

SANDWICH FIA SIMULTANEOUS MULTIDETERMINATION OF CATIONIC SPECIES IN WATERS

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ABSTRACT

The use of the sandwich technique to perform different biparametric determinations of cationic species in waters is described in order to exploit its general performance in which sampling rate, reagent consumption and analytical range is concerned. To achieve this aim a laboratory-made 14 ports rotatory valve is used. Its construction and working mechanism, namely the possibility of this valve enabling the insertion of a sample plug sandwiched between two plugs of different reagents into the carrier stream, are outlined. With this valve three manifolds were developed: Fe(II)/total iron, Cr(VI)/total iron, Al/Cu by normal and reverse FIA modes determinations, respectively, with sampling rates varying between 60 and 120 h⁻¹. Comparative analysis of the results obtained with proposed methodologies and those of the reference methods were also performed showing correlation coefficients varying between 0.988 in determinations for total iron with system for determination of Fe(II)/total iron, and 0.999 in determinations of Cr(VI) and Cu (by reverse FIA mode). The results obtained showed a relative standard deviation lower than 3.7%.

Keywords: 14 ports rotatory injection valve, sandwich technique, cationic species in waters.

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INTRODUCTION

Characterization of natural or residual waters involves laboratorial evaluation of different constituents of which cationic species are a good example. To facilitate this task different approaches to the development of multidetection flow-injection systems for simultaneous determinations have been carried out.

The most obvious solution was achieved by the use of either, several detectors in series or multichannel detectors¹. However, the costs involved are relatively high. Other systems in which the flowing sample plug was split into two channels and then subject to different chemical treatment downstream have alternatively been proposed. The analytes or products of chemical reactions were then simultaneously monitored in both channels, or after flux convergence into a single detector²⁻⁶. The use of the same flow system to perform different determinations based on flow reagent substitution was also proposed⁷. Multidetermination following the above mentioned options was based on the principle that analytical signals obtained resulted from all potential analyte contained in each sample plug. Together with the reagent continuous flow this aspect leads to a significant consumption of reagent per determination and low total sampling rate is inherent to the use of a single system in sequential multidetermination purposes.

By resorting to the sandwich technique, in which an on-line^{8,9} or multiway¹⁰⁻¹⁴ injectors are used, or even more recently, to the technique of sequential injection analysis¹⁵, the reaction is limited to the reagent/sample interface, which, in turn enabled the detection of more than one analytical signal without subdivision of the sample injected plug. Under these conditions the volume of the reagent used for each determination could be reduced¹⁶ and by using single channel systems, sequential biparametric determinations of different species, in each interface of contact between the sample and the carrier, could be carried out.

In this paper the potentialities of the sandwich technique in implementation of simple setups for simultaneous biparametric determination of different cationic species in waters are assessed, using colorimetric detection. The use of multiport injection devices enables three consecutive loops allowing simultaneous injection of reduced volumes of reagents thereby reducing costs. Additionally, the possibility

of opting for the reverse FIA mode, herein exemplified in the biparametric determination of aluminium and copper, is considered as an alternative when improvement in sensitivity and detection limits, without any considerable decrease in the sampling rate, is required.

EXPERIMENTAL

Reagents and solutions

Analytical grade reagents and deionized water (conductivity less than $0.1 \mu\text{S cm}^{-1}$) were used throughout the experiments.

Standard solutions of iron(III), copper and aluminium were prepared by appropriate dilutions of 1000 mg dm^{-3} SpectrosoL stock solutions (BDH Limited, England). Standard solutions of chromium(VI) were obtained by dilution of a stock solution (1000 mg dm^{-3}) which was prepared by weighing and dissolving potassium dichromate in water. A 1000 mg dm^{-3} stock solution of iron(II) was obtained by weighing ammonium iron(II) sulfate hexahydrate and dissolving it in 0.02 mol dm^{-3} hydrochloric acid as described elsewhere¹⁷.

A stock solution of 1,5-diphenylcarbazide 12.5 g dm^{-3} was prepared in ethanol. Standard working solutions were prepared daily, by diluting 10 times with water an appropriate volume of the stock solution.

Determination of iron(II) and total iron was carried out by using a solution of 1,10-phenanthroline monohydrate obtained by dissolving 2 g in 100 cm^3 ethanol and making up the volume to 1 dm^3 in doubly deionized water. An acetic acid/ammonium acetate buffer solution, prepared as described elsewhere¹², and a solution of hydroxylamine hydrochloride at 200 g dm^{-3} were also used.

