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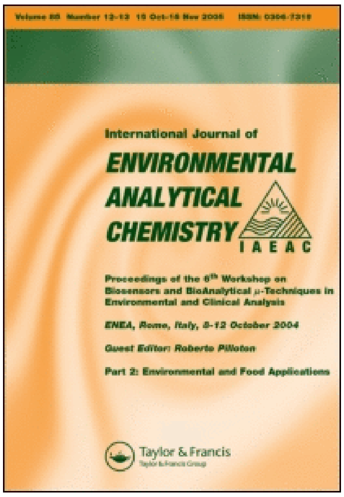

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NOVEL FLOW INJECTION APPROACHES TO ENVIRONMENTAL ANALYSIS

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An overview of the state of the art in Flow Injection Analysis for environmental control is presented The contributions to single- and multi-parameter determinations and potential of this technique for speciation are considered. Improvements resulting from the on-line use of separation techniques, of easy implementation, make an excellent feature which allows the user to address problems arising from complex matrices and/or low analyte concentration

KEY WORDS: Flow injection analysis, environmental, review.

INTRODUCTION

Flow Injection Analysis, FIA, has consolidated as a very useful automatic technique for the routine control of parameters in different areas of social interest. Its simplicity, its capacity to lead itself to the development methods with high sampling frequencies and its versatility and flexibility for adaption to different types of analytes and samples are responsible for its currently widespread use in routine environmental monitoring. One feature derived from the rapidity of FIA determinations is the possibility to perform measurements in real or near-real time. Environmental chemistry is one of the fields where these features are more highly valued; this is to because deterioration of the environment requires fast and efficient solutions to the new problems confronting chemists and authorities every day.

Many authors have considered the potential of FIA for the resolution of environmental problems since its advent; thus, as shown in our review in 1985[1] a number of methods have been developed for the control of different pollutants. There have been so many contributions since that date that a new overview showing in a systematic way the advances in the last few years and present trends in FIA-environmental control is required.

The diffrent methods reviewed here are classified according to whether the determination involves one of several analytes. Because the methods proposed so far for the control of pollutants in air are single-parameter, those in

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section A are further divided according to whether the material assayed is water or air. Section B is devoted to multiparameters determinations including speciation.

SINGLE-PARAMETER CONTROL

The facility with which liquid samples can be manipulated compared to gaseous samples has fostered the development of methods for the former, which are discussed first here.

Determinations in Water

There is a general trend to the use of separation and/or pre-concentration techniques which approach the proposed methods to real problems involving complex sample matrices and analytes at very low concentrations. Methods involving innovative reactions, the coupling of separation techniques and new detection systems are commented on below.

One parameter commonly controlled in most types of water is alkalinity, which has traditionally been determined by titration. This technique can be implemented in an FIA system at a rate of 30 samples/h, or greater,[2] which results in fast monitoring analyses (no discussion will be made here about the accuracy of the term 'FIA titration', the reader is instead referred to the work of specialists).[3-6]

Methods not involving a separation technique must be highly sensitive and require an analyte concentration in the sample calling for a strong dilution lowering the concentration of potential interferents below their 'active' level. This is the case with the photometric determination of iron based on the reaction between perbromate and iodide, induced by this metal.[7]

The on-line preconcentration-separation coupled with catalytic determination of cobalt in sea and river water proposed by Yamane *et al.*[8] makes use of two column to concentrate and separate the analyte, packed with silica-immobilized 8-quinolinol and a strongly acidic cation-exchange resin, respectively (Figure 1a) The preconcentration step in PC is performed by continuously pumping the sample through it, eluting the analyte by injecting through E a hydrochloric acid solution which drives the metal ion to the separation column, SC. The cobalt eluted from this last column catalyzes the indicator reaction (protocatechuic acid/hydrogen peroxide). A detection limit of 5×10^{-3} ng/ml is achieved. Intermittent pumping has been used by Zolotov *et al.*[9] for preconcentration-separation and determination of lead and copper with the configuration depicted in Figures 1b and 1c, respectively. In the first case, the preconcentration and column washing step is carried out in the loop of the injection valve, after which the pump 1 is stopped and pump 2 started to perform the elution, mixing with the reagents and monitoring at the detector. The copper determination is carried out in a special reverse FIA (r-FIA) system; the alternate functioning of pumps P1 and P2 compels the sample (P1) or a buffer solution (P2) in which the eluent is injected to circulate through the system. The sampling rate achieves ranges between 1 and 50 samples/

