# Flow-injection analysis of substances in water. Part I. Anions. A critical review*

**Jacobus F. 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 anions in water is given, highlighting the possibilities of FIA methods in this area, such as methods for the determination of sulphate, sulphide, chloride, residual chlorine, nitrite, nitrate, phosphate, silicate, cyanide and alkalinity.

## Introduction

A large number of water samples are submitted to routine water laboratories every day to satisfy increasing demands for analyses. To supply required data timeously and effectively, it would be an advantage to have a rapid, accurate and reliable system like a flow-injection analyser (FIA) available.

Flow-injection analysis (FIA) has become a well accepted technique in analytical chemistry. Since its introduction about a decade ago, more than 1 000 articles on FIA were published of which the number on water forms the majority.

The basic characteristics of flow-injection analysis (FIA) are the absence of air bubbles and the rapid injection of an aqueous sample into a continuously moving unsegmented carrier stream of water or reagent solution. The injected sample forms a slug or zone that is processed in a manifold system and transported into a flow-through detection system. The concept of FIA depends upon 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, immediately when the sample is injected. Since no air bubbles are involved, there is no need to control the air bubble size and air bubble pattern, whilst pulsation is reduced because of the absence of air bubbles. Among the advantages are flexibility, reliability and reproducibility as well as ease of automation and increased sample throughput.

In this paper, the first of a series, a critical review of FIA applications for the determination of anions in water samples is presented.

## Sulphate (Table 1)

A number of methods have been adapted to FIA for the determination of sulphate in water (Table 1). The spectrophotometric methods include the methylthymol blue method, the dimethylsulphonazo-III-(sulphonazo-III) procedure and the barium sulphate turbidimetric method.

Madsen and Murphy (1981a) reported a FIA procedure for the determination of sulphate in rain water using the automated methylthymol blue method. Samples were drawn through a cation-exchange column in the sample line in order to eliminate interferences from some cations. This procedure is very sensitive with a detection limit of 0,1 mg/ℓ, but has a narrow linear range (0,1 to 6,0 mg/ℓ) and samples with higher sulphate values had to be diluted manually before analysis. The method is not very precise (RSD of 4,1%) and with a rate of 20 samples $h^{-1}$, the throughput is rather low, when compared with a normal sample capacity of about 40 to 60 samples $h^{-1}$.

Reijnders *et al.* (1979, 1980) was the first group to report on the sensitive determination of sulphate in environmental samples by FIA using the barium chelate of dimethylsulphonazo-III (DMSA) as indicator. Interfering cations were also eliminated by using a cation-exchange column in the sample line. The procedure, furthermore, still uses an air bubble pattern in the manifold system. Although the method is very sensitive with a detection limit of about 0,25 mg/ℓ of sulphate, the precision at this limit was poor (24%). The same concept was also used by Kondo *et al.* (1982) for the sensitive determination of sulphate ion in river water, but without air segmentation. This method is more precise than the above-mentioned one, but suffers from a relatively low sample throughput (30 samples $h^{-1}$). The procedure also has a limited calibration range (0 to 30 mg/ℓ). Nakashima *et al.* (1984) have devised the former procedure by incorporating the cation exchanger into the analytical manifold instead of the sample line. Standard deviations of between 0,94 and 1,2% for 6 to 10 mg/ℓ sulphate were obtained with a limit of detection of 0,2 mg/ℓ. This method also has a narrow working range with a calibration curve which is linear up to 14 mg/ℓ.

The method that appears to be used almost universally is the barium sulphate turbidimetric procedure. The turbidity is measured at 420 nm. The accuracy and precision therefore depend critically on the crystalline form and size distribution of the light-scattering particles in the suspension. The degree of suspension is controlled by several factors and therefore the concentrations related to reagents and precautions preparing the reagents must be strictly followed. This suits the FIA concept as every standard and sample can be treated exactly the same due to the constant flow dynamics of the system. Hydrochloric acid is added to the barium chloride carrier solution to prevent the formation of precipitates of carbonate, chromate, sulphite, phosphate and oxalate of barium which may interfere.

Krug *et al.* (1977) first adapted the turbidimetric sulphate procedure to FIA using various types of flow systems with more than one reagent or carrier stream, but with a manifold tubing with inside diameter of 1,0 mm. A sampling rate of 180 samples $h^{-1}$ was achieved, the concentration range was extended to 140 mg/ℓ with a good precision (0,85%), but the sample volume injected is still high (400 µℓ).

Basson and Van Staden (1978) improved on the 40 samples $h^{-1}$ for the segmented barium sulphate turbidimetric procedure. The sampling rate was increased to about 200 samples $h^{-1}$ and the flow diagram simplified to a single carrier reagent stream with

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TABLE 1
SULPHATE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, prevalve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Rain water | 20 | 0,1-6,0 | 4,1 | 1 100 | Methylthymol blue | Sequential addition of reagents to a water carrier stream. Cation-exchange column in sample line before valve | Spectrophotometry | Madsen and Murphy (1981a) |
| Rain, potable, percolation water | 60 | 0-6,7 | 24 | 250 | Dimethylsulphonazo(III) indicator | Sequential addition of reagents to a water carrier stream. Cation-exchange column in sample line before valve. | Spectrophotometry | Reijnders *et al.* (1979) |
| River water | 30 | 0-30 | 1 | 80 | Dimethylsulphonazo(III) indicator | Sequential addition of reagents to a reagent carrier stream. Samples treated with cation-exchanger before injection. | Spectrophotometry | Kondo *et al.* (1982) |
| Natural water | – | 0,2-14 | 1,2 | 130 | Dimethylsulphonazo(III) indicator | Sequential addition of reagents to a carrier stream. Cation-exchanger incorporated into manifold system. | Spectrophotometry | Nakashima *et al.* (1984) |
| Natural waters | 180 | 20-140 | 0,85 | 400 | Barium sulphate turbidimetric | Pre-combination of reagents into a single line carrier stream before injection. | Spectrophotometry | Krug *et al.* (1977) |
| Natural waters | 200 | 50-200 | 3,9 | 100 | Barium sulphate turbidimetric | Single line carrier stream | Spectrophotometry | Basson and Van Staden (1978) |
| Natural waters | 200 | 20-500 | 2 | 200 | Barium sulphate turbidimetric | Sequential addition of reagents to a water carrier stream. Sample split into two conduits. | Spectrophotometry | Basson and Van Staden (1981) |
| River and sea water | – | 40-160 | 1-2 | 200 | Alkaline barium sulphate – EDTA solution, samples acidified | Single line carrier stream | Spectrophotometry | Baban *et al.* (1980) |
| Surface, ground and domestic water | 60 | 50-200 | 0,95 | 60 | Barium sulphate turbidimetric | Single line carrier stream. Alkaline-buffer-EDTA solution alternately injected between water samples | Spectrophotometry | Van Staden (1982b) |
| Natural waters | 120 | 1-30 | 1 | 500 | Barium sulphate turbidimetric | Sequential addition of reagents to a water carrier stream. Intermittent replacement of reagent stream by an alkaline-EDTA solution controlled by an injector commutator | Spectrophotometry | Krug *et al.* (1983) |

Table 1 continued

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Surface, ground and domestic water | 60 | 50-200 | 1 | 60 | Barium sulphate turbidimetric | Single line carrier stream. Alkaline-buffer-EDTA solution alternately injected between water samples. Automated pre-valve sample filtration in packed activated carbon tube | Spectrophotometry | Van Staden (1982c) |
| Surface, ground and domestic water | 60 | 50-200 | 1 | 60 | Barium sulphate turbidimetric | Single line carrier stream. Alkaline-buffer-EDTA solution alternately injected between water samples. Automated pre-valve sample filtration through activated carbon filter paper. | Spectrophotometry | Van Staden (1986c) |
| Surface, ground and domestic water | 60 | 50-200 | 1 | 60 | Barium sulphate turbidimetric | Double channel system (one blank) | Spectrophotometry | Van Staden (1986c) |
| Surface, ground and domestic water | 120 | 1 600-6 000 | 1 | 200 | Barium sulphate turbidimetric | Dialysis | Spectrophotometry | Van Staden (1986c) |

an inside manifold tube diameter of 0,38 mm. The precision was however unacceptable. (3,9%). Polyvinyl alcohol (Krug *et al.*, 1977) and gelatin (Basson and Van Staden, 1978) have been used to stabilise the barium sulphate suspension in order to obtain a relatively good precision.

Basson and Van Staden (1981) also reported an automated method for the simultaneous determination of chloride and sulphate in natural waters. The sample zone (200 μℓ) is split into two analytical manifolds, one for chloride and the other for sulphate. The calibration range for sulphate is extended to 500 mg/ℓ and a high sample throughput (200 samples $h^{-1}$) is obtained. Precision is improved by using gelatin as protective colloid and thymol to prevent bacterial growth.

One of the problems associated with the barium sulphate turbidimetric procedure, is the build-up of barium sulphate precipitate in the flow system which tends to settle in the flow cell. This leads to low precision and ultimately blocks the manifold. The addition of an alkaline buffer-EDTA solution to redissolve the accumulated barium sulphate precipitate is one way of overcoming this problem.

Baban *et al.* (1980) used a carrier solution of barium (II) ions with an excess of EDTA in alkaline medium (pH 10) to dissolve any accumulated precipitate. Precipitation occurs under the very acidic conditions of the well-defined sample zone (pH 1,5) in the analytical manifold where a pH-gradient in the sampling zone is established. The precipitate is, however, redissolved outside this zone by the self-cleansing action of the excess alkaline-EDTA carrier solution. By using pH-gradients and alkaline-EDTA a sufficiently stable barium sulphate suspension is obtained, which obviates the use of protective colloids such as polyvinyl alcohol or thymol gelatin. The precision is 1 to 2%, but no sampling rate is mentioned.

Van Staden (1982b) used a different approach by utilising 60 μℓ water samples from one loop of a two-position sampling valve alternating with an alkaline buffer-EDTA solution (100 μℓ) from the second loop which was injected into a barium sulphate-thymol-gelatin single line carrier stream. This obviates acidification (and dilution) of water samples, reduces baseline drift and improves precision to better than 1%. It also ensures that the residual precipitate, coating the walls of the flow cell, is redissolved and the system kept clean. Krug *et al.* (1983) used the same approach, rinsing the analytical path through intermittent replacement of the reagent stream by an alkaline EDTA solution. In this case both sample injection and the sequence of the alternating streams are controlled by an electronically operated injector-commutator. The method is precise (1%) and a relatively high sampling rate (120 samples $h^{-1}$) was achieved, due to a very high flow rate, combined with a 0,8 m inside diameter manifold tubing as well as 500 μℓ sample volumes injected.

The other problems associated with the barium sulphate turbidimetric procedure are suspended solids, the presence of organic substances and colour in samples which interferes at 420 nm. Van Staden (1982c) solved this problem by using a similar automated method previously described (Van Staden, 1982b) together with automated pre-valve sample filtration in a packed activated carbon tube as part of the sample line. This method was improved by switching to active carbon filter paper (Van Staden, 1986c). This ensures a great improvement in accuracy of some water samples with no loss in other features. A double channel system (with one channel as blank) was also proposed (Van

Staden, 1986c) for heavy coloured samples where the automated prevalve sample filtration system failed. A dialyser unit as part of the manifold to facilitate automated dilution was also used (Van Staden, 1986c) for industrial effluents with a relatively high sulphate content. The method is suitable for the determination of sulphate in the range 1 600 to 6 000 mg/ℓ at a sample frequency of 120 $h^{-1}$ with a precision of better than 1%.

1,6% by using the above-mentioned spectrophotometric procedure. They also extended the concentration range to 532 mg/ℓ at a sampling throughput of 120 $h^{-1}$ by stream splitting. A single sample is split, channelled through two different reaction lines with different line lengths and tube inside diameters, rejoined and transported to a single detector. The precision deteriorates, however, to about 4,3%, probably as a result of instability due to

TABLE 2
SULPHIDE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Industrial waste | 210 | 0,5-45 | 1 | 65 | Methylene blue method | Single line carrier stream, reagents merged before injection of sulphide | Spectrophotometry | Leggett *et al.* (1981) |
| Sewage effluents | 60 | 0,32-3200 | 2 | 100 | Standard antioxidant buffer containing sufficient ascorbic acid antioxidant in alkaline medium with small background levels of sulphide | Single line carrier stream | Sulphide ion-selective electrode | Glaister *et al.* (1985) |
| Industrial | – | 3,2-3 200 | – | – | – | – | Sulphide ion-selective electrode | Duffield *et al.* (1980) |

## Sulphide (Table 2)

The methylene blue spectrophotometric procedure has been adapted by Leggett *et al.* (1981) for determining the sulphide content in solutions containing sodium sulphide and hydrogen sulphide. The two reagents, N,N-dimethylaniline sulphate and iron(III)ammonium sulphate, both in acidic medium are merged automatically before injection of 65 μℓ alkaline sulphide samples. The method is suitable for sulphide (concentration range 0,5 to 45 mg/ℓ) analysis in industrial waste waters at a rate of 210 $h^{-1}$ and is precise (1%). The sulphide ion-selective electrode as sensing membrane has also been studied by Duffield *et al.* (1980) and Glaister *et al.* (1985) for the determination of sulphide in industrial processes and sewage effluents. Cascade and flow-through electrode modes were studied. Sample volumes of 100 μℓ were injected into a single line carrier stream of standard antioxidant buffer containing sufficient ascorbic acid antioxidant in alkaline medium with small background levels of sulphide. Other details are summarised in Table 2.

## Chloride (Table 3)

One of the most frequently used methods for the determination of chloride in water systems, is by measuring, spectrophotometrically at 480 nm, the colour of an iron(III)thiocyanate complex formed (Table 3). This is enhanced by the simplicity of the reaction and the ease of incorporation into a simple FIA manifold system.

The intensity of the red-coloured complex ion $FeSCN^{2+}$ is directly proportional to the amount of chloride present.

Ruzicka *et al.* (1976) described a simple single line manifold for the low level determination of chloride between 7 and 177 mg/ℓ at a rate of 300 samples $h^{-1}$ with a precision of better than

splitting. Sample splitting was also used in an automated method for the simultaneous determination of chloride and sulphate in natural water (Basson and Van Staden, 1981). The sample zone (200 μℓ) is split into two analytical manifolds, one for chloride and the other for sulphate. The calibration range for chloride is extended to 500 mg/ℓ and a relatively high sample frequency (200 samples $h^{-1}$) is obtained with a precision of 1,3%. Due to the formation of other (higher) iron(III)thiocyanate complexes, $Fe(SCN)_n$ (n = 2 to 5), the calibration curve, although extended, is non-linear. The addition of a complexing agent to the chloride colour reagent improves linearity somewhat. Slanina *et al.* (1980a) designed a computer-controlled multichannel continuous flow system for the simultaneous determination of nitrate, chloride and ammonium ions in small samples of rain water. A single sample is channelled via three independant valves which sample simultaneously. Chloride is determined spectrophotometrically via iron(III)thiocyanate in a single line manifold system. The sample frequency (18 to 35 $h^{-1}$) is rather slow and precision (8 to 10%) not so good, although 1 000 μℓ sample is injected. The linear range (0 to 14 mg/ℓ) is also limited. Van Staden (1985), extended the linear range to about 800 mg/ℓ by using an automated pre-valve dilution technique. The application of a Fe(II)/Hg-tripyridyl-s-triazine system for the photometric trace analysis (0,01 to 10 mg/ℓ) of chloride in air and water was also reported (Rössner and Schwedt, 1983). Although the method is not so precise, it is sensitive enough for the purpose needed. A more sensitive, specific and selective determination procedure for chloride ($1,1 \times 10^{-3}$ to $1,5 \times 10^{-2}$ mg) has also been reported by Miyazaki *et al.* (1984). The FIA system is based on the specific and selective reaction between the chloride anion and fluorescein with potassium bromate as oxidant in an acidic flow.

TABLE 3
CHLORIDE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Natural waters | 200 | 20-500 | 1,3 | 200 | Iron(III)thiocyanate complex | Sequential addition of reagents to a water carrier stream. Sample split into two conduits | Spectrophotometry | Basson and Van Staden (1981) |
| Brackish waters | 300 | 7-177 | 1,56 | 400 | Iron(III)thiocyanate complex | Single line carrier stream | Spectrophotometry | Ruzicka *et al.* (1976) |
| Brackish waters | 120 | 7-532 | 4,23 | 400 | Iron(III)thiocyanate complex | Single line carrier stream split through two different tubes and rejoined | Spectrophotometry | Ruzicka *et al.* (1976) |
| Rain water | 18-35 | 0,2-15 | 8-10 | 1 000 | Iron(III)thiocyanate complex | Single line carrier stream | Spectrophotometry | Slanina *et al.* (1980a) |
| Surface, ground and domestic water | 92 | 0-800 | 1,2 | 40 | Iron(III)thiocyanate complex | Sequential addition of reagents of a water carrier stream. Automated pre-valve sample dilution | Spectrophotometry | Van Staden (1985) |
| Natural waters | – | 0,01-10 | 8 | 300 | Fe(II)/Hg-tripyridyl-s-triazine system | Sequential addition of reagents to a reagent carrier stream | Spectrophotometry | Rössner and Schwedt (1983) |
| Water | 15 | $1,1x10^{-3}$ $-1,5x10^{-2}$ | – | 71,8 | Fluorescein-$KBr0_3$ | Single line carrier stream | Spectrophotometry | Miyazaki *et al.* (1984) |
| River water | 15 | 0-14 | – | 500 | Silver nitrate turbidimetric | Sequential addition of reagents to a reagent carrier stream. Cation-exchange column in carrier stream line | Spectrophotometry | Zaitsu *et al.* (1984) |
| River water | – | 5-40 | 2,1 | 300 | Potassium nitrate for ionic strength adjustment | Single line carrier stream. | Ion-selective electrode | Trojanowicz and Matuszewski (1983) |
| Water | 120 | 5-5 000 | 1,7 | 30 | Potassium nitrate for ionic strength adjustment | Single line carrier stream | Tubular ion-selective electrode | Van Staden (1986a) |

The product is detected at 530 nm in an alkaline flow. The limit of detection is $3,5 \times 10^{-4}$ mg. Zaitsu *et al.* (1984) also applied a silver nitrate turbidimetric procedure for the FIA determination of chloride in river water. The method is based on the turbidimetric measurement at 440 nm of a silver chloride suspension in nitric acid medium. A cation-exchange column is incorporated into the carrier stream line to eliminate interferences. The method is applicable for chloride concentrations between 0 and 14 mg/ℓ, but has a very low sampling rate of 15 samples $h^{-1}$.

Although the majority of FIA publications are devoted to spectrophotometric detection, the use of electrochemical detection for chloride has also been described recently. Trojanowicz and Matuszewski (1983) used a silver/silver chloride electrode for the determination of chloride in river water in the range 5 to 40 mg/ℓ with a precision of 2,1%. The working range was extended to 5 000 mg/ℓ by Van Staden (1986) using a homemade coated tubular solid-state chloride-selective electrode. A sample throughput (30 μℓ samples) of 120 $h^{-1}$ with a precision of better than 1,7% is obtained. Interferences are similar to those found in batch analysis with Ag/AgCl electrodes, but are less severe in the flow system; pH has no effect in the range 2 to 12. The main drawback of this electrode, however, is the severe interference of mercury(II)ions.

TABLE 4
RESIDUAL CHLORINE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Sea water | 160 | 1,4-38,4 | - | 60 | Methyl orange method | Single line carrier stream, automated premix of reagents | Spectrophotometry | Leggett *et al.*(1982) |
| Sea water | 288 | 0,18-18,1 | - | 60 | o-tolidine method | Single line carrier stream | Spectrophotometry | Leggett *et al.*(1982) |
| Town water supplies, swimming pools | 252 | 1,78-17,8 | - | 65 | N,N-diethyl-p-phenylene diamine(DPD) indicator and phosphate buffer | Single line carrier stream | Spectrophotometry | Leggett *et al.*(1983) |
| Tap water | 40-60 | 0,1-5,0 | 1 | 600 | Buffered electrolyte solution | Sequential addition of reagents to a reagent carrier stream | Iodide selective electrode | Trojanowicz *et al.*(1982) |

## Residual chlorine (Table 4)

Three spectrophotometric determinations for residual chlorine (hypochlorite) have been reported by Leggett *et al.* (1982, 1983). The first method is based on decolorisation of methyl orange in pH 2 buffer solution, the second on the formation of a yellow complex with o-tolidine and the third (Leggett *et al.*, 1983) employing the reaction of free chlorine with a mixture of N,N-diethyl-p-phenylene diamine (DPD) indicator and phosphate buffer to form a pink product. The authors improved the detection limit of 2 mg/ℓ obtained with methyl orange to 0,3 mg/ℓ with the DPD indicator. The DPD method was successfully employed in the determination of residual chlorine in town water supplies and swimming pools at a rate of 252 samples $h^{-1}$. Trojanowicz *et al.* (1982) measured residual chlorine at a rate of 40 to 60 samples $h^{-1}$ in tap water using a potentiometric system composed of an iodide-selective electrode and platinum electrode sensing the iodine-iodide ratio. More details are given in Table 4.