Assessment of aluminium was carried out using a solution of eriochrome cyanine R (ECR), at 0.8 g dm^{-3} and a solution of 2.2 g dm^{-3} cetyltrimethylammonium bromide (CTA) in $\text{HCl } 0.1 \text{ mol dm}^{-3}$, respectively. To minimize interference of iron a solution containing 35 g dm^{-3} 1,10-phenanthroline and 2 g dm^{-3} hydroxylamine hydrochloride¹⁸ was used. A 1,2-diaminoethane buffer solution (0.07 mol dm^{-3} in 1,2-diaminoethane dihydrochloride and 0.03 mol dm^{-3}

in 1,2-diaminoethane), was also prepared.

Copper was assessed using a solution of 1.65 g dm^{-3} cuprizone in 17% ethanol in water (v/v) and 0.4 mol dm^{-3} citric acid in 0.6 mol dm^{-3} ammonia solution.

Apparatus

The analysis of the sample contents of total iron and copper by the reference methods was carried out by an atomic absorption spectrophotometer Pye Unicam SP9. For the remaining species a Hitachi U 2000 spectrophotometer was used.

Construction of FIA manifolds was carried out with a Jenway 6105 spectrophotometer equipped with a flux cell Hellma, Ref. 178.713 QS with an optic volume of $8 \mu\text{l}$, connected to a BD 111 Kipp & Zonen recorder. Peristaltic pumps (Gilson Minipuls 2) with 4 or 8 channels were used to drive liquids through tygon, Ismatec tubes of appropriate diameter.

Manifolds were constructed from 0.5 and 0.8 mm PTFE tubing supplied by Omnifit.

A 14 ports rotatory injection valve, depicted in Fig. 1, was made up of a brass plate (BP) with 14 equidistant holes of 1.0 mm internal diameter, arranged in a circular configuration, to which an equal number of teflon tubes (T) were fixed. Attachment of the brass plate to the remaining valve components was accomplished by a teflon plate (TP) with 14 holes concentric with the former. The whole assembly rested on a teflon covering (TC), on the inner side of which there was a teflon rotor (TR) whose movement was controlled by the movement of a pin (P) between two stoppers created by an opening on the brass basis (BB) which supported the whole assembly. The rotor was laid on a bearing ring (B) to minimize rotatory friction. The surface of the rotor in contact with the teflon plate had 7 cavities, 0.5 mm deep, which enabled intercommunication between consecutive pairs of tubes.

Rotation of the handle (H) connected to the rotor, enabled alternation in the position of the cavities and interchange of communication between pairs of tubes.

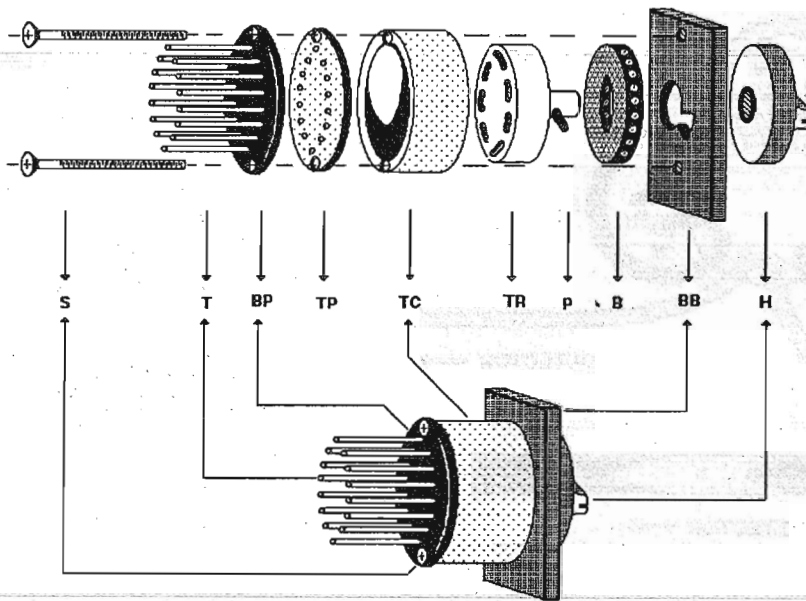


Fig. 1. Exploded view of the 14 ports rotatory valve. S - screws; T - tubes; BP - brass plate; TP - teflon plate; TC - teflon covering; TR - teflon rotor; P - pin; B - bearing; BB - brass basis; H - handle.