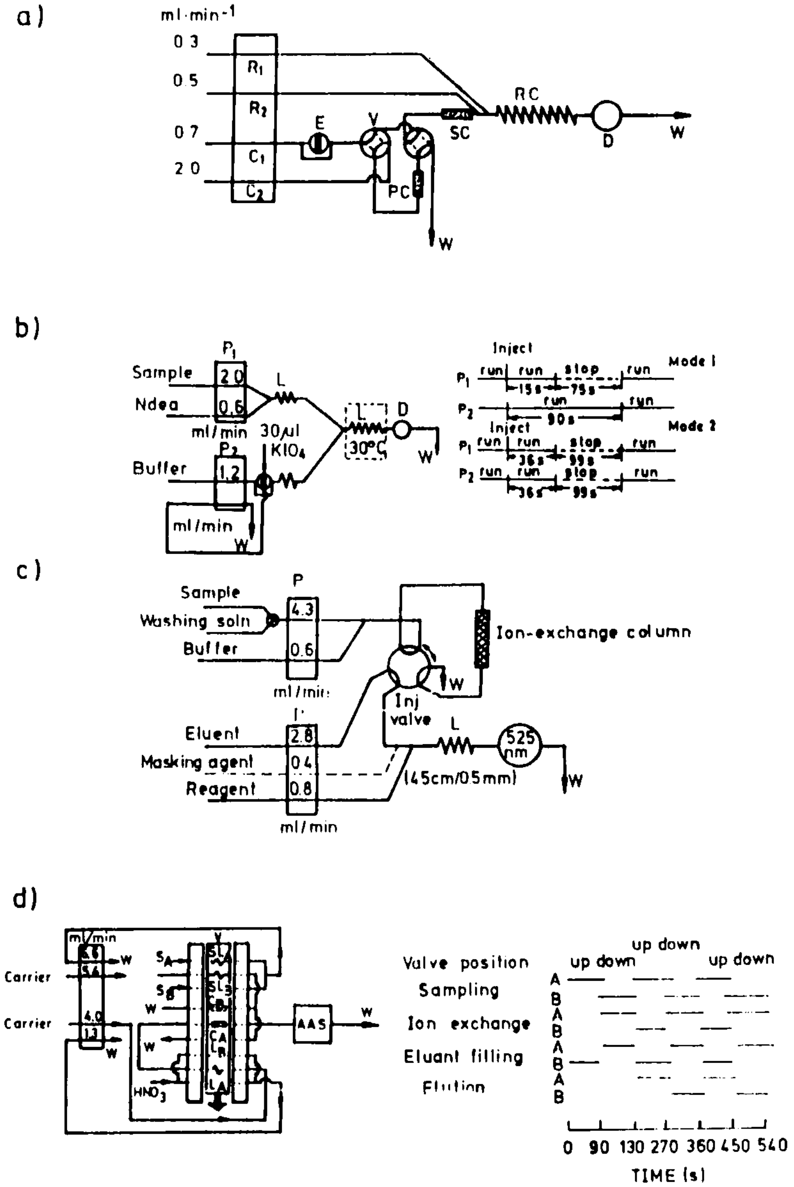

Figure 1 FIA-separation technique coupling manifolds. (a) Continuous-flow system for the determination of cobalt in sea and river water. R1 1.0 M sodium carbonate; R2 indicator mixture; C1, eluent; C2, carrier; E, sliding valve; V, double 4-way valve; PC, preconcentration column; SC, separation column; RC, reaction coil; D, detector; W, waste (ref. 8). (b) Schematic diagram for the catalytic determination of manganese(II). P1, P2, peristaltic pumps; L1, L2, mixing coils; L3, reaction coil. The two operation modes of the pumps; the stop and go sequences are controlled by a micro-processor (ref. 9). (c) Schematic diagram for determination of lead (ref. 9). (d) Dual-column on-line preconcentration system and the corresponding program for the preconcentration process. Subscripts A and B represent channels A and B, respectively, multifunctional rotary valve (V) parts: S_A and S_B, sample; SL_A, SL_B, sample loop; C_A, C_B, ion-exchange column, L_A, L_B, eluant loop (ref. 10).

h, depending on the preconcentration interval. A means of accelerating this step has been reported by Fang *et al.*,[10] who used the system depicted in Figure 1d. It consists of a three-layer sandwich valve analogous to a commutation injector with three 3:2:3 commutations sections and two parallel sample loops, two eluant loops and two ion-exchange columns arranged on the same rotor. As the rotor is rotated manually at regular intervals, the sampling, ion-exchange and elution processes are done sequentially and alternately on the two columns. The manifold has been used for the determination of nickel, copper, lead and cadmium by atomic absorption at a frequency of 40/h using sample volumes of 5 ml. A single-channel system with the column located immediately after the injection system has been used by Pereiro *et al.*[11] for the determination of aluminium in water by atomic absorption and/or inductively coupled plasm atomic emission spectrometry.