## Nitrite (Table 5) and nitrate (Table 6)

Nitrite (Table 5) and nitrate (Table 6) have been determined successfully by FIA using modifications of the Shinn reaction (Shinn, 1941). In the case of the determination of nitrate, the nitrate is first reduced to nitrite with copperised cadmium. In the Shinn reaction the nitrite is diazotised with sulphanilamide and the product coupled with N-(1-naphthyl)ethylenediammonium dichloride to form a highly coloured azodye which is measured at 520 nm. The Shinn modification for nitrite gives excellent results with FIA. Anderson (1979) adapted this reaction for the simultaneous determination of nitrate and nitrite in sea, tap and waste water. Although the sample (200 μℓ) is split into two conduits (one for nitrate and the other for nitrite), the precision (1%) for both components is still very good. The sampling rate of 30 samples $h^{-1}$ is, however, not very high. The author included a reductor tube packed with copperised cadmium granules as part of the nitrate plus nitrite analytical manifold line to facilitate reduction of nitrate. Gine *et al.* (1980) combined the merging zone principle with the Shinn reaction for the simultaneous determination of nitrate and nitrite. By using a special injector-commutator operating in two positions (one for nitrate plus nitrite and the other for nitrite alone), they increased the sampling rate to 90 samples $h^{-1}$ with a precision of 0,5% for nitrite and 1,5% for nitrate. By using a pre-valve in-valve reduction technique Van Staden (1982a) was able to use the Shinn modification for the simultaneous determination of nitrate and nitrite in water at a rate of 72 determinations $h^{-1}$. One loop of a two-position sampling valve is replaced by a copperised cadmium tube for the reduction of nitrate to nitrite. Nitrite from the samples as well as nitrite formed in the reduction prodecure is sampled by a second valve and introduced into the flow system. The two sampling valves are synchronised in such a way that two peaks are obtained, one corresponding to the nitrate plus nitrite and the other to the nitrite only. The same concept as above was also used by Johnson and Petty (1983b) for the simultaneous determination of nitrate and nitrite.

A more sensitive spectrophotometric method for the determination of nitrite in natural waters has also been described by Nakashima *et al.* (1983). The reaction is based on the diazotation of nitrite with p-aminoacetophenone and coupling of the product with m-phenylenediamine at pH 1,5 to 3,0 to form a product which was measured at 460 nm. With a sampling rate of 30 samples $h^{-1}$, the limit of detection is $2 \times 10^{-4}$ mg/ℓ for 650 μℓ sample injected which also yields a good precision. ($\leq$ 1,3%).

By using reversed flow-injection analysis (rFIA) Fogg and Bsebsu (1984) sequentially determined phosphate and nitrite in water. Nitrite has been analysed by injecting acidic bromide reagent into a sample carrier stream with a voltammetric glassy carbon electrode as sensing device. The results are summarised in Table 5.

The spectrophotometric determination of nitrate takes place in two main consecutive steps: reduction to nitrite and diazotation. The diazotation part has successfully been applied to FIA as indicated, but the efficiency of the reduction from nitrate to nitrite is dependant on the metal used in the reductor, the preparation and conditioning of the reduction column, the pH of the solution and the activity of the metal surface. In the case of both copperised cadmium column and tube reductors there is a tendency in decreasing accuracy which is the result of a decline in reduction ability of the reductors. The primary cause of the decline in reduction efficiency is the decrease in the surface of the cadmium, precipitation of hydroxides on the cadmium and the reduction of oxygen which reduces the amount of copper in the cadmium tube. Van Staden *et al.* (1986b) designed a FIA system which extended the lifetime of the copperised cadmium tube.

TABLE 5
NITRITE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Sea, tap, waste water | 30 | 2,3-92 | 1 | 200 | Diazotation of nitrite with sulphanilamide. Coupling of product with N-(1-naphthyl)-ethylenediam-monium dichloride | Sequential addition of reagents to a reagent carrier stream. Sample split into two conduits | Spectrophotometry | Anderson (1979) |
| Water | 90 | 0,1-0,5 | 0,5 | 75 and 15 | Diazotation of nitrite with sulphanilamide. Coupling of product with N-(1-naphthyl)-ethylenediam-monium dichloride | Merging zones | Spectrophotometry | Gine *et al.*(1980) |
| Water | 72 | 0,1-0,5 | 0,83 | 75 | Diazotation of nitrite with sulphanilamide. Coupling of product with N-(1-naphthyl)-ethylenediam-monium dichloride | Sequential addition of reagents to a water carrier stream | Spectrophotometry | Van Staden (1982a) |
| Sea water | 75 | 4,6-1 840 | 1 | 20 | Diazotation of nitrite with sulphanilamide. Coupling of product with N-(1-naphthyl)-ethylenediam-monium dichloride | Sequential addition of reagents to a reagent carrier stream | Spectrophotometry | Johnson and Petty (1983b) |
| Natural waters | 30 | 0-0,03 | 1,3 | 650 | Diazotation of nitrite with p-amino-acetophenone. Coupling of product with m-phenylenediamine at 30°C | Sequential addition of reagents to a reagent carrier stream. Line filter in manifold | Spectrophotometry | Nakashima *et al.* (1983) |
| Water | – | $2,3x10^{-3}$ $-2,3x10^{-2}$ | – | 100 (reagent) | Acidic bromide reagent | Reagent injection into a sample carrier stream | Voltammetry | Fogg and Bsebu (1984) |

They incorporated a copper tube before the copperised cadmium tube in the reaction manifold preventing the relatively rapid decrease in activity which directly influences the accuracy. The precision of the method is good ($\leqslant$ 1,5%) but the procedure is not fast (50 samples $h^{-1}$).

A solution of hydrazine, Zn(II) and Cu(II) was also used for the reduction of nitrate to nitrite (Madsen, 1981b) before applying the Shinn reaction. Despite the large volume of sample injected (1 000 μℓ), a reproducibility of 3% was reported for nitrate values between 1,0 and 10 mg/ℓ in rain-water samples, which is not as precise as expected. The sample frequency of 40 samples $h^{-1}$ is also relatively low.

An UV-spectrophotometric determination of nitrate using a perchloric acid manifold system was also reported by Slanina *et al.* (1978). This system was modified by the same group (Slanina *et al.*, 1980a) for the simultaneous determination of nitrate, chloride and ammonium ions in small samples of rain water. From a routine laboratory's viewpoint the single line system provides a relatively high sample throughput (120 samples $h^{-1}$), but with a reproducibility of 3% which is not so precise as the Shinn modifications. The results obtained from the multichannel system are, however, relatively poor (18 to 35 samples $h^{-1}$ with a precision of 10%).

Hansen *et al.* (1977) determined nitrate in waste water and air by using a home-made nitrate-selective electrode in an alkaline (pH 9,5) borax electrolyte medium to which glycine was added. Ninety samples $h^{-1}$ are analysed and the method is suitable to determine nitrate in the range 0,62 to 620 mg/ℓ with a coefficient of variation of 1 to 2%.

## Phosphate (Table 7)

The FIA colorimetric determination of phosphate is based on the complexation of orthophosphate with acidic molybdate. The two most commonly used colorimetric methods available for phosphate determination are either the yellow-coloured vanadomolybdate for relatively high phosphate concentrations or the molybdenum blue procedure for relatively low phosphate concentrations. The molybdenum blue procedure was applied by Hirai *et al.* (1981) for the determination of ortho and polyphosphates in various environmental waters. Although a sample plug of 500 μℓ was inserted into a system with a reactor of 30 m x 0,5 mm inside diameter (which gives a residence time of about 4 min), maintained at 140°C, a fairly high sample rate of

TABLE 6
NITRATE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Rain water | 18 – 35 | 0,2-2,0 | 10 | 200 | Perchloric acid | Single line carrier stream | Spectrophotometry | Slanina *et al.* (1980a) |
| Sea water | 30 | 6,2-1 240 | 1 | 200 | Reduction of nitrate to nitrite with copperised cadmium granules. Diazotation of nitrite with sulphanilamide. Coupling of product with N-(1-naphthyl)ethylenediammonium dichloride | Sequential addition of reagents to a reagent carrier stream. Sample split into two conduits. Reductor tube packed with copperised cadmium granules in manifold line | Spectrophotometry | Anderson (1979) |
| Water | 90 | 1,0-5,0 | 1,5 | 75 and 15 | The same as Anderson (1979) | Merging zones | Spectrophotometry | Gine *et al.* (1980) |
| Water | 72 | 1,0-5,0 | 1,96 | 75 | The same as Anderson (1979). A copperised cadmium tube is used | Sequential addition of reagents to a water carrier stream. Copperised cadmium tube used as a pre-valve in-valve reductor | Spectrophotometry | Van Staden (1982a) |
| Sea water | 75 | 6,2-2 480 | 1 | 20 | The same as Van Staden (1982a) | Sequential addition of reagents to a reagent carrier stream | Spectrophotometry | Johnson and Petty (1983b) |
| Natural waters | 50 | 0,2-2 | 1,5 | 300 | The same as Van Staden (1982a) | Sequential addition of reagents to a water carrier stream. Copper and copperised cadmium tubes in manifold line | Spectrophotometry | Van Staden *et al.*(1986b) |
| Rain water | 40 | 1,0-10 | 3 | 1 000 | Reduction of nitrate to nitrite with hydrazine. Diazotation of nitrite with sulphanilamide. Coupling of product with N-(1-naphthyl)ethylenediammonium dichloride | Sequential addition of reagents to a water carrier stream | Spectrophotometry | Madsen (1981) |
| Rain, surface waters | 120 | 0,1-40 | 3 | 500 | Perchloric acid | Sequential addition of reagents to a water carrier stream | Spectrophotometry | Slanina *et al.* (1978) |
| Waste waters, air | 90 | 0,62-620 | 1-2 | 300 | An alkaline (pH 9,5) borax electrolyte solution to which glycine was added | Sequential addition of reagents to a reagent carrier stream | Ion-selective electrode | Hansen *et al.*(1977) |

30 $h^{-1}$ was still achieved. A very low detection limit of 0,01 mg/ℓ P is reached, but the method is not as precise (4%) as expected. Using the same reaction approach Korenaga and Okada (1984) were able to increase the precision to 0,7% (for 0,01 to 10 mg P/ℓ) but the sampling rate dropped dramatically to 10 $h^{-1}$, which from a routine water laboratory's viewpoint is slow. Janse *et al.* (1983) used simplex optimisation to improve the FIA molybdenum blue procedure. Tin(II)chloride solution, with hydrazinium sulphate as stabiliser (to counter for the drift in baseline, caused by the instability of the tin(II)chloride solution) is used as reductant. The authors increased the sampling rate to 180 samples $h^{-1}$ with a linear calibration range from 0,04 to 2,50 mg/ℓ P. Johnson and Petty (1983a) also applied the molybdenum blue procedure for the determination of phosphate in sea water,

TABLE 7
PHOSPHATE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Water | – | 0,48-48 | – | 100 (reagent) | Acidic molybdate reagent | Reagent injection into a sample carrier stream | Voltammetry | Fogg and Bsebsu (1984) |
| Environmental waters | 30 | 0,1-9,5 | 4,0 | 500 | Molybdenum blue procedure | Sequential addition of reagents to a water carrier stream | Spectrophotometry | Hirai *et al.*(1981) |
| Waste water | 10 | 0,01-10 | 0,7 | 310 | Molybdenum blue procedure | Sequential addition of reagents to a reagent carrier stream | Spectrophotometry | Korenaga and Okada (1984) |
| Water | 180 | 0,04-2,50 | – | 200 | Molybdenum blue procedure | Sequential addition of reagents to a water carrier stream | Spectrophotometry | Janse *et al.*(1983) |
| Sea water | 90 | $4,7x10^{-3}$ -0,38 | 1,5 | 20 (reagent) | Molybdenum blue procedure | Reagent injection into a sample carrier stream | Spectrophotometry | Johnson and Petty (1983a) |
| River water | 40 | 0,01-0,08 | – | 240 (40) | Molybdate-malachite green | Sequential addition of reagent to a reagent carrier stream | Spectrophotometry | Motomizu *et al. (1983)* |

TABLE 8
SILICATE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ $SiO_2$ | Precision % | Sample volume injected μℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Well and river waters | 60 | 2-100 | 1,7 | – | Yellow molybdosilicic acid | Sequential addition of reagents to a water carrier stream. Different types used including merging zones | Spectrophotometry | Yokoyama *et al.* (1982) |
| Sea water | 40 | 0,02-1,0 | 0,5 | – | Heteropoly molybdenum blue complex | Sequential addition of reagents to a water carrier stream. Different types used including merging zones | Spectrophotometry | Yokoyama *et al.*(1982) |
| Sea water | 80 | 0,12-6,0 | 1 | 20 (reagent) | Molybdenum blue | Reagent injection into a sample carrier stream | Spectrophotometry | Thomsen *et al.*(1983) |
| Water | 164 | 1-5 | 1,6 | 164 | Molybdenum blue | Sequential addition of reagents to a water carrier stream | Spectrophotometry | Van Staden (1979) |

but used reversed flow-injection analysis where a reagent was injected into a sample carrier stream. A sampling rate of 90 $h^{-1}$ and a coefficient of variation of 1,7% (working range of $4,7 \times 10^{-3}$ to 0,38 mg/ℓ) is possible.

Despite the short reactor of 80 cm at a temperature of only 50°C with 20 μℓ of reagent injected, the sensitivity was increased to $4,7 \times 10^{-3}$ mg/ℓ as detection limit. A very sensitive flow-injection determination of phosphate in river water with malachite green and ammonium heptamolybdate as a complexing agent in acidic medium was described by Motomizu *et al.* (1983). Although this method has a lower limit of detection, the reported frequency of analysis (40 samples $h^{-1}$) and the linear range (0,01 to 0,8 mg/ℓ) are comparatively poor. Voltammetric detection and reversed flow-injection analysis formed the basis of

TABLE 9
CYANIDE

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected µℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Industrial effluents, waste water | 100 | $0,4x10^{-3}$ -$4,0x10^{-3}$ | 2 | 30 | Alkaline electrolyte solution | Single line carrier stream | Amperometric flow-through detector | Pihlar *et al.*(1979) |
| Surface ground waters | 60-70 | $1x10^{-3}$-several mg/ℓ | – | 240 | Alkaline electrolyte solution | Single line carrier stream, lead grain column incorporated into manifold | Amperometric flow-through detector | Ma *et al.*(1981) |
| Waste water | 40 | $0,3x10^{-3}$ -$100x10^{-3}$ | 3,4 | 200 | Hydrogen cyanide liberated from acidified carrier stream, diffused into an alkaline collector stream and detected | Sequential addition of reagents to a reagent carrier stream gas diffusion cell in manifold system | Ion-selective electrode | Okumoto *et al.*(1984) |
| Industrial waste waters | 20 | 0,1-1,0 | 0,8 | 136,3 | Chloramine-T, pyridine, barbituric acid dye reaction | Sequential addition of reagents to a reagent carrier stream | Spectrophotometry | Rios *et al.*(1984) |
| Industrial waste waters | 28 | 0,3-5,0 | 0,8 | 98,8 | Chloramine-T, pyridine, barbituric acid dye reaction | Injection of pyridine-barbituric acid reagent into a buffer-chloramine-T sample carrier stream | Spectrophotometry | Rios *et al.* (1984) |

TABLE 10
ALKALINITY

| Sample matrix | Sampling rate per hour | Concentration range mg/ℓ | Precision % | Sample volume injected µℓ | Chemistry | Manifold (valve, pre-valve) technique | Detector | Reference |
|---|---|---|---|---|---|---|---|---|
| Surface, ground, domestic waters | 120 | 40-400 | 1,4 | 50 | Bromocresolgreen method | Sequential addition of reagent into a water carrier stream | Spectrophotometry | Van Staden and Van Vliet(1984) |
| Surface, ground, domestic waters | 120 | 20-800 | 1,1 | 200 | Acid linear-response buffer | Sequential addition of reagent into a reagent carrier solution | pH-electrode | Basson and Van Staden (1980) |
| Surface, ground, domestic waters | 120 | 20-800 | 0,8 | 28 | Acid linear-response buffer | Sequential addition of reagent into a reagent carrier stream | pH-electrode | Van Staden (1986d) |

a procedure designed by Fogg and Bsebsu (1984) in which 100 µℓ of an acidic molybdate reagent was injected into a stream of phosphate solution. No sampling rate is given. For more details see Table 7.

## Silicate (Table 8)

The FIA spectrophotometric determination of silicate, similar to the concept used for phosphate, is based on the formation of a yellow molybdosilicic acid complex or its reduced heteropoly blue complex form. Both methods were used by Yokoyama *et al.* (1982), the yellow method in the concentration range 2 to 100 mg/ℓ ($SiO_2$) at a rate of 60 samples $h^{-1}$ (precision 1,7%) and the blue method in the concentration range 0,02 to 1,0 mg/ℓ ($SiO_2$) at a rate of 40 samples $h^{-1}$ (precision 0,5%). Ascorbic acid was used as the reductant and oxalic acid to remove phosphate interference. Thomsen *et al.* (1983) developed a reversed flow-injection procedure for the determination of reactive silicate in sea water using the molybdenum blue method, preferring stannous chloride as reductant. A detection limit of 0,03 mg/ℓ ($SiO_2$) was achieved and a relative precision of better than 1% for silicate concentrations above 0,60 mg/ℓ. Van Staden (1979) also designed a FIA procedure in the range 1 to 5 mg/ℓ ($SiO_2$) using the reduced molybdosilicic acid method with ascorbic and oxalic acid. The method is suitable for analysis at a rate of up to 164 samples $h^{-1}$ with a precision of better than 1,6%.

## Cyanide (Table 9)

The use of an amperometric flow-through detector for the FIA determination of cyanide in water has been studied by two groups, Pihlar *et al.* (1979) and Ma *et al.* (1981). (Table 9). In both cases the sample is injected into an alkaline single line elec-

trolyte carrier stream. Ma *et al.* (1981), however, inserted a lead-grain column into the manifold system for on-line pretreatment of samples. The method reported by Pihlar *et al.* (1979) is suitable for the determination of cyanide in industrial effluents and waste water at a sampling rate of 100 $h^{-1}$ with a precision of 2% (sampling range 0,4 x $10^{-3}$ to 4,0 x $10^{-3}$ mg/ℓ). A sampling rate of 60 to 70 $h^{-1}$ was achieved by Ma *et al.* (1981) in surface ground waters. Okumoto *et al.* (1984) interfaced FIA with a cyanide-selective electrode to screen waste-water samples from metal plating processes. Although the sampling range obtained by Pihlar *et al.* (1979) was extended to 0,10 mg/ℓ, the method is not so precise (3,4%). Spectrophotometric detection was also applied in the determination of cyanide in industrial waters (Rios *et al.*, 1984), in both a normal FIA as well as a reversed FIA mode. In the normal mode the carrier consists of a mixture of chloramine-T solution and buffer into which the sample is inserted. The method is very precise (0,8%) for cyanide concentrations between 0,1 and 1,0 mg/ℓ, but the sample frequency drops to 20 $h^{-1}$. In the reversed FIA mode, where a pyridine-barbituric acid reagent is injected into a buffer-chloramine-T sample carrier stream, the concentration range is extended to 5,0 mg/ℓ with the same precision (0,8%) as the normal FIA system. The sample frequency increases to 28 $h^{-1}$.

### Total alkalinity (Table 10)

Total alkalinity has been determined successfully in surface, ground and domestic waters by FIA using the colorimetric bromocresolgreen indicator modification and electrometric titrations. Van Staden and Van Vliet (1984) applied the bromocresolgreen indicator method at a rate of up to 120 samples per hour. The method is precise (1,4%) but the working range is limited (40 to 400 mg/ℓ). Colour and turbidity in samples may interfere. These interferences were eliminated by Basson and Van Staden (1980) and Van Staden (1986d) in designing a single-point titration system. In this system the sample is reacted with an acid linear-response buffer solution and the pH of the resulting solution is measured with a glass electrode in a flow-through assembly. Although a sampling rate of up to 120 samples $h^{-1}$ with reproducibility of better than 1,1% was obtained for water samples with a total alkalinity between 20 and 800 mg/ℓ, the corresponding calibration curves were non-linear in the first attempt (Basson and Van Staden, 1980). A more precise (0,8%) and linear system for the same concentration range was obtained by Van Staden (1986d) in a second attempt using other modifications as well as components in the acid linear response buffer.

Slanina *et al.* (1980b) evaluated the performance of a cascade fluoride-selective membrane electrode in a flow-injection system under manual or active computer control. Rain-water samples (500 µℓ) are injected into a water carrier stream, a total ionic strength adjustment buffer (TISAB) is added further downstream and the processed sample plug is fed into the detector. Although the response of the fluoride-selective membrane electrode is not Nernstian, 60 determinations per hour are possible in the concentration range 20 x $10^{-3}$ to 200 x $10^{-3}$ mg/ℓ with a typical precision of 3%. Despite the sample volume of 700 µℓ used by Van den Winkel *et al.* (1983) for the potentiometric determination of fluoride in potable waters in the concentration range 0,1 to 5 mg/ℓ their system was not as precise (5%) as the one by Slanina *et al.* (1980a). Deguchi *et al.* (1983) designed a photometric FIA procedure for the determination of trace amounts of iodide ion in rain water using the catalytic reduction of sulphatocerium(IV)ion by arsenic trioxide in sulphuric acid medium. The sampling rate is 30 samples $h^{-1}$ with a precision of 10% (concentration range 0 to 50 x $10^{-3}$ mg/ℓ). The detection limit is 1 x $10^{-3}$ mg/ℓ.

## Conclusion

The potential use of different FIA systems for anions in water laboratories is illustrated. Widespread application of FIA methodologies is possible and the rate at which FIA analysers are implemented in routine water laboratories is increasing.

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