The valve had three independent and consecutive loops which enabled injection of a sample plug sandwiched between two plugs of different reagents into the main carrier stream (Fig. 2 A). Two interfaces of contact reagent/sample of distinct analytical use were thus established.

Following optimization of the manifolds, an analytical signal was obtained after introduction of each sample which was made up of two peaks corresponding to the concentration of each species and a valley corresponding to an almost non-reaction zone in the sample plug's centre (Fig. 2 B).

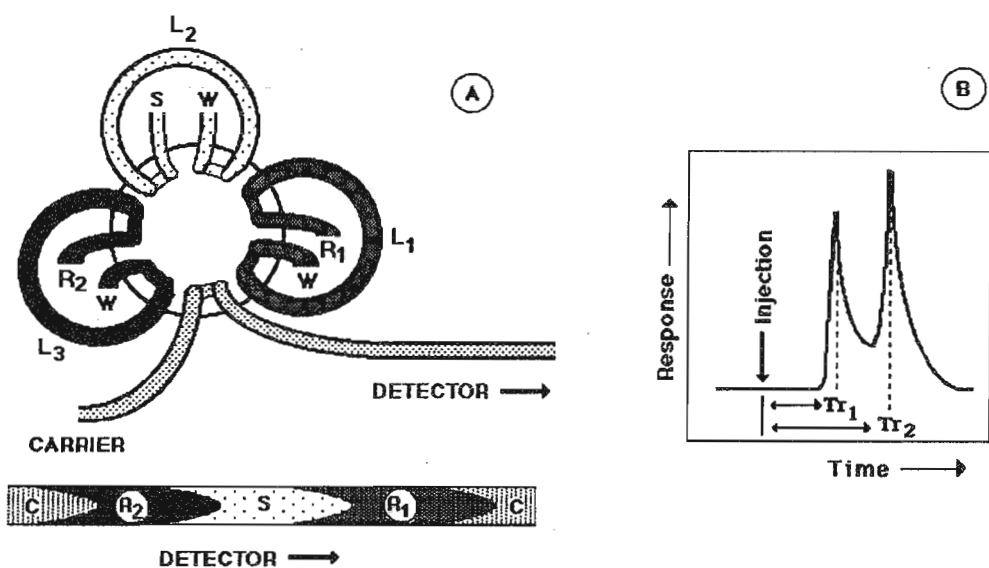


Fig. 2. Diagram showing working mode of the injection valve. (A) Load position and the diagram of the reagent/sample/reagent sequencing in the injection position (B) FIA signal obtained by the flow of the complex formed in each interface trough the reactor. Tr_1 and Tr_2 are the residence times at the first and second interfaces, respectively.

RESULTS AND DISCUSSION

Development of the manifolds was conditioned by the use of a single device for colorimetric detection. This option influenced the type of the chemical reactions involved in the development of colour for determination of the various species tested, so that the resulting coloured complexes showed either common absorbance maximum or enabled the alternative of a compromising wavelength.

Optimization of FIA manifolds was carried out in two stages. Initially the flow-system variables were optimized so as to obtain a transient signal with two distinct peaks which guaranteed the highest possible sampling rate. In a second step the volume of the reagents were optimized, so as to attain a good compromise between sensitivity and the linear analytical range.

Biparametric determination of iron(II) and total iron

Determination of iron(II) and total iron was carried out by determining Fe(II) at the V_1/V_2 interface, whereas total Fe was determined at V_2/V_3 (Fig. 3), since, in the latter, pre-quantitative reduction of Fe(III) to Fe(II) was necessary. The monitored transient peaks corresponded hence to the passage of ferroin, a complex formed with iron(II), through the detector ($\lambda=510$ nm).

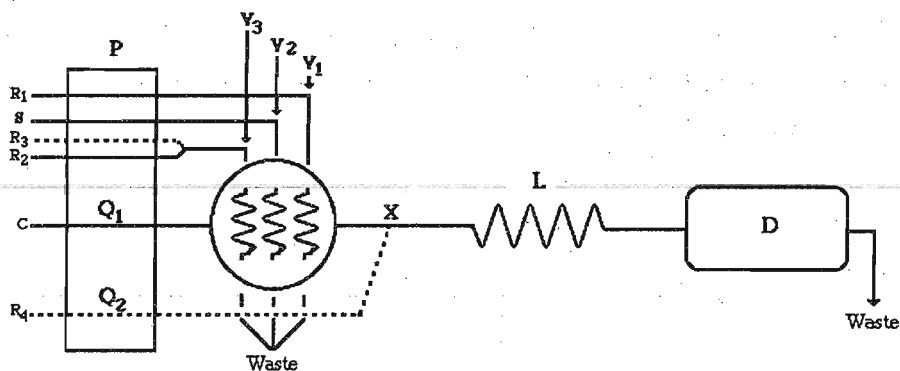


Fig. 3. Diagram of the constructed flow manifolds. P - peristaltic pump; C - carrier; R_1 , R_2 , R_3 , R_4 - reagent solutions; Q_1 , Q_2 - reagent streams; V_1 , V_2 , V_3 - injection volumes; L - coil length; D - detector; X - merging point; --- optional channels (see text).

Achievement of transient signals with two very distinct peaks was a function of various parameters, namely the carrier flow rate, the injected sample, the reagent volume V_1 and the reactor length (L). Poorer separation of the two peaks in the transient signal, would be a consequence of greater dispersion, as a result of an increase in the sample residence time in the reactor (either due to an increase in its length and/or the loop volume V_1 , or due to a decrease of the carrier rate). Distinct peaks were only obtained, for a length of the reactor of 100 cm (0.8 mm i.d.) and the flow rate of addition of the buffer, Q_2 , of 0.5 ml min^{-1} at the merging point X, for

sample volumes greater than 600 μl . The selected flow rate, $Q_1=5.0 \text{ ml min}^{-1}$, corresponded to the best compromise between sensitivity and sampling rate. The intensity of the peak corresponding to the determination of total iron increased with an increment in the volume of the injected sample up to 700 μl (Fig. 4 A). For V_1 fixed at 100 μl , a lower definition of the valley until complete overlapping ($L=200 \text{ cm}$) of the two peaks, corresponded to an increase in the length of the reactor (Fig. 4 B).

Prior to its passage through the reactor the sample flowed through the loop containing the reagent used in the determination of Fe(II) and thus its effect on the separation of the two peaks was also studied. As expected, an increase in the volume of this loop produced lower definition of the two peaks similar to that observed with an increase in the length of the reactor. Only one peak was observed for a volume of 350 μl .

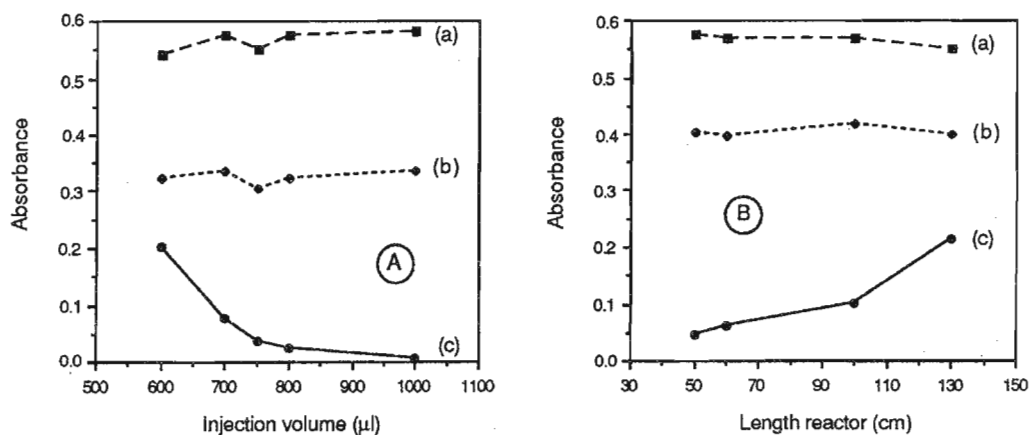


Fig. 4. (A) Effect of the injected sample volume on peak values of (a) total iron; (b) iron(II); and (c) valley between two peaks (Sample solution at a concentration of 5.00 mg dm^{-3} for total iron and 3.00 mg dm^{-3} for iron(II)) and (B) Effect of the length of the reactor on peak values of (a) total iron; (b) iron(II); and (c) valley between two peaks (Sample solution at a concentration of 5.00 mg dm^{-3} for total iron and 3.00 mg dm^{-3} for iron(II)).

The volume of the reagent inserted through V_1 also conditioned the linear range for the determination of Fe(II). After successive calibrations, the smallest volume of reagent to be inserted which caused simultaneously a maximum analytical range without compromising the definition of the analytical signal was, therefore, determined. Adjustment of reactor length to 50 cm, V_2 to 700 μl and the flow rate of the carrier to 5.0 ml min^{-1} , produced a linear range up to 5 mg dm^{-3} , with a limit of detection of 0.2 mg dm^{-3} , without an overlap of the two transient peaks (Table 1).

Table 1: Performance of the proposed methods

Determination	Linear Regression			Upper limit (mg dm^{-3})	Detection limit ^b (mg dm^{-3})	R.s.d. ^c (%)	Conc. for r.s.d. (mg dm^{-3})	Sampling rate/ h^{-1}
	Intercept	Slope	r^a					
Iron(II) and Total Iron								
Iron(II)	- 0.021	0.128	1.000	5.00	0.22	0.5	3.70	120
Total Iron	- 0.003	0.114	1.000	7.00	0.17	3.7	0.80	120
						0.8	4.50	
						2.1	1.90	
Chromium(VI) and Total Iron								
Chromium(VI)	0.067	0.185	0.999	4.00	0.08	2.4	1.87	70
Total Iron	- 0.016	0.086	1.000	10.00	0.38	1.0	2.46	70
						1.1	1.32	
						0.7	7.15	
Aluminium and Copper								
Aluminium (normal FIA)	0.005	1.532	0.999	0.200	0.0007	1.7	0.032	70
Copper (normal FIA)	- 0.022	0.059	0.996	3.00	0.039	1.1	0.164	70
						1.0	0.99	
						0.5	2.97	
Aluminium (reverse FIA)	0.003	1.832	0.999	0.200	0.0006	2.4	0.045	60
Copper (reverse FIA)	- 0.054	0.169	0.999	3.00	0.016	0.9	0.133	60
						0.7	1.00	
						0.9	2.91	

a) Correlation coefficient.

b) Assessed according to reference 19.

c) Relative standard deviations determined after ten repeated injections.

The volume of the analytical reagent mixture inserted in loop V_3 (200 μl), and used in the above mentioned trials, was kept in the optimized system as it was the lowest volume capable of producing maximum sensitivity and a linear calibration

up to 7 mg dm^{-3} . For lower volumes of reagent there was a decrease in sensitivity as a consequence of greater dispersion of the reagent under the adopted flow rate.

Several hydroxylamine hydrochloride solutions with concentrations ranging from 100 to 400 g dm^{-3} were tested with the purpose of achieving complete reduction of iron(III) to iron(II). Intensity of the analytical signal was observed to be independent of hydroxylamine concentration in the range between 200 and 400 g dm^{-3} .

The final setup proposed for the determination of iron(II) and total iron consisted on intercalating a $700 \mu\text{l}$ sample into the carrier stream together with $150 \mu\text{l}$ of 1,10-phenanthroline and $200 \mu\text{l}$ of a 1:1 (v/v) solution of 1,10-phenanthroline and hydroxylamine hydrochloride.

Biparametric determination of chromium(VI) and total iron

For the determination of Cr(VI) and total iron a tubular reactor with 0.5 mm inner diameter was used. The analytical wavelength was adjusted to 526 nm which corresponded to the point of intersection between spectra of the two absorbents with highest molar absorption coefficient.

During the optimization procedure, conclusions similar to those mentioned above for the effect of the length of the reactor, the volumes V_1, V_2 and the rate Q_1 (Fig. 3) on the analytical signal definition, were also drawn. A compromise was established between sensitivity and sampling rate for a 250 cm reactor length, a 3 ml min^{-1} carrier flow rate (Q_1), a $800 \mu\text{l}$ sample volume (V_2), and a $150 \mu\text{l}$ and $200 \mu\text{l}$ for V_1 and V_3 , respectively.

Following optimization of the volume and composition of the reagents for development of colour, in the final setup used for water analysis, the sample was inserted in a carrier, sandwiched between a V_1 1:3 (v/v) mixture of sulfuric acid and 1,5-diphenylcarbazide and a V_3 1:1:1 (v/v/v) mixture of 1,10-phenanthroline, hydroxylamine hydrochloride and acetic acid/ammonium acetate buffer.

Calibration graphs obtained under optimum conditions were linear up to 4 mg dm^{-3} for chromium(VI) and up to 10 mg dm^{-3} for total iron. Values obtained for detection limits, linearity of calibration lines, measurement repeatability and

sampling rates are listed in Table 1.

Biparametric determination of aluminium and copper

In the system developed for the determination of aluminium and copper, reaction at the leading edge of the sample zone produced a peak corresponding to a complex formed with aluminium, whereas the second peak was related to the concentration of copper in the sample. Determinations were carried at 595 nm.

In the reaction of aluminium, it was necessary not only to assess the effect of reagent concentration in the respective peak, but also to determine the most suitable relationship between the concentration of the reagent for the development of the colour and the cationic surfactant, so as to achieve improved sensitivity. The most adequate molar ratio was 1:5. This was obtained by keeping the reagent for the development of the colour at a fixed concentration and varying CTA concentration. This confirmed earlier results¹⁸ obtained for this determination.

In this system, variation of the flow rate of the carrier solution, for a 65 cm (0.8 mm i.d.) reactor length, influenced separation of the two peaks obtained for both determinations. For a 0.6 ml min^{-1} flow rate the minimum value corresponded to 10 and 25% of the first and second peaks respectively, whereas for a 2.4 ml min^{-1} flow rate (Q_1) these values were reduced to 4 and 10%.

Following optimization of the volume and composition of the reagents for the development of colour, it was established that the sample ($V_2=500 \mu\text{l}$) was intercalated in $V_1=30 \mu\text{l}$ and $V_3=20 \mu\text{l}$ in the final setup (Fig. 3). The solution inserted in V_1 was obtained by pre-mixing of the colour reagent with 1,2-diaminoethane buffer. The colour reagent solution consisted of a 6:7:2 (v/v/v) of ECR, CTA and a solution of 1,10-phenanthroline and hydroxylamine hydrochloride. A 1:1 (v/v) solution of cuprizone and citric acid-ammonia solution was inserted at V_3 .

Under these conditions it was possible to determine aluminium levels between 0.0007 and 0.2 mg dm^{-3} and copper levels between 0.04 and 3 mg dm^{-3} at a sampling rate of 70 h^{-1} (Fig. 5).