Anionic surfactants in water can be determined by a spectrophotometric method involving flow injection coupled with solvent extraction. Eight cationic dyes forming ion-pairs and various extraction solvents have been assayed. The sampling rate was 20 samples/h. The calibration graphs are linear up to 3×10^{-5} M of anionic surfactant for injection volumes of 300 μl. The method has been applied to the determination of anionic surfactants in river water.[12]

An automated flow-injection system with gas-diffusion separation-preconcentration and spectrophotometric detection has been used for the determination of total cyanide in waste waters.[13] The novel combination of a gas-diffusion separator with a sampling valve enables efficient on-line separation, preconcentration and sampling of cyanide. A sampling frequency of 40/h, a detection limit of 0.006 μg/ml and a preconcentration factor of 3.5 are achieved for a 20-ml sample. The relative standard deviation is 1.4% at the 0.5 μg/ml level. The results obtained with this method are in good agreement with those found by the standard manual spectrophotometric method.

A solid–liquid separation technique recently incorporated into FIA, precipitation, has proved to be useful in environmental monitoring for the direct determination of cationic and indirect of anionic pollutants by AAS. The method proposed for the determination of chloride by precipitation with silver ion makes use of normal and reverse FIA. In both cases, the precipitated AgCl is retained on a stainless-steel filter and the absorbance decrease arising from the decreased silver concentration in the carrier resulting from the formation and retention of the solid compound is monitored by n-FIA. In the reverse mode, the injection of the silver ion solution yields a peak whose height is inversely proportional to the concentration of the analyte in the sample, which is continuously circulated through the system.[14] Because the precipitate is retained on the filter, a cleaning step is required each 150–250 samples. The procedure used for the determination of lead allows its preconcentration besides its separation. It is based on the use of r-FIA in a two-channel system where the sample is merged with an ammonia solution, the precipitate formed during a preselect interval being retained on the filter. Elution and monitoring are effected after injection of an adequate volume of HNO_3. The analyte can thus be determined in the range 1.2–1500 ng/ml at sampling frequencies between 1 and 15/h, with an r.s.d. less than 3.6%.[15]

Preconcentration in the detection cell has been carried out electrochemically in environmental analysis with subsequent potentiometric[16,17] or voltammetric[16] stripping of the species deposited on the electrode (metals in all cases) and by use of ion-exchange phase-absorptiometry for Cr(VI)[18] and Fe(III)[19] determinations. Jagner *et al.* have developed a method for the determination of mercury(II) in tap water by flow potentiometric and constant-current stripping with gold, platinum and carbon fibre working electrodes.[16] Compared to gold and glassy carbon disc electrodes, the fibre electrodes give increased sensitivity and stability and are considerably simpler to handle. The gold-coated carbon fibre electrode gives a higher background than the gold fibre electrode in both the potentiometric and constant-current stripping modes. Mercury(II) can be determined in the presence of a 10^5-fold (molar) amount of copper(II) by constant-current stripping in media with chloride concentration below 0.05 M. The detection limit for mercury(II) after 10 min of electrolysis is 45 nl/l at the 3σ level. Schulze *et al.*[17] have designed a flow-cell with flexible deposition efficiency for a serial dual-detection system based on potentiometric stripping analysis and atomic absorption spectrometry, whose performance have been tested by applying it to the determination of lead in water.[18] Ion-exchange phase-absorptiometry has been applied to the determination of trace amounts chromium(VI) in natural waters. The product of the reaction of chromium(VI) with 1,5-diphenylcarbazide (DPC) is introduced into a carrier solution stream in the flow system. The increase in absorption caused by the coloured complex sorbed on a cation exchanger, with which the light-path of the flow-through cell is partly filled is monitored. The detection limit is as low as 0.5 ng of chromium. Cations such as calcium and background electrolytes present in natural waters at high concentration cause a change in the background attenuation. For fresh water, this effect can only be counteracted by passing the sample solution through a small hydrogen-form cation-exchange column. For sea water, it is necessary to use a calibration graph prepared at a concentration similar to those in the sample solution. Another method using integrating retention by an ion-exchanger in the photometric flow-cell for the determination of iron based on the Fe(III)-thiocianate complex formation was recently proposed.[19] The method has good selectivity, with a determination limit of 10 ng/ml and a linear range between 10 and 400 ng/ml. Different types of measurements (peak height, absorbance increment, tangent curve) with their own inherent advantages are made. The method has been applied to the determination of the analyte in natural water, with an average recovery of 100.2% and average deviation of the recovery with respect to 100% of 2.5%.

Finally, it is worth mentioning two contributions to FIA configurations and/or detection systems successfully applied in environmental control, Johnson *et al.*[20] have proposed a reagent injection flow system with automatic control of the volume of reagent to be injected. The sensitivity of the measurements can be adjusted over a wide range by changing the injection volume. The system also eliminates problems in photometric determinations arising from the refractive index effects and from light scattering by suspended particles in the sample by using a light-emitting diode photometer to measure changes in light transmission. Special care is taken to optimize the signal-to-noise ratio because the expected absorbances are somewhat low. A large diameter flow-cell (2.2 mm i.d., 1 cm path length, 40 μl capacity) increases the signal through exposure of a larger active area of the photodiode. Absorbances as small as 0.00004 can thus be measured. The

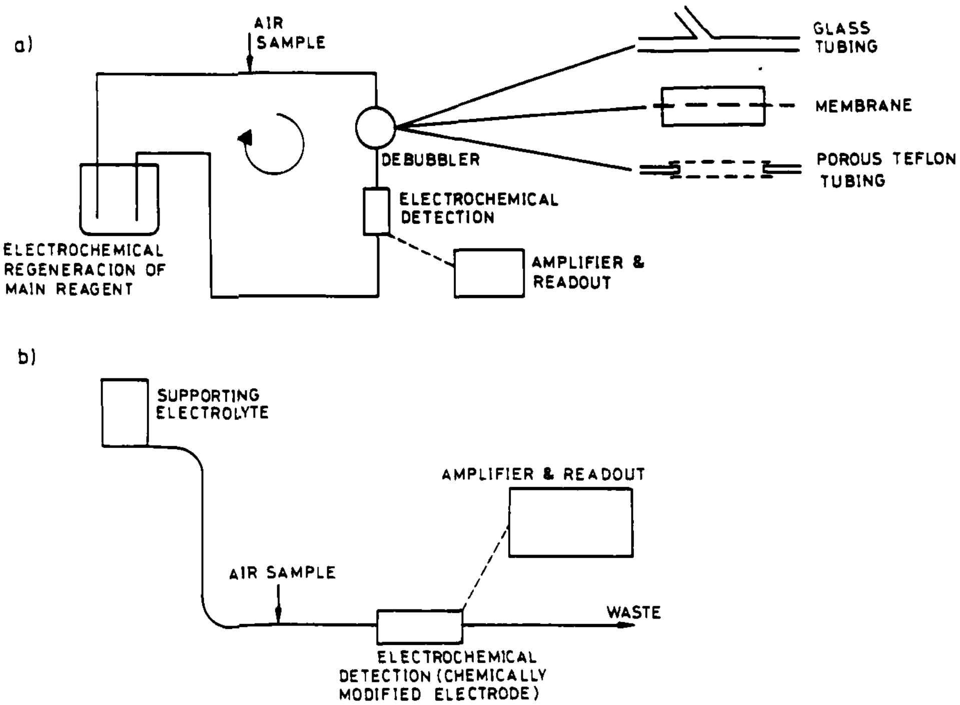

Figure 2 Manifolds for the determination of gas pollutants with direct injection of the analyte and electrochemical detection. (a) With electrochemical regeneration of the main reagent and several types of debubbler. (b) With a chemically modified electrode and no debubbler.

capabilities of this system were tested by using it to determine hydrogen peroxide in sea water at nanomolar levels. The concentration of analyte was determined through a coloured condensation product, with detection limits of 12 nM.[20] Worsfold and Clinch[21] have designed a spectrophotometric field monitor for water quality parameters which they applied to the determination of phosphate in natural water with a reverse FIA configuration. The dual-beam photometric detector incorporating light-emitting diodes and photodiodes is enclosed in a 20 cm^3 box. This dual configuration allows the untreated sample to be passed through the reference cell before reagent addition and passage through the sample cell. The response is linear over the range 0–2000 μg/l phosphate-phosphorus ($r = 0.9992$) and the limit of detection (2σ) is 12 μg/l phosphorus.

Determinations in Air

The determination of parameters in gases involves additional problems which have deferred applications in this field. Nevertheless, the methods proposed in the last few years, all of which involve direct injection of the pollutant, have a vast potential.

An interesting sequel of direct determinations have been implemented by exploiting the reversible behaviour of the Fe(II)–Fe(III) complexes with ligands of the 1,10-phenanthroline family. In an almost evolutionary manner, Mottola *et al.*

have developed a series of methods based on the redox chemistry of such complexes on oxidant and reductant pollutants.[22–27] The emphasis on these determinations has been directed towards electrochemical detection. The earlier examples utilized reaction at the liquid–gas interface and more recently, such detection has been accomplished by means of chemically modified electrodes incorporating the reversible redox couple directly on the surface electrode. An example of detection as a result of redox chemistry at the liquid–gas interface is the work of Rios *et al.*[22] Sulphur dioxide in air samples from power plant fume can be determined and industrial hygiene measurements can be accomplished without the need for preconcentration by detecting with a carbon paste working electrode the iron(II) complex (ferroin) resulting from the $SO_2(g)$ reduction of the binuclear iron(III)-1,10-phenanthroline complex. The continouos flow system (Figure 2A) used in this application involves electrochemical regeneration of the iron(III) binuclear complex[23] and the use of a debubbler before the detection point. The determination of an oxidizing pollutant has been illustrated by Nyasulu and Mottola[24] with the NO_2 oxidation of tris (1,10-phenanathroline)-iron(II) to its iron(III) analogue, also at gas–liquid interface. The authors also used a closed loop system with electrochemical regeneration of main reagent and accomplished debubbling either by gas-diffusion through a gas-permeable membrane or directly by means of Gore-Tex miroporous Teflon tubing.

More recently, the direct incorporation of the reversible redox couple has been accomplished by its immobilization on the surface of a carbon paste electrode[25] and oxidative electropolymerization on a glassy carbon electrode (Figure 2B).[26] Chemical modification of the carbon paste electrode was accomplished by direct admixing of the iron complexes with 4,7-diphenyl, 1,10-phenanthroline; the oxidative electropolymerization involved the electrochemistry of the iron(II) complex of 5-amino-1,10-phenanthroline. This electrode has been evaluated for electrochemical response to oxidizing and reducing pollutants by direct injection of the air samples without the need for debubbling.[27]

MULTIPARAMETER DETERMINATIONS AND SPECIATION

The determination, whether sequential or simultaneous, of several analytes of interest in environmental analysis by use of a single-FIA system can be based on the different behaviour of the analytes with a common reagent, on the features of the detection system or on the manipulation of the FIA system with the aid of selective chemical reaction and/or the use of different detection systems. The singular features of speciation require separate treatment.

Multiparameter Determinations

A fluorimetric differential-kinetic determination of silicate and phosphate in waters based on the different rates of formation of their molybdo-heteropoly acids has been proposed. The monitored product is thiochrome, formed by oxidation of thiamine by the heteropoly acid. The FIA configurations used, which involve single injection and splitting-confluence points, and a dual simultaneous injection and merging point, respectively, allow measurements to be performed at two different times on each injection. The method permits the determination of the above-mentioned anions in the range 30–600 ng-ml in ratios from 1:10 to 10:1 and can be applied to samples of running and bottled water with good results. The sampling frequency achieved is 60/h.[28]

The use of a suitable detector allows simultaneous determinations to be implemented in straightforward FIA set-ups. A fast detector (e.g. a diode array spectrophotometer-DAS-) has been used for the resolution of binary and ternary mixtures of organic isomers (o-, m- and p-naphthol) based on the use of the same indicator reaction (coupling of a diazonium salt to the hydroxylated compound). This is a typical situation in which the FIA technique offers distinct advantages over the conventional methodology involving the use of precursors for the *in situ* generation of an unstable reagent in a continuous and controlled manner instead of the use of an unstable reagent *per se*. The differences in the absorption spectra of the products formed from the isomers are small, so that a suitable computer program allows monitoring at several wavelengths and processing of the absorbance data at each wavelength, ultimately allowing one to select those which result in the smallest errors in the resolution of the mixtures. Whereas FIA enhances the differences in the chemical behaviours of these systems, the detector emphasises the small differences in the monitored signals; the combined use of both avoids the separation step commonly employed in analyses involving closely related compounds.[29]

The use of fast scan detectors has also proved to be useful for the multidetermination of pollutants. A fast-scan monochromator and a storage oscilloscope have been employed in soil extracts with relative standard deviations in the range 2.5–4.6%. A novel standardization method based on the gradual dispersion of standard into the solution sample zone has been proposed to accomplish multicomponent standard addition at different sample/standard ratios in a single injection.[30] The potential of the use of a fast-scan voltammetric detector for individual and joint determinations of phenol compounds in water from different sources has been exploited. A cyclic voltammetric unit for potential scans connected to a cell with three electrodes has been used for the simultaneous determination of phenol, guaiacol and 2,4-dichlorophenol at levels lower than 1 μg/ml. The resolution and hence the selectivity in electrode multiprocesses can be improved by derivatizing the i–E recordings.[31]

The versatility of Flow Injection Analysis is more clearly shown when the manipulation of the configuration makes possible the multidetermination. The use of a conventional single-beam photometric detector allows the determination of two or three pollutants in a sample if a manifold based on r-FIA mode is used (Figure 3a);[32] this involves the use of a selecting and two injection valves for the merging of one of the reagents and injection of other selective reagents for the determination of each analyte (cyanide and nitrite),[33] or includes two selecting valves for the sample conditioning (buffer, masking agents, etc.) the reagent being inserted through a sole injection valve.[34]

The determination of analytical parameters in drinking water has been carried

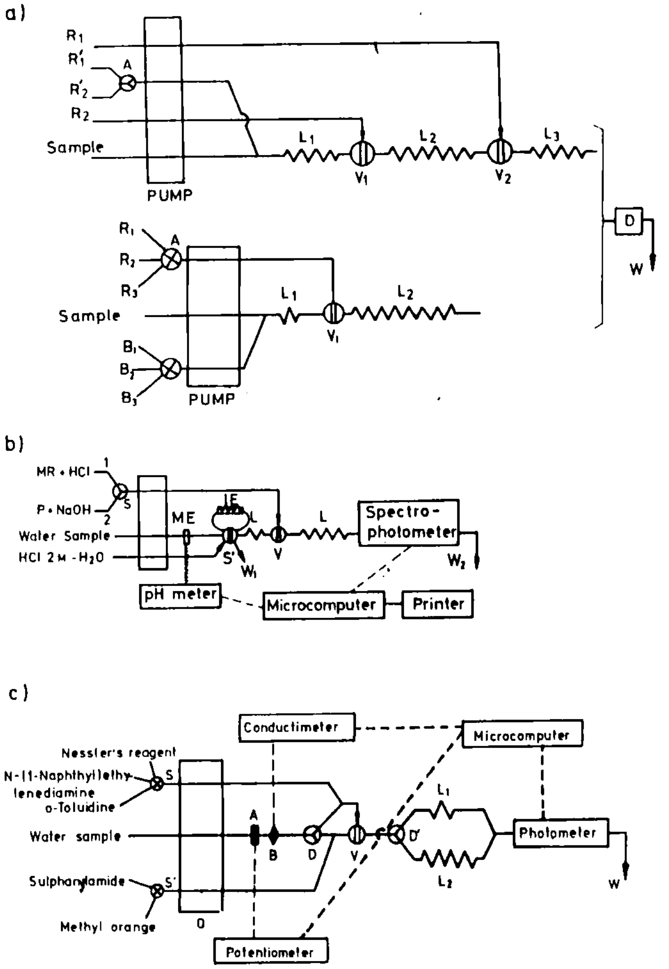

Figure 3 Configurations used for multideterminations. (a) Schematic diagram for determination of anions and cations. (b) Manifold for sequential determination of pH, alkalinity and total ionic concentration. MR, methyl red; P, phenolthalein; ME, microelectrode; IE, ion-exchange column (ref. 36). (c) FIA system for the determination of pH, conductivity, residual chlorine and ammonium and nitrite ions (ref. 37). For details, see text.

out by using different configurations both in the normal and in the reverse mode. One sequential determination of calcium and magnesium (hardness) in natural, drinking and bottled water is based on an FIA titration with photometric detection by using conventional chemical systems, e.g. murexide-EDTA for calcium and eriochrome black-T-EDTA for the sum of calcium and magnesium, the concentration of the latter being obtained by difference. The use of a selecting valve for the carrier (EDTA-NaOH or EDTA-ammonia buffer) and another for selecting the indicator to be admixed with the sample prior to injection is indispensable.[35] The r-FIA mode has been used to determine pH, alkalinity and total ionic concentration[36] and pH, conductivity, residual chlorine, ammonium and nitrite.[37] The former involved the configuration depicted in Figure 3b. The cell including the glass-calomel microelectrode was inserted into the sample stream prior to the injection or merging with the reagents. In addition to a valve for selection of the reagent to be injected through Vi, another injection valve ensures the alternate use of the ion-exchanger mirocolumn located in its loop. In the filling position, the sample does not pass through the loop and the selection and injection of the methyl red-HCl stream allows the determination of alkalinity. In the emptying position, the microcolumn releases an amount of protons equivalent to that of retained ions, which are titrated by injection the phenolphthalein-NaOH solution. A more complex manifold offers the possibility to use the reverse mode and, occasionally, the normal mode (Figure 3c), and allows the determination of the five above-mentioned parameters. The general scheme includes three detectors: potentiometric and conductimetric for the continuous monitoring of pH and conductivity, and photometric for the rest of the analytes. It also includes two diverting valves, D and D′, two selecting valves, S and S′, and one injection valve, V. The data obtained in the monitoring of pH and conductivity performed prior to any confluence or injection point, are collected and treated by a microcomputer. Valves S and S′ allow for selection of the photometric reagents required for the determination of ammonium, nitrite and chloride by sequentially inserting the reagent through valve V. Both selecting valves are used for nitrite determination (confluence of the sulfanilamide channel and injection of N(1-naphthyl) ethylendiamine solution). The determination of ammonium only requires the injection of the Nessler reagent, so that S′ remains inactive. The chloride determination can be performed in two different ways depending on the presence or absence of nitrite in the sample. If there is no nitrite, valve S selects the o-toluidine injection and the channel from S′ is unnecessary; the presence of nitrite calls for an n-FIA configuration, which is set up by switching valve D; this allows the sample stream to fill the loop of the injection valve, whilst S′ incorporates the stream of the suitable carrier-reagent (methyl orange). The length of the channel prior to the photometric detector must be very short for the determination of nitrite and residual chlorine and ten-fold longer for that ammonium ion and chlorine with o-toluidine, valve D′ allows selecting one or the other channel as required.

Speciation of Pollutants

FIA makes an excellent tool for speciation of elements and compounds, as shown by a number of workers.[38] The methods proposed in this area of environmental analysis, of great interest at present, have been developed according to two criteria. (a) the use of a single indicator reaction for one of the species and addition of a redox agent to transform the other into the one which undergoes the indicator reaction and (b) the use of several detectors allowing discrimination between two different states with or without the aid of a chemical reaction for some species.

Redox reagents used to change the oxidation state of a species can be used in solution or on solid reactors. The photometric determination or arsenium as arsenite-arsenate is carried out with the aid of a manifold including a selecting

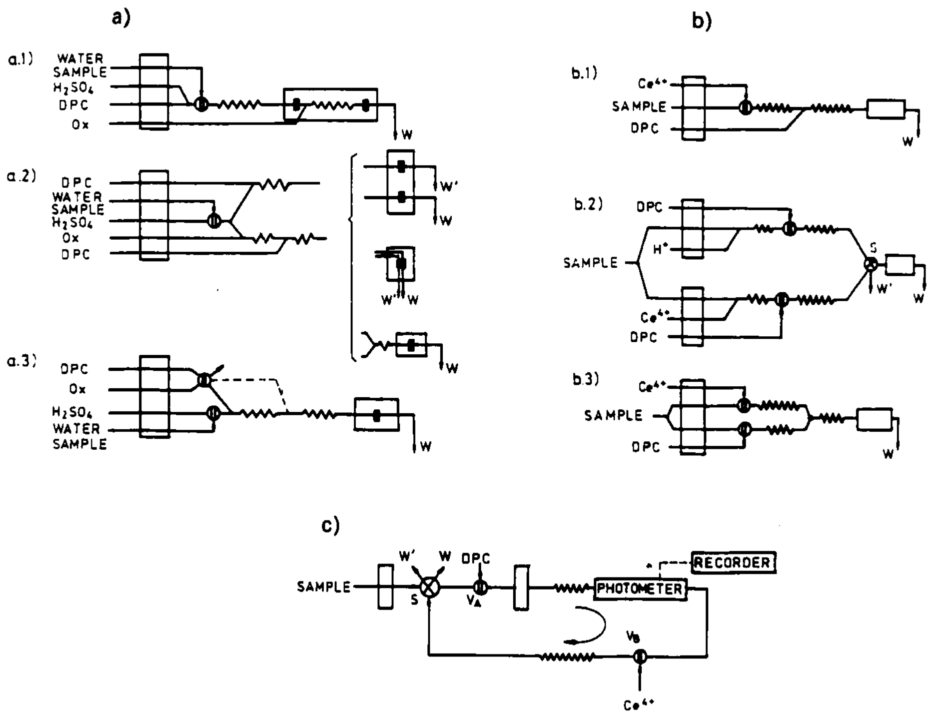

Figure 4 Configurations designed for speciation of chromium. (a) Normal-FIA manifolds (ref. 41); (b) Reverse-FIA manifolds (ref. 42); (c) Open-closed system (ref. 44). For details, see text.

