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GAS DIFFUSION WITH PRECONCENTRATION FOR THE DETERMINATION OF FLUORIDE IN WATER SAMPLES BY FLOW INJECTION

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Summary—The preconcentration of fluoride is achieved on-line by converting it to trimethylsilane which then diffuses through a gas permeable membrane to be absorbed in a stationary sodium hydroxide acceptor stream. This stream is enclosed in the sample loop of an injection valve and after preconcentration, the fluoride sample is flushed into a flow injection manifold for spectrophotometric analysis by the zirconium/alizarin S procedure at 520 nm. The method is suitable for fluoride analysis in the range 0.1–10 mg/l at a sampling rate of 17/hr. Phosphate does not interfere and aluminium and iron can be tolerated at 200 and 500 times the fluoride concentration, respectively. The LOD was calculated to be 0.055 mg/l and LOQ was found to be 0.18 mg/l.

Many reports have appeared on the use of gas diffusion in flow injection analysis for different gaseous species but few have given details of this methodology for the analysis of fluoride.

Valcarcel and de Castro[1] described a gas diffusion–flow injection (GD–FIA) system for fluoride analysis which was first developed by Macdonald and Wu[2] and presented at a conference by these authors. According to the former, 40–200 μl samples were injected into an aqueous carrier which merged with an acidified hexamethyldisiloxane (HMDS) stream to produce trimethylfluorosilane (TMFS), which in turn diffused through a Teflon membrane into an alkaline acceptor stream and the fluoride was detected spectrophotometrically by the Alizarin Fluorine Blue method. A surfactant was added to improve the diffusion at the membrane and pyrophosphate was added to the acid carrier to eliminate interferences from ions which form complexes with fluoride. A manifold design was not presented[1] and other details such as sample throughput, TMFS reaction conditions and diffusion cell methods were not available.

Recently, a slightly more detailed description of an automated GD–FIA method was presented by Fang *et al.*[3] This procedure involved separation and preconcentration of the fluoride on-line, the latter serving to enhance the sensitivity of the technique. The sample was acidified by merging with a stream of 8M sulfuric acid solution and heated to 78°C while passing through a 280 cm coil. Hydrogen fluoride formed in the donor stream diffused through a Teflon membrane in the gas diffusion unit to be preconcentrated for a set time period in a static alkaline recipient solution enclosed in the sample loop of an injection valve. At the end of that time, the injector was activated and the carrier transported the absorbed sample downstream where it merged with lanthanum/alizarin complexone solution to be determined spectrophotometrically at 620 nm. Fluoride was determined in waste water at a sample rate of 40/hr with a detection limit of 0.1 mg/l. Aluminium still interfered but it was claimed[4] that there was a considerable improvement in the concentration of aluminium ion which could be tolerated in the system compared with that by the direct colorimetric procedure without separation by gas diffusion.

Dingli *et al.*[5] reported that hexamethyldisilazane (HMDSA) was a more suitable accelerating reagent than hexamethyldisiloxane in simple diffusion experiments as the latter was limited in its practical application owing to its instability. Yoshida *et al.*[6] were able to mask aluminium successfully at 500 times the concentration of fluoride in the classical Alizarin Fluorine Blue colorimetric method by the addition of a small volume of concentrated phosphoric acid in the acid mixture. In this paper, these and other

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improvements are introduced into a gas diffusion–flow injection system with preconcentration for the analysis of fluoride and the method is applied to the analysis of water samples; spectrophotometric detection of fluoride was carried out using the zirconium/alizarin sulfonate complex at 520 nm.[7]

EXPERIMENTAL TECHNIQUES

Instrumentation

Four different gas diffusion modules were investigated.

Module I. The Tecator Chemifold V module consists of two Perspex blocks, each with a straight shallow groove of dimensions 75 mm long, 2 mm wide and 0.2 mm deep (surface area/volume ratio = 5:1).

Module II. A module was constructed which consisted of two Perspex blocks, each with a straight channel of dimensions 65 × 2 × 0.8 mm (surface area/volume ratio = 1.7:1).

Module III. A module constructed from two Teflon blocks, each with a spiral channel of dimensions 90 mm long, 0.5 mm wide and 0.3 mm deep (surface area/volume ratio = 3.8:1).

Module IV. Similar to Module III in design and material with channel dimensions 190 mm long, 0.7 mm wide and 0.3 mm deep (surface area/volume ratio = 4.4:1).

The cross section of the channel in Module I was rectangular whereas the channels in the other modules were hemispherical. A Teflon membrane was sandwiched between the blocks and the blocks were sealed by screws or a clamp.

The water bath used to heat the acidified sample stream in the long reaction coil consisted of a 500 ml round-bottomed flask with a wide lip placed in a temperature controlled heating mantle.

Electron micrographs were obtained using a Siemens Autoscan Microscope. The membranes were mounted on aluminium stubs using double-sided adhesive tape and sputter-coated with gold, using a Balzers Union Vacuum deposition unit (model FL-9496), to minimize the distortion of images due to charging of the specimens during the electron beam irradiation.

Membranes

Several fluorinated polymer membranes were tested in the gas diffusion modules.

(i) Teflon plumbing tape (Dorf Industries Pty. Ltd., Clayton, Victoria, Australia). Average thickness, 0.075 mm; specific gravity, 0.4 g/cm^3. Electron microscopy showed oval-shaped pores, approximately 10 μm long and 1 μm wide.

(ii) Unasco Teflon (Shamban) tape (Unasco Pty. Ltd., North Melbourne, Victoria, Australia). Thickness, approx. 0.14 mm; specific gravity, 1.6 g/cm^3. Electron microscopy revealed a mixture of pