectors have been implemented as sensors in the FIA determination of calcium in water (Table 2) and this plays a key role in the formulation of the FIA system used in this regard.

Calcium was determined simultaneously with magnesium, sodium and potassium in a simple, rapid automated procedure by using atomic absorption spectrophotometry as sensor for both calcium and magnesium (Basson and Van Staden, 1980). Samples drawn from a sampler were injected into a water carrier stream, reagents added downstream and the samples splitted to a dual-beam atomic absorption and dual-beam flame photometer for detection. This allowed the simultaneous determination of calcium, magnesium, sodium and potassium at a sampling rate of up to 128/h (approximately 500 analyses per hour) with a precision of better than 2,7% for calcium in surface, ground and domestic water. An on-line preconcentration flow-injection system with inductively coupled plasma atomic emission spectrometry (ICP) as detector was also proposed for the determination of calcium amongst a variety of ultra-trace metals (barium, beryllium, cadmium, cobalt, copper, lead, magnesium, manganese, nickel and zinc) in tap-water and rain-water runoff (Hartenstein *et al.*, 1985). A miniature column of Chelex-100 was used as preconcentrator. The procedure could not be described as very successful as the sampling rate of 12 to 20 determinations per hour was less than the conventional ICP sample throughput of 30 to 60/h.

Spectrophotometry with a variety of organic colour-forming reagents was, however, used in the majority of FIA systems for the determination of calcium. Hansen *et al.* (1978) exploited o-cresolphthalein complexone as colour-forming reagent injecting aliquots of 30 μℓ waste water at a rate of 100 to 110/h into a FIA system covering a concentration range of 1 to 30 mg/ℓ. The authors also proposed a potentiometric FIA method for the determination of calcium for the same type of water samples employing a single line FIA system (aliquots of 30 μℓ, sampling rate 100 to 110/h) and covering a concentration range of 20 to 400 mg/ℓ. Borate buffer at pH 9,4 with sodium chloride as ionic strength

TABLE 2
CALCIUM

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Waste waters	100-110	1-30	–	30	o-Cresolphthalein complexone reagent	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Hansen *et al.* (1978)
Waste waters	100-110	20-400	–	30	Borate buffer at pH 9,4. Sodium chloride as ionic strength adjustment buffer	Single line carrier stream	Ion-selective electrode	Hansen *et al.* (1978)
Surface, ground and domestic water	128	10-125	2,7	200	Lanthanum nitrate solution in a cesium and lithium medium	Sequential addition of reagent to a water carrier stream followed by sample splitting. Simultaneous analysis of 4 elements with a single sample	Atomic absorption spectrophotometry	Basson and Van Staden (1980)
Natural waters	180	0-500	1	200	Glyoxal bis (2-hydroxyanil) as colour-forming reagent	Merging zones	Spectrophotometry	Jacintho *et al.* (1981)

TABLE 2 (continued)

Tap and pond water	80	0,8-7,2	–	20	Exchange reaction between calcium and the zinc complex of ethylene glycol bis (2-aminoethyl-ether) tetraacetic acid (EGTA) in the presence of 4 (2-pyridylazo)-resorcinol (PAR)	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Nakagawa *et al.* (1983)
Potable and raw water	–	0,7-4000	~2%	50	Tetraborate buffer at pH 9,4. Sodium chloride as ionic strength adjustment buffer	Single line carrier stream	Ion-selective electrode	Frend *et al.* (1983)
Natural and tap waters	40	1,2-3,9	1,12	50	Hydroxynaphthol blue as complex forming agent	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Uchida *et al.* (1985)
Tap and well water	60	20-2000	0,2	200	Titration with EDTA with calmagite as indicator	Pseudotitrations with the aid of a microcomputer-controlled analyser	Spectrophotometry	Koupparis *et al.* (1985)
Well, river and waste water	60-90	2-4000	3,5	100	Sodium chloride as ionic sttength adjuster containing 10^{-6} mol/ℓ calcium chloride to stabilise the baseline	Single line carrier stream	Tubular PVC membrane ion-selective electrode	Alonso *et al.* (1986)
Tap and rain runoff water	12-20	1x10^{-3}-0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrometry	Hartenstein *et al.* (1985)
Water	100	4-32	–	–	Exchange reaction between calcium and the zinc complex of EGTA	Single line carrier stream	Spectrophotometry	Qingxun (1984)
Natural, drinking, urban and bottled water	30-35	2-400	1,5	1 800	FIA titration of calcium with EDTA and murexide and calcium and magnesium with EDTA and eriochrome black T	Sequential addition of reagents to a reagent carrier stream. Simultaneous determination of calcium and magnesium using different indicators	Spectrophotometry	Canete *et al.* (1987)

adjustment buffer was used as carrier stream and the method also allowed the simultaneous determination of pH and calcium. The merging-zones approach was employed by Jacintho *et al.* (1981) using glyoxal bis (2-hydroxyanil) as sensitive and selective spectrophotometric reagent for the determination of calcium in natural waters. With the merging zones concept the intermediate complex which was formed, was added to the sample zone in a reproducible manner obviating any instability which placed restrictions on the method. A sampling rate of 180/h was achieved covering the range of 0 to 500 mg/ℓ with a precision of less than 1% which indicated that the procedure gave excellent results. A method was also proposed (Uchida *et al.*, 1985) for the determination of calcium in natural and tap waters with spectrophotometric detection using hydroxynaphthol blue as complex forming indicator. The sampling rate was rather slow, 40/h, with a narrow linear range (1,2 to 3,9 mg/ℓ) and a precision of 1,12%. The indirect spectrophotometric determination of calcium in the presence of interferences like magnesium, phosphate and

sulphate was described by Nakagawa *et al.* (1983). The method is based on the exchange reaction between the calcium and the zinc complex of ethylene glycol bis (2-aminoethylether) tetraacetic acid (EGTA) in the presence of 4- (2-pyridylazo) resorcinol (PAR)

$$Ca + Zn(EGTA) + 2PAR \rightleftharpoons Zn(PAR)_2 + Ca(EGTA).$$

The results obtained are summarised in Table 2. The features of a similar procedure (Qingxun, 1984) are also outlined in Table 2. FIA titration with EDTA was applied by Koupparis *et al.* (1985) for the determination of calcium in tap and well water using calmagite as indicator (Table 2). The same concept was adapted by Canete *et al.* (1987) for the simultaneous determination of calcium and magnesium (water hardness) in natural, drinking, urban and bottled water using EDTA and murexide for calcium and EDTA and eriochrome black T for the sum of calcium and magnesium (Table 2). Tubular PVC membrane electrodes (Frend *et al.*, 1983; Alonso *et al.*, 1986) have also been proposed as sensors for the FIA determination of calcium in water. The performances of these FIA-ion-selective systems are outlined in Table 2.

Magnesium

In most of the publications reported to date, magnesium was determined simultaneously (Basson and Van Staden, 1980; Canete *et al.*, 1987), sequentially (Alonso *et al.*, 1986) or by using the same detector (Hartenstein *et al.*, 1985) sequentially in a single channel system for single determinations. More details are given in Table 3. Magnesium was also determined spectrophotometrically by a magnesium ligand complex formed (Wada *et al.*, 1983b), or by a method based on the inhibitory ef-

TABLE 3
MAGNESIUM

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Surface, ground and domestic water	128	0-100	1,8	200	Lanthanum nitrate solution in a cesium and lithium medium	Sequential addition of reagent to a water carrier stream followed by sample splitting. Simultaneous analysis of 4 elements with a single sample	Atomic absorption spectrophotometry	Basson and Van Staden (1980)
Tap and pond waters	80	0,2-2,4	0,66	40	Magnesium ligand complex (magnesium-CPR chelate)	Sequential addition of reagent to a reagent carrier stream	Spectrophotometry	Wada *et al.* (1983b)
Well, river and waste water	60-90	0-10	–	100	Sodium chloride as ionic strength adjustor containing 10^{-6} mol/ℓ calcium chloride to stabilise the base line. Added for ion-selective electrode	Single line carrier stream	Atomic absorption spectrophotometry	Alonso *et al.* (1986)
Tap and rain water	12-20	1×10^{-3} – 0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrometry	Hartenstein *et al.* (1985)
Natural, drinking, urban and bottled water	30-35	2×10^{-3} – 0,28	1,5	1 800	FIA titration of calcium with EDTA and murexide and calcium and magnesium with EDTA and eriochrome black T	Sequential addition of reagents to a reagent carrier stream. Simultaneous determination of calcium and magnesium using different indicators	Spectrophotometry	Canete *et al.* (1987)
Drinking waters	60	0,5-8	2	125	Method based on the inhibitory effect of Mg (II) on the succinimidedioxime (SIDO) oxidation catalysed by Mn (II)	Sequential addition of reagents to a reagent carrier stream. Reaction proceeds at 35 °C	Spectrophotometry	Forteza *et al.* (1987)

fect of Mg (II) on the succinimidedioxime (SIDO) oxidation catalysed by Mn (II) (Forteza *et al.*, 1987). A very stable magnesium chelate around pH 10 is formed in the reaction between magnesium and 1-(2-hydroxy-3-sulfo-5-chloro-1-phenylazo)-2-naphthol-3,6-disulfonic acid (CPR) which is detected at 510 nm. An excellent precision of 0,66% was achieved for the determination of magnesium in tap and pond waters at a sampling rate of 80/h in the range 0,2 to 2,4 mg/ℓ. In the procedure proposed by Forteza *et al.* (1987) a sample frequency of 60/h was obtained, the range extended to 0,5 to 8 mg/ℓ, but the precision dropped to 2%.

Potassium and sodium

Sodium (Table 5) and potassium (Table 4) have been determined simultaneously in a simple, rapid procedure using flame photometry as detector (Basson and Van Staden, 1980). Four elements were determined simultaneously (the other two being calcium and magnesium) from a single sample at a rate of approximately 500 analyses/h. For more details see Tables 4 and 5. A solvent extraction-flow-injection procedure with spectrophotometric detection was also described for the determination of potassium in river water. The sampling rate of 50/h is rather slow, but the method is very sensitive. Unfortunately no precision was given.

Iron

The majority of methods described up to now for the determination of iron, made use of spectrophotometric detection based on the formation of coloured products of iron with ferrozine (Dutt *et al.*, 1976), 1,10-phenanthroline (Mortatti *et al.*, 1982b), bathophenanthroline (Rios *et al.*, 1985), 2-(3,5-dibromo-2-pyridylazo) -5-[N-ethyl-N- (3-sulfopropyl) amino] phenol (Wada *et al.*, 1983a) and 2-nitroso-5- (N-propyl-N-sulphopropylamino) phenol (Ohno and Sakai, 1987). Broekaert and Leis (1979) used a low-power argon plasma with Meinhard nebuliser for the FIA-inductively-coupled plasma atomic emission spectrophotometric determination of iron at a sample frequency of 60/h in the range 0,05 to 20 mg/ℓ in waste-water samples. Although 500 µℓ samples were used, the precision of 4 to 7% was rather poor. Dutt *et al.* (1976, 1977) used a closed flow-through system for the determination of iron with ferrozine (Dutt *et al.*, 1976) or thiocyanate (Dutt *et al.*, 1977). Repetitive determinations were obtained based on sample injection into a chamber in a closed loop system of circulating reagent. Reagent consumption was restricted to a minimum which resulted in reducing operating cost and time as the authors claimed a sample throughput of up to 350/h. An excellent procedure for the determination of iron in natural waters was proposed by Mortatti *et al.* (1982b), measuring the absorbance of the iron (II)-1,10-phenanthroline complex at

TABLE 4
POTASSIUM

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (µℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Surface, ground and domestic water	128	0-40	1,7	200	Lanthanum nitrate solution in a cesium and lithium medium	Sequential addition of reagent to a water carrier stream followed by sample splitting. Simultaneous analysis of 4 elements with a single sample	Flame photometry	Basson and Van Staden (1980)
River water	~50	0-3,9	–	100	Dibenzo-18-crown-6	Sequential addition of reagents to a reagent carrier stream followed by solvent extraction	Spectrophotometry	Iwachido *et al.* (1986)

TABLE 5
SODIUM

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (µℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Surface, ground and domestic water	128	0-150	2,1	200	Lanthanum nitrate solution in a cesium and lithium medium	Sequential addition of reagent to a water carrier stream followed by sample splitting. Simultaneous analysis of 4 elements with a single sample	Flame photometry	Basson and Van Staden (1980)

TABLE 6
IRON

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Lake and tap water	–	0-45	1,5	1 000	Ferrozine	Closed loop system. Kinetic analysis	Spectrophotometry	Dutt *et al.* (1976)
Waste waters	60	0,05-20	4-7	500	–	Single line carrier stream	Inductively-coupled plasma atomic emission spectrophotometry	Broekaert and Leis (1979)
Natural waters	180	0,1-30	1	100	1,10-phenanthroline method	Sequential addition of reagents to a reagent carrier stream with injector-commutator	Spectrophotometry	Mortatti *et al.* (1982b)
Potable waters	30	0,02-0,44	–	200	2- (3,5-dibromo-2-pyridylazo) -5-[N-ethyl-N-(3-sulfopropyl) amino] phenol reagent	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Wada *et al.* (1983a)
Waste waters	34	0,1-3,0	0,15	–	Bathophenanthroline	Reagent injection into a sample carrier stream (reversed flow-injection analysis)	Spectrophotometry	Rios *et al.* (1985)
Boiler and well water	25	0-0,10	1	120	2-Nitroso-5-[N- propyl-N-sulphopropyl-amino) phenol	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Ohno and Sakai (1987)
Industrial waters	350	22-56	–	2 500	Thiocyanate	Closed loop system	Spectrophotometry	Dutt *et al.* (1977)

512 nm. Ascorbic acid was used to reduce any iron (III) to iron (II). The proposed procedure covered the range 0,1 to 30 mg/ℓ at a sampling rate of 180/h with a precision of better than 1%. Rios *et al.* (1985) improved the previous procedure by proposing a more sensitive method (0,1 to 3,0 mg/ℓ) with excellent precision (0,15%) using bathophenanthroline as reagent and a reversed flow-injection system for the simultaneous determination of iron with copper and aluminium. More details on the other spectrophotometric procedures are given in Table 6.

Copper

Various flow-injection procedures have been developed for the determination of copper in water. These include spectroscopic methods with inductively-coupled plasma atomic emission spectrometry (Broekaert and Leis, 1979; Hartenstein *et al.*, 1985) and atomic absorption spectrophotometry (Olsen *et al.*, 1983; Fang *et al.*, 1984a, 1984b; Marshall and Mottola, 1985) as well as electrochemical methods with polarography (Frenzel and Brätter, 1986) and ion-selective electrodes (Van der Linden and Oostervink, 1978; Van Staden and Wagener, 1987; Zolotov *et al.*, 1987). At this stage the results obtained with inductively-coupled plasma atomic emission spectrometry do not seem to be very promising as the precision is rather poor (4 to 7%) when the sampling rate is about 60/h (Broekaert and Leis, 1979) or the sampling rate of 12 to 20/h with FIA cannot even match the conventional sampling procedures (Hartenstein *et al.*, 1985). Better results were obtained with FIA-atomic absorption spectrophotometry. Olsen *et al.* (1983) implemented a simple flow-injection system, the FIA star unit, where a sample frequency of 250/h was attainable for sea-water samples ranging from 0,1 to 10 mg/ℓ with a very good precision. With on-line preconcentration using a microcolumn of Chelex-100 the sampling rate dropped to between 30 and 60/h, which is still fairly good. The other atomic spectrophotometric procedures used either Chelex-100 or silica-immobilised 8-quinolinol as preconcentrator and the features of these methods are given in Table 7.

Maleate buffer at pH 6,25 (Van der Linden and Oostervink, 1978) or acetate buffer at pH 4,7 to 4,8 (Van Staden and Wagener, 1987; Zolotov *et al.*, 1987) with potassium nitrate as ionic strength adjuster were used as carrier and reagent streams. Van Staden and Wagener (1987) also used formaldehyde to retard oxidation of the membrane and sodium fluoride as additional reagents and a tubular mode electrode. The procedures described ranges from very sensitive (less than 1,0 mg/ℓ), in which copper was determined either directly with sequential addition of reagents to a reagent carrier stream (sample volume

TABLE 7
COPPER

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Waste waters	60	0,05-20	4-7	500	–	Single line carrier stream	Inductively-coupled plasma atomic emission spectrophotometry	Broekaert and Leis (1979)
Tap water	–	0,064-0,64	–	1 300	Maleate buffer at pH 6,25 with potassium nitrate as ionic strength adjustment buffer	Sequential addition of reagents to reagent carrier stream	Ion-selective electrode (cascade as well as tubular mode)	Van der Linden and Oostervink (1978)
Sea water	180-250	0,1-10	–	150	Sulphuric acid	Single line carrier stream	Atomic absorption spectrophotometry	Olsen *et al.* (1983)
Sea water	60	5×10^{-3} – 2×10^{-2}	3,2	–	Chelex-100 used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984a)
Tap, sea and polluted water	40	0,025-0,10	4,1	5 000	Chelex-100 used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984b)
Waste waters	44	0,3-4,0	0,51	–	Complex formation reaction between Cu (II) and cuprizone	Reagent injection into a sample carrier stream (reversed flow-injection analysis)	Spectrophotometry	Rios *et al.* (1985)
Water (EPA and tap)	15	0,005-0,500	–	10 000	Silica-immobilised 8-quinolinol as preconcentrator. Hydrochloric-nitric acid used as eluant	Sequential addition of reagent to reagent carrier stream. Ion-exchange column in manifold	Atomic absorption spectrophotometry	Marshall and Mottola (1985)
Tap water	200	1×10^{-3} mg/ℓ level	–	500	Mercury (II) as carrier stream	Single and two-channel system	Polarography	Frenzel and Brätter (1986)
Tap and rain water	12-20	1×10^{-3} – 0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrometry	Hartenstein *et al.* (1985)
Effluent and tap water	80	0,5-912	1,8	30	Acetate buffer (pH 4,8) in sodium fluoride, formaldehyde with potassium nitrate as ionic strength adjustment buffer	Sequential addition of reagents to a reagent carrier stream	Ion-selective electrode (tubular mode)	Van Staden and Wagener (1987)
Sea water and waste waters	–	0,005-1,0	6,3	300	Acetate buffer at pH 4,7	Single line carrier stream with preconcentration on a minicolumn of Chelex-100 resin	Ion-selective electrode	Zolotov *et al.* (1987)

1 300 µℓ) or via preconcentration on a minicolumn of Chelex-100 resin (50 to 500 mℓ sample concentrated, 300 µℓ injected), to a range between 0,5 to 912 mg/ℓ (sample volume 30 µℓ, precision 1,8%). Electrodes in the cascade mode (Van der Linden and Oostervink, 1978; Zolotov *et al.*, 1987) as well as the tubular mode (Van Staden and Wagener, 1987; Van der Linden and Oostervink, 1978) were used as sensors. A polarographic-FIA procedure for the determination of copper in tap water in the very low µg/ℓ level was proposed by Frenzel and Brätter (1986). Aliquots of 500 µℓ were injected into a de-aerated carrier containing mercury (II) in hydrochloric acid solution. The instrumentation used permitted a sample throughput of 200/h, but unfortunately no precision was given.

A very successful spectrophotometric procedure for the determination of copper in waste waters was described by Rios *et al.* (1985). The complex formation reaction between Cu (II) and cuprizone was used as indicator reaction in a reversed flow-injection system where copper was simultaneously determined with iron and aluminium. The precision of 0,51% was excellent.

Aluminium

Spectrophotometric methods with a variety of indicators appeared to be used almost universally for the determination of aluminium in water and were by far superior in analytical performance when compared with spectroscopic methods such as atomic absorption and inductively coupled plasma atomic emission spectrometry. Although a very low concentration level (10 to 300 µg/ℓ) with an ion-exchange (microcolumn loaded with Amberlite IRA-400) preconcentration procedure was reached, the precision of 6% with inductively coupled plasma atomic emission spectrometry as detector was rather poor. The precision of 2,7% obtained with atomic absorption spectrometry for the range 0,1 to 5 mg/ℓ is not very much better.

Royset (1985, 1986, 1987) compared various chromogenic reagents for the flow-injection determination of aluminium in water in a series of publications. The best performance was obtained for the reaction between aluminium and eriochrome cyanine R in cetyltrimethylammonium bromide at a pH of 7,5. The detection limit was 1 µg/ℓ Al and calibration graphs were linear up to 0,8 or 4 mg/ℓ (injection loops 200 or 10 µℓ respectively). Good reproducibility (precision of 0,7%) and a high sample throughput (120/h) were reported on samples from surface and leachate water. Interference from phosphate and fluoride was to a large extent obviated at pH 7,5 and dissolved organic carbon up to 20 mg/ℓ C could be tolerated. Of 40 elements tested, only iron, beryllium, lanthanum and cerium caused strong interference and the effect of iron was masked (<2 mg/ℓ). The spectrophotometric procedure by Wyganowski *et al.* (1982) for

TABLE 8
ALUMINIUM

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (µℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
River water	20	0-0,3	–	160	Bromopyrogallol red in presence of n-tetradecyltrimethylammonium bromide	Sequential addition of reagent to a reagent carrier stream	Spectrophotometry	Wyganowski *et al.* (1982)
Water	90	0,01-0,1	0,3	790	Chromazurol S	Sequential addition of reagents to a water carrier stream	Spectrophotometry	Zoltzer and Schwedt (1984)
Waste waters	42	0,06-0,80	0,62	–	Eriochrome cyanine R	Reagent injection into sample carrier stream (reversed flow-injection analysis)	Spectrophotometry	Rios *et al.* (1985)
Water	–	>5x10^{-3}(PCV) >0,100(A) >5x10^{-3}(ECR) >5x10^{-3}(ECR/CTA)	1-2(PCV) 5-10(A) 1-2(ECR) 1-2(ECR/CTA)	Varied	(a) Pyrocatechol violet (PCV) (b) aluminon (A) (c) eriochrome cyanine R(ECR) (d) eriochrome cyanine R with cetyltrimethylammonium bromide(ECR/CTA)	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Royset (1985)
Natural waters, surface and leachate water	100	3-10	2	200 or 10	Pyrocatechol violet	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Royset (1986)
Surface and leachate water	120	0,8-4	0,7	200 or 10	Eriochrome cyanine R and cetyltrimethylammonium bromide	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Royset (1987)
Tap waters	–	0,01-0,3 (ICP) 0,1-5 (AAS)	6(ICP) 2,7(AAS)	75	Minicolumn of Amberlite IRA-400 serving as preconcentrator	Single line carrier stream with minicolumn for preconcentration	Inductively coupled plasma atomic emission spectrometry (ICP) and atomic absorption spectrometry (AAS)	Garcia *et al.* (1987)

the determination of aluminium in river water with bromopyrogallol red and n-tetradecyltrimethylammonium bromide appeared to be very sensitive, but the sample throughput was rather low and unfortunately no precision was given. The two best spectrophotometric procedures were, however, reported by Zoltzer and Schwedt (1984) and Rios *et al.* (1985). In the determination of aluminium by means of chromazurol S a sampling rate of 90/h in the range 0,01 to 0,10 mg/ℓ was achieved with an excellent precision of 0,3% (Zoltzer and Schwedt, 1984). Simultaneous determination of aluminium with copper and iron in waste waters by reversed flow-injection analysis was presented by Rios *et al.* (1985) using eriochrome cyanine R as the chromogenic reagent. Excellent performance, with a precision of 0,62% for the range 0,06 to 0,8 mg/ℓ at 42 samples/h, was obtained.

For more details see Table 8.

Lead

The majority of flow-injection methods adapted for the determination of lead in water used spectroscopic detection. The results obtained with inductively coupled plasma atomic emission spectrometry again do not seem to be very promising as the sample throughput of 12 to 20/h with FIA cannot even match the conventional sampling procedures (Hartenstein *et al.*, 1985). Olsen *et al.* (1983) reported better results with FIA-atomic absorption spectrophotometry attaining a sample throughput of 250 samples/h for sea-water samples in the range 0 to 20 mg/ℓ with good precision. The rate dropped to between 30 and 60 samples/h when an on-line preconcentration column of Chelex-100 was incorporated as part of the FIA system, which in comparison with other methods is still fairly good. Details of other preconcentration FIA-AAS systems are outlined in Table 9. Zolotov *et al.* (1987) reported a FIA method for the determination of lead in the range 0,7 to 100 μg/ℓ, which was based on spectrophotometric detection of the lead IV/(2-pyridylazo) resorcinol (PAR) complex at 525 nm after on-line preconcentration of the sample (5 to 50 mℓ) on a minicolumn filled with Chelex-100 or Dowex 1-X8 resin. Although a sampling rate of 30/h was achieved, the precision of 12,0% was not as good as expected. Frenzel and Brätter (1986) proposed a flow-injection potentiometric stripping analysis procedure for the fast sequential measurement of zinc, lead and copper in tap water at very low μg/ℓ level. Samples of 500 μℓ were injected into a de-aerated car-

TABLE 9
LEAD

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Natural waters	50	0,02-0,50	2	–	Dithiozone	Extraction	Spectrophotometry	Mortatti *et al.* (1982a)
Sea water	180-250	0-20	–	150	Sulphuric acid	Single line carrier stream	Atomic absorption spectrophotometry	Olsen *et al.* (1983)
Sea water	60	0,025-0,10	3,2	–	Chelex-100 used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector	Atomic absorption spectrophotometry	Fang *et al.* (1984a)
Tap, sea and polluted water	40	0,1-0,5	4,1	5 000	Chelex-100 used as preconcentrator. Nitric acid used as eluant.	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984b)
Tap water	200	1×10^{-3} level	–	500	Mercury (II) as carrier stream	Single and two-channel system	Polarography	Frenzel and Brätter (1986)
Tap and rain water	12-20	1×10^{-3} – 0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrometry	Hartenstein *et al.* (1985)
Sea water and waste waters	30	7×10^{-3} – 0,10	12,0	5 000	Reaction of lead (IV) with (2-pyridylazo) resorcinol (PAR)	Single line carrier stream with preconcentration on a minicolumn of Chelex-100 resin	Spectrophotometry	Zolotov *et al.* (1987)
Potable water	–	0,0-0,10	12,0	250	Activated alumina used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with preconcentration on a minicolumn	Atomic absorption spectrometry	Zhang *et al.* (1988)

rier containing mercury (II) in hydrochloric acid solution. A sample throughput of 200/h was possible, but unfortunately no precision was given.

A flow-injection system for the determination of low concentrations of lead in natural waters was also reported by Mortatti *et al.* (1982a). The method was based on the injection of a suitable volume of sample into an inert carrier stream with further addition of a buffer-masking solution and dithiozone in carbon tetrachloride. After phase separation in a special chamber, the coloured complex was directed towards spectrophotometric detection at 520 nm. The system was characterised by a sampling rate of 50/h in the range 20 to 500 $\mu g/\ell$ with good precision (<2%).

Chromium

The photometric determination of chromium (VI) in water as the 1,5-diphenylcarbazide complex appears to be used universally as the complex forms rapidly, has a high absorptivity at 540 nm, while the method is highly selective at pH 1 to 2. Jorgensen and Regitano (1980) proposed a FIA method for the determination of chromium (VI) in natural waters in the range 0,1 to 20,0 mg/ℓ at a sample throughput of 70/h with a precision of 1,26%. Ruz *et al.* (1985) extended the procedure using several different configurations for simultaneous and sequential photometric speciation of Cr (VI) and Cr (III), based on reversed flow-injection analysis and completely continuous modes. For more details see Table 10.

Zinc

The various proposed flow-injection systems for the determination of zinc in water include spectroscopic methods using inductively-coupled plasma atomic emission and atomic absorption spectrometry as well as potentiometric stripping analysis as detecting systems. The procedures and outstanding features of these methods have been discussed in detail in the section on copper and are similar for zinc. Other details are summarised in Table 11.

A small column packed with immobilised bovine carbonic anhydrase was also used for the determination of traces of zinc in spring water, based on the measurement of recovered esterase activity of the metal-free apoenzyme after taking up zinc from the sample solution. The activity increase, after passing sample solution, was measured by injecting substrate solution into the buffer

TABLE 10
CHROMIUM

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected ($\mu\ell$)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Natural waters	70	0,1-20	1,26	20	Chromium (VI)-1,5-diphenylcarbazide complex	Single line carrier stream	Spectrophotometry	Jorgensen and Regitano (1980)
Natural and waste waters	30	0,1-5,0	1	–	1,5-diphenylcarbazide	Reversed flow-injection analysis. Simultaneous determination	Spectrophotometry	Ruz *et al.* (1985)
Natural and waste waters	100	0,2-3,5	3	–	1,5-diphenylcarbazide	Reversed flow-injection analysis. Sequential determination	Spectrophotometry	Ruz *et al.* (1985)

TABLE 11
ZINC

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected ($\mu\ell$)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Waste waters	60	0,05-20	4-7	500	–	Single line carrier stream	Inductively coupled plasma atomic emission spectrometry	Broekaert and Leis (1979)
Sea water	180-250	0-2,0	–	150	Sulphuric acid	Single line carrier stream	Atomic absorption spectrophotometry	Olsen *et al.* (1983)
Sea water	60	0,025-0,10	3,2	–	Chelex-100 used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984a)

TABLE 11 (continued)

Tap, sea and polluted water	40	0,1-0,5	4,7	5 000	Chelex-100 used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984b)
Tap water	200	1×10^{-3} level	–	500	Mercury (II) as carrier stream	Single and two-channel system	Polarography	Frenzel and Brätter (1986)
Spring water	–	1×10^{-5} – 4×10^{-4}	4,9	–	Bovine carbonic anhydrase immobilised on cyanogen bromide-activated Sepharose 4B dipicolinic acid used to remove zinc from enzyme column	Single line carrier stream with enzyme column	Spectrophotometry	Kashiwabara *et al.* (1985)
Tap and rain water	12-20	1×10^{-3} – 0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrometry	Hartenstein *et al.* (1985)
Waters	80	1-10	1	300	Zincon method	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Koupparis and Anagnostopoulou (1986)

TABLE 12
CADMIUM

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Waste waters	60	0,05-20	4-7	500	–	Single line carrier stream	Inductively coupled plasma atomic emission spectrometry	Broekaert and Leis (1979)
Sea water	180-250	0,01-0,100	–	150	Sulphuric acid	Single line carrier stream	Atomic absorption spectrophotometry	Olsen *et al.* (1983)
Sea water	60	5×10^{-3} – 2×10^{-2}	3,2	–	Chelex-100 used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984a)
Tap, sea and polluted water	40	0,025-0,10	4,7	5 000	Chelex-100 used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984b)
Tap water	200	1×10^{-3} level	–	500	Mercury (II) as carrier stream	Single and two-channel system	Polarography	Frenzel and Brätter (1986)
Tap and rain water	12-20	1×10^{-3} – 0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrophotometry	Hartenstein *et al.* (1985)

stream, which was carried to the column, followed by spectrophotometric detection of the product, p-nitrophenol, at 400 nm. The method is extremely sensitive, 1 x 10^{-5} to 4 x 10^{-4} mg/ℓ zinc, with a precision of 4,9% (Kashiwabara *et al.*, 1985). An automated flow-injection method for the determination of zinc in water, based on the zincon method with differential demasking of the cyanide metal complexes with cyclohexanone was also described by Koupparis and Anagnostopoulou (1986). Excellent results were obtained for zinc concentrations in the range 1 to 10 mg/ℓ at a sample throughput of 80/h. The precision was better than 1% and a detection limit of 0,05 mg/ℓ is possible.

Cadmium

The FIA procedures and outstanding features obtained for the determination of cadmium in water were similar to those obtained for copper and are discussed in detail in the copper section. Other details are given in Table 12.

Nickel

Similar results as those given for copper were obtained for the determination of nickel in water by Fang *et al.* (1984b), Broekaert and Leis (1979) and Hartenstein *et al.* (1985)(Table 13). The best flow-injection technique for the determination of trace amounts of nickel was however, given by Fang *et al.* (1984c). An on-line ion-exchange preconcentration system (60 to 80 mesh chelating resin with a salicylic acid functional group) prior to AAS determination was used. A sample throughput of 40/h in the range 10 to 500 μg/ℓ was obtained with a precision of 1,5%.

Cobalt

By using chelating resins as preconcentrators Fang and Zhang (1987) achieved an enrichment factor of 48 for the on-line preconcentration of cobalt in water samples. A sample frequency of 60/h was obtained with a precision of 1,7% at the 40 μg/ℓ level. A very sensitive catalytic method had also been developed for the spectrophotometric determination of cobalt in sea water (Kawashima *et al.*, 1985). A sampling rate of 30/h was achieved in the range 0,04 to 0,20 μg/ℓ with a precision of 4,0%. For more details see Table 14.

Manganese

The formaldoxime method had been applied successfully by Gine *et al.* (1979) to the spectrophotometric determination of manganese in natural waters, because of its high sensitivity and the rapid formation of a stable coloured complex. The method was suitable for the determination of manganese in the range 0,2 to 2,0 mg/ℓ at a sampling rate of about 135/h with a precision of better than 1%. Inductively coupled plasma atomic emission spectrometry was also used as detection system (Broekaert and Leis, 1979; Hartenstein *et al.*, 1985) for the flow-injection analysis of manganese and similar results as previously described for copper were obtained.

A flow-injection analytical method based on the catalytic ac-

TABLE 13
NICKEL

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Tap, sea and polluted water	40	0,1-0,4	4,7	5 000	Chelex-100 used as preconcentrator. Nitric acid used as eluant	Single line carrier stream with dual-column ion-exchange preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984b)
Tap and surface water	40	0,01-0,5	1,5	5 000	Chelating resin used as preconcentrator	Single line carrier stream with miniature ion-exchange column and preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1984c)
Waste waters	60	0,05-20	4-7	500	–	Single line carrier stream	Inductively coupled plasma atomic emission spectrometry	Broekaert and Leis (1979)
Tap and rain water	12-20	1x10^{-3} – 0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrometry	Hartenstein *et al.* (1985)

TABLE 14
COBALT

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Tap and rain water	12-20	1×10^{-3} – 0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrometry	Hartenstein *et al.* (1985)
Sea water	30	4×10^{-5} – 2×10^{-4}	4,0	187	Phenyl-p-phenylenediamine	Sequential addition of reagents to a reagent carrier stream	Spectrophotometry	Kawashima *et al.* (1985)
Water	60	0-0,100	1,7	–	Chelating resins used as preconcentrator	Single line carrier stream with miniature ion-exchange column and preconcentration valve on injector-commutator	Atomic absorption spectrophotometry	Fang *et al.* (1987)

TABLE 15
MANGANESE

Sample matrix	Sampling rate per hour	Concentration range mg/ℓ	Precision %	Sample volume injected (μℓ)	Chemistry	Manifold (valve, prevalve) technique	Detector	Reference
Water	135	0,2-2	1	350	Formaldoxime method	Sequential addition of reagents to a water carrier stream	Spectrophotometry	Gine *et al.* (1979)
Waste waters	60	0,05-20	4-7	500	–	Single line carrier stream	Inductively coupled plasma atomic emission spectrometry	Broekaert and Leis (1979)
Tap and rain water	12-20	1×10^{-3} – 0,10	–	–	2 mol/ℓ nitric acid as eluant	Preconcentration with ion-exchange column in sample loop of electronically operated proportional injector	Inductively coupled plasma atomic emission spectrometry	Hartenstein *et al.* (1985)

tion of molybdenum on the oxidation of iodide by hydrogen peroxide in acidic medium was proposed by Fang and Xu (1983). The triiodide formed was measured spectrophotometrically at 350 nm. With 200 μℓ sample injections a sample throughput of 90/h was obtained over a linear range of 1 to 1 000 μg/ℓ (detection limit 0,7 μg/ℓ) with a precision of 1,9%. See Table 15 for more information.

Conclusion

The potential and great capability of different FIA systems in water laboratories is demonstrated. It appears that flow-injection analysis has taken a prominent place in routine water laboratories where a widespread application of FIA methodologies is possible.

References

ALONSO, J, BARTROLI, J, LIMA, JLFC and MACHADO, AASC (1986) Sequential flow-injection determinations of calcium and magnesium in waters. *Anal. Chim. Acta.* **179** 503-508.

BASSON, WD and VAN STADEN, JF (1980) Simultaneous determination of sodium, potassium, magnesium and calcium in surface, ground and domestic water by flow-injection analysis. *Fresenius Z. Anal. Chem.* **302** 370-374.

BERGAMIN, FH, REIS, BF, JACINTHO, AO and ZAGATTO, EAG (1980) Ion exchange in flow injection analysis. Determination of ammonium ions at the μg/ℓ level in natural waters with pulsed Nessler reagent. *Anal. Chim. Acta.* **117** 81-89.

BETTERIDGE, D (1978) Flow injection analysis. *Anal. Chem.* **50** 832A-846A.

BROEKAERT, JAC and LEIS, F (1979) An injection method for the sequential determination of boron and several metals in waste-water

samples by inductively-coupled plasma atomic emission spectrometry. *Anal. Chim. Acta.* **109** 73-83.
CANETE, F, RIOS, A, LUQUE DE CASTRO, MD and VALCARCEL, M (1987) Determination of analytical parameters in drinking water by flow-injection analysis. Part 2. Simultaneous determination of calcium and magnesium. *Analyst* **112** 267-270.
DUTT, VVSE, ESKANDER-HANNA, A and MOTTOLA, HA (1976) Kinetically assisted equilibrium-based repetitive determination of iron (II) with ferrozine in flow-through systems. *Anal. Chem.* **48** 1207-1211.
DUTT, VVSE, SCHEELER, D and MOTTOLA, HA (1977) Repetitive determination of iron (III) in closed flow-through systems by series reactions. *Anal. Chim. Acta.* **94** 289-296.
FANG, Z and XU, S (1983) Determination of molybdenum at μg/ℓ levels by catalytic spectrophotometric flow-injection analysis. *Anal. Chim. Acta.* **145** 143-150.
FANG, Z, RUZICKA, J and HANSEN, EH (1984a) An efficient flow-injection system with on-line ion-exchange preconcentration for the determination of trace amounts of heavy metals by atomic absorption spectrometry. *Anal. Chim. Acta.* **164** 23-39.
FANG, Z, XU, S and ZHANG, S (1984b) The determination of trace amounts of heavy metals in waters by a flow-injection system including ion-exchange preconcentration and flame atomic absorption spectrometric detection. *Anal. Chim. Acta.* **164** 41-50.
FANG, Z, XU, S and ZHANG, S (1984c) Determination of trace amounts of nickel by on-line FIA ion-exchange preconcentration atomic absorption spectrometry. *Fenxi Huaxue* **12** 997-999.
FANG, Z, XU, S and ZHANG, S (1987) Fundamental and practical considerations in the design of on-line column preconcentration for flow-injection atomic spectrometric systems. *Anal. Chim. Acta.* **200** 35-49.
FORTEZA, R, CERDA, V, MASPOCH, S and BLANCO, M (1987) Spectrophotometric determination of magnesium (II) by flow-injection analysis using succinimidedioxime. *Analusis* **15** 136-139.
FREND, AJ, MOODY, GJ, THOMAS, JDR and BIRCH, BJ (1983) Flow-injection analysis with tubular membrane ion-selective electrodes in the presence of anionic surfactants. *Analyst* **108** 1357-1364.
FRENZEL, W and BRÄTTER, P (1986) Flow-injection potentiometric stripping analysis – A new concept for fast trace determinations. *Anal. Chim. Acta.* **179** 389-398.
GARCIA, MRP, GARCIA, MED and MEDEL, AS (1987) Flow-injection ion-exchange preconcentration for the determination of aluminium by atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry. *Journal of Analytical Atomic Spectrometry* **2** 699-703.
GINE, MF, ZAGATTO, EAG and BERGAMIN, FH (1979) Semi-automatic determination of manganese in natural waters and plant digests by flow-injection analysis. *Analyst* **104** 371-375.
HANSEN, EH, RUZICKA, J and GHOSE, AK (1978) Flow-injection analysis for calcium in serum, water and waste waters by spectrophotometry and by ion-selective electrode. *Anal. Chim. Acta.* **100** 151-165.
HARTENSTEIN, SD, CHRISTIAN, GD and RUZICKA, J (1985) Applications of an on-line preconcentrating flow-injection analysis system for inductively coupled plasma atomic emission spectrometry. *Can. J. Spectrosc.* **30** 144-148.
IWACHIDO, T, ONODA, M and MOTOMIZU, S (1986) Determination of potassium in river water by solvent extraction-flow-injection analysis. *Analytical Sciences* **2** 493-494.
JACINTHO, AO, ZAGATTO, EAG, REIS, BF, PESSENDA, LCR and KRUG, FJ (1981) Merging zones in flow-injection analysis. Part 6. Determination of calcium in natural waters, soil and plant materials with glyoxal bis (2-hydroxyanil). *Anal. Chim. Acta.* **130** 361-368.
JORGENSEN, SS and REGITANO, MAB (1980) Rapid determination of chromium (VI) by flow-injection analysis. *Analyst* **105** 292-295.
KASHIWABARA, K, HOBO, T, KOBAYASHI, E and SUZUKI, S (1985) Flow-injection analysis for traces of zinc with immobilized carbonic anhydrase. *Anal. Chim. Acta.* **178** 209-215.
KAWASHIMA, T, MINAMI, T, ATA, M, KAMADA, M and NAKANO, S (1985) Catalytic determination of ultratrace amounts of cobalt by flow-injection analysis. *J. of Flow-injection Analysis* **2** 40-49.
KOUPPARIS, MA, ANAGNOSTOPOULOU, P and MALMSTADT, HV (1985) Automated flow-injection pseudotitration of strong and weak acids, ascorbic acid and calcium, and catalytic pseudotitrations of aminopolycarboxylic acids by use of a microcomputer-controlled analyzer. *Talanta* **32** 411-417.
KOUPPARIS, MA and ANAGNOSTOPOULOU, PI (1986) Automated flow-injection spectrophotometric determination of zinc using zincon: Applications to analysis of waters, alloys and insulin formulations. *Analyst* **111** 1311-1315.
KRUG, FJ, RUZICKA, J and HANSEN, EH (1979) Determination of ammonia in low concentrations with Nessler's reagent by flow-injection analysis. *Analyst* **104** 47-54.
KRUG, FJ, REIS, BF, GINE, MF, ZAGATTO, EAG, FERREIRA, JR and JACINTHO, AO (1983) Zone trapping in flow-injection analysis. Spectrophotometric determination of low levels of ammonium ion in natural waters. *Anal. Chim. Acta.* **151** 39-48.
KUWAKI, T, AKIBA, M, OSHIMA, M and MOTOMIZU, S (1987) Determination of ammoniacal nitrogen in water by FIA with a gas-diffusion unit. *Bunseki Kagaku* **36** T81-T84.
MARSHALL, MA and MOTTOLA, HA (1985) Performance studies under flow conditions of silica-immobilised 8-Quinolinol and its application as a preconcentration-tool in flow-injection/atomic absorption determinations. *Anal. Chem.* **57** 729-733.
MISAKA, H, MOTOMIZU, S and TOEI, K (1985) Fluorimetric determination of ammonia in river water by flow-injection analysis. *Bunseki Kagaku* **34** 518-521.
MORTATTI, J, KRUG, FJ and BERGAMIN, FH (1982a) Spectrophotometric determination of lead in natural waters and plant material by a flow-injection system. *Report to the Energ. Nucl. Agric., Piracicaba* **4** 82-98.
MORTATTI, J, KRUG, FJ, PESSENDA, LCR, ZAGATTO, EAG and JORGENSEN, SS (1982b) Determination of iron in natural waters and plant material with 1,10-phenanthroline by flow-injection analysis. *Analyst* **107** 659-663.
MOTTOLA, HA (1981) Continuous flow analysis revisited. *Anal. Chem.* **53** 1312A-1316A.
NAKAGAWA, G, WADA, H and WEI, C (1983) Spectrophotometric determination of calcium with a flow-injection system. *Anal. Chim. Acta.* **145** 135-141.
OHNO, N and SAKAI, T (1987) Spectrophotometric determination of iron in boiler and well waters by flow-injection analysis using 2-nitroso-5- (N-propyl-N-sulphopropylamino) phenol. *Analyst* **112** 1127-1130.
OLSEN, S, PESSENDA, LCR, RUZICKA, J and HANSEN, EH (1983) Combination of flow-injection analysis with flame atomic-absorption spectrophotometry: Determination of trace amounts of heavy metals in polluted sea water. *Analyst* **108** 905-917.
OSHIMA, F (1981) Flow-injection analysis of ammonium nitrogen in environmental waters. *Fukuoka Kyoiku Daigaku Kiyo* **31** 57-65.
PAINTON, CC and MOTTOLA, HA (1981) Chemical kinetic contributions to practical dispersion in flow-injection analysis. *Anal. Chem.* **53** 1713-1715.
QINGXUN, W (1984) Spectrophotometric determination of calcium by flow-injection analysis. *Jion Daxue Tiran Kexue Xue Bao* **3** 113-117.
RANGER, CB (1981) Flow-injection analysis: Principles, techniques, applications, design. *Anal. Chem.* **53** 20A-32A.
REIJN, JM, VAN DER LINDEN, WE and POPPE, H (1980) Some theoretical aspects of flow injection analysis. *Anal. Chim. Acta.* **114** 105-118.
RIOS, A, LUQUE DE CASTRO, MD and VALCARCEL, M (1985) New approach to the simultaneous determination of pollutants in waste waters by flow-injection analysis. Part II. Cationic pollutants. *Analyst* **110** 277-281.
ROYSET, O (1985) Comparison of four chromogenic reagents for the flow-injection determination of aluminium in water. *Anal. Chim. Acta.* **178** 223-230.
ROYSET, O (1986) Flow-injection spectrophotometric determination of aluminium in water with pyrocatechol violet. *Anal. Chim. Acta.* **185** 75-81.
ROYSET, O (1987) Flow-injection spectrophotometric determination of aluminium in natural water using eriochrome cyanine R and cationic surfactants. *Anal. Chem.* **59** 899-903.
RUZ, J, RIOS, A, LUQUE DE CASTRO, MD and VALCARCEL, M (1985) Simultaneous and sequential determination of chromium (VI) and chromium (III) by unsegmented flow methods. *Fresenius Z. Anal. Chem.* **322** 499-502.
RUZICKA, J and HANSEN, EH (1980) Flow-injection analysis. Principles, applications and trends. *Anal. Chim. Acta.* **114** 19-44.
RUZICKA, J and HANSEN, EH (1981) *Flow-injection analysis.* Wiley, New York.
SLANINA, J, BAKKER, F, BRUYN-HES, A and MÖLS, JJ (1980) A computer-controlled multichannel continuous flow analysis system applied to the measurement of nitrate, chloride and ammonium