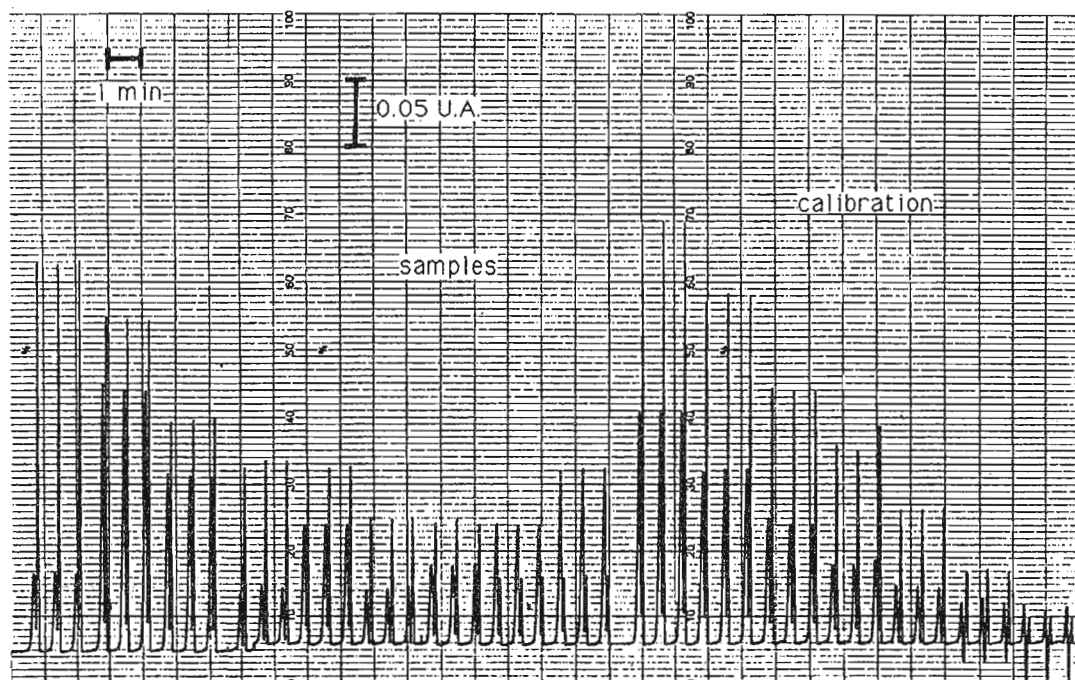


Fig. 5. Recorder output obtained in the biparametric determination of aluminium and copper in natural waters corresponding (from right to the left) to the triplicate injection of a blank and six standards between $0.025\text{-}0.200\text{ mg dm}^{-3}$ for aluminium and $0.050\text{-}3.00\text{ mg dm}^{-3}$ for copper, and nine samples.

Reverse FIA determination of aluminium and copper

The application of the sandwich technique was also tested for the possibility of operating in the reverse FIA mode in aluminium and copper biparametric determination. In this case, not only was the sample injected through V_2 but the carrier solution, deionized water, was also replaced by the sample flow. Thus, the quantity of the sample which interacts with the reagent is increased since there is a reaction at both interfaces of the reagent zones. An increase in sensitivity was then achieved by decreasing the limits of detection. There was a slight decrease in the sampling rate due to the need of filling the reactor with a new sample prior to each injection. By interposing of a three way valve at C it was possible to facilitate this

operation achieving sampling rates of 60 h⁻¹ (Table 1).

Water analysis

The quality of the results obtained by the proposed methodologies for the analysis of different species in natural and residual waters were comparatively assessed with the results from the respective reference methods. A relation of the type $C_f = C_0 + SC_r$ was established between the FIA results (C_f) and the reference method results (C_r) (Table 2).

Reference methods were based on the monitoring of the complex formed in the reaction of chromium(VI) and iron(II) with 1,5-diphenylcarbazide and 1,10-phenanthroline, respectively, by molecular absorption spectrophotometry, whereas total iron was evaluated by atomic absorption spectrophotometry²⁰. Aluminium was also assessed by molecular absorption spectrophotometry following reaction with eriochrome cyanine R whereas copper was assessed by atomic absorption spectrophotometry²¹.

Table 2: Comparison of the results obtained by FIA (C_f) methods and by reference methods (C_r)

	Parameters of equation $C_f = C_0 + SC_r$			Measured concentration range (mg dm ⁻³) by reference method ^b
	C_0	S	r^a	
Iron(II) and Total Iron				
Iron(II)	- 0.097	0.975	0.993	0.74 - 4.83
Total Iron	- 0.158	1.001	0.988	0.93 - 6.70
Chromium(VI) and Total Iron				
Chromium(VI)	0.036	1.010	0.999	0.52 - 3.26
Total Iron	-0.010	0.938	0.994	0.35 - 8.20
Aluminium and Copper				
Aluminium (normal FIA)	- 0.007	1.031	0.994	0.018 - 0.191
Copper (normal FIA)	- 0.031	1.003	0.993	0.47 - 2.94
Aluminium (reverse FIA)	0.0005	0.992	0.993	0.018 - 0.191
Copper (reverse FIA)	0.108	0.955	0.999	0.47 - 2.94

a) Correlation coefficient.

b) Results obtained for 20 water samples.

The values of the slopes obtained for all the determinations varied between 0.938 and 1.031. Such figures were assessed for total iron in biparametric determination of Cr(VI)/total iron and aluminium by normal FIA mode, respectively. Overall linear regression lines showed intercepts close to zero. The correlation coefficients values assessed in all determinations varied between 0.988 and 0.999. These figures were obtained in the assessment of total iron in biparametric determination of Fe(II)/total iron and chromium(VI) and copper by the reverse FIA mode respectively.

CONCLUSIONS

The use of a multiport rotatory injection valve can foster the development of simple design and easy operation systems based on the sandwich technique with low reagent consumption in biparametric determinations. This was shown by analysing different pairs of cations in waters which involved distinct colorimetric reactions. The manifolds showed the possibility of biparametric determination at a satisfactory sampling rate. There was a fairly good agreement between the results obtained and those of the reference methods.

Application of this kind of valves can also be easily extended to uniparametric determinations in which the sample is intercalated in a reduced reagent volume or to determinations in which the sample must be dispersed prior to a colour-developing reaction in chasing-zones mode.

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