valve allowing or avoiding the merging of the sample with the oxidant (KIO_3 solution) prior to contact with the indicator reagent (molybdate-ascorbic acid).[39] The Cr-DPC-Ce(IV) system has been used to design a large number of configurations for speciation of this element as Cr(VI)-Cr(III), some of which are depicted in Figure 4. They simplify the configuration previously proposed by Bubnis *et al.*[40] which required the use of three peristaltic pumps, an injector and two-channel flow-through valve. Configurations based on n-FIA (Figure 4A)[41] involve the use of a dual-beam spectrophotometer with the sample and reference cells located in series and with the confluence of the oxidant between both (a.1); with splitting the injected plug (a.2) and use of the same detector with the cell aligned in parallel, or with a single-channel spectrophotometer and two cells aligned in the optical path, or with a confluence point prior to a single flow-cell. The sequential determination can be performed with configuration a.3 by having or not the Ce(IV) solution merge prior to that of DPC.

Configurations making use of r-FIA mode (Figure 3B)[42] allow the continuous monitoring of Cr(VI) and sporadic of Cr(III) by injecting an oxidant (b.1), the sequential determination of both oxidation states by selecting the suitable subsystem through S (b.2), or the simultaneous determination of both oxidation states by the asymmetric merging zones mode (b.3) (a large plug of DPC reacts at its head with Cr(VI) present in the sample to yield a peak, and mixes at its tail with the small plug of oxidant, which acts on Cr(III) giving rise to a second peak resulting from contribution of both oxidation states). This last configuration also involving monitoring of the sample pH and a microcomputer to collect the data from both detector has been used to obtain more information on speciation. The data are treated by a program taking account the constant of the equilibria in which both oxidation states of chromium are involved. The calculation of the concentration of up to nine different species of chromium is thus achieved.[43] Finally, an open-closed system such as that depicted in Figure 4C make possible this speciation by inserting the DPC and the oxidizing reagent simultaneously through the two injection valves.[44] A similar configuration has been used for iron speciation based on the injection of 1,10-phenanthroline and hydroxylamine solutions.[45]

A copperised cadmium redox column located in the loop of the secondary valve of a nested system has been used for the simultaneous speciation of nitrogen as nitrite–nitrate. The first subplug of the loop of the main valve provides a peak due to nitrite, and the second, which passes through the solid reactor, provides a peak made up of the contribution from both oxidation states.[46]

An electrochemical detector has been used by Nakayama *et al.* to discriminate between different forms of iodine[47] by the performing electrochemical oxidation of iodide to iodine quantitatively and concentrating it on a carbon wool electrode in a preconcentration cell. The iodate is previously reduced to iodine by a chemical reagent. The resulting amperometric current is proportional to the iodide or idodate concentration in the original solution. The sensitivity is 0.4–0.5 $\mu A/\mu g$ I^- and the detection limit is 5 ng of I^-.

Although the use of two detectors rises the cost of the instrumentation, it dramatically simplifies the set-up. Lynch *et al.* have designed a very simple configuration with two serial optical detectors (molecular and atomic for the speciation of chromium and iron, allowing the determination of one of the oxidation states (Cr(VI) with DPC and Fe(II) with 1,10-phenanthroline) by the photometer and the sum of both by AAS.[48]

FINAL REMARKS

The numerous major contributions of FIA to environmental control in the last years testify its virtually inexhaustible potential. New configurations have been designed, new separation techniques have been incorporated and new detectors have been used to suit methods to the type of sample and analyte concerned.

Possibly, the trends in this area should be aimed to the development of completely automated methods for continuous control, of special usefulness in the different stations of a survey network, to the multiparameter determinations in water and to broaden the scope of pollutants determinable in gaseous samples. With the rare exception of straightforward samples, the on-line coupling with a separation technique (of easy implementation in FIA configurations) allows for increased selectivity and sensitivity in the proposed methodologies.

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