ions in small samples of rain water. *Anal. Chim. Acta.* **113** 331-342.
STEWART, KK (1981) Flow-injection analysis: A review of its early history. *Talanta* **28** 789-797.
UCHIDA, K, TOMODA, M and SAITO, S (1985) Determination of calcium by flow-injection analysis with hydroxynaphthol blue. *Bunseki Kagaku* **34** 568-572.
VALCARCEL, M and LUQUE DE CASTRO, MD (1987) *Flow-injection analysis*. Ellis Horwood Limited Publishers, Chichester.
VAN DER LINDEN, WE and OOSTERVINK, R (1978) Construction and behaviour of a micro flowthrough copper (II) -selective electrode. *Anal. Chim. Acta.* **101** 419-422.
VANDERSLICE, JT, STEWART, KK, ROSENFELD, AG and HIGGS, DJ (1981) Laminar dispersion in flow-injection analysis. *Talanta* **28** 11-18.
VAN SON, M, SCHOTHORST, RC and DEN BOEF, G (1983) Determination of total ammoniacal nitrogen in water by flow-injection analysis and a gas diffusion membrane. *Anal. Chim. Acta.* **153** 271-275.
VAN STADEN, JF (1981) Some application aspects of flow-injection analysis. Paper presented at Symposium on Flow-injection and Other Unsegmented Continuous-flow Sample Processing Systems, Div. Anal. Chem., 182nd ACS National Meeting, New York, August 1981.
VAN STADEN, JF (1989) Chapter 3. Basic components and automation. In: Burguera, JL (Editor) *Flow-injection Atomic Spectroscopy*. Marcell Dekker Inc., New York.
VAN STADEN, JF (1987) Flow-injection analysis of substances in water. Part 1. Anions. A critical review. *Water SA* **13** 197-208.
VAN STADEN, JF and WAGENER, CCP (1987) Flow-injection analysis with a coated tubular solid-state copper (II) -selective electrode. *Anal. Chim. Acta.* **197** 217-227.
WADA, H, NAKAGAWA, G and OHSHITA, K (1983a) Spectrophotometric determination of traces of iron with 2-(3,5-dibromo-2-pyridylazo) -5-[N-ethyl-N- (3-sulfopropyl) amino] phenol and its application in flow-injection analysis. *Anal. Chim. Acta.* **153** 199-206.
WADA, H, YUCHI, A and NAKAGAWA, G (1983b) Spectrophotometric determination of magnesium by flow-injection analysis with a ligand buffer for masking calcium. *Anal. Chim. Acta.* **149** 291-296.
WYGANOWSKI, C, MOTOMIZU, S and TOEI, K (1982) Spectrophotometric determination of aluminium in river water with bromopyrogallol red and n-tetradecyltrimethylammonium bromide by flow-injection analysis. *Anal. Chim. Acta.* **140** 313-317.
YOUXIAN, Y (1987) Merging zones flow-injection analysis of nitrite-nitrogen and ammonia-nitrogen in natural waters. *Fenxi Huaxue* **15** 454-457.
ZHANG, Y, RIBY, P, COX, AG, McLEOD, CW, DATE, AR and CHEUNG, YY (1988) On-line preconcentration and determination of lead in potable water by flow-injection atomic absorption spectrometry. *Analyst* **13** 125-128.
ZOLOTOV, YU A, SHPIGUN, LK, KOLOTYRKINA, I YA, NOVIKOV, EA and BAZANOVA, OV (1987) The trace determination of some heavy metals in waters by flow-injection spectrophotometry and potentiometry. *Anal. Chim. Acta.* **200** 21-33.
ZOLTZER, D and SCHWEDT, G (1984) Comparison of continuous-flow (CFA) and flow-injection (FIA) techniques for the photometric determination of traces of aluminium in water and soil samples. *Fresenius Z. Anal. Chem.* **317** 422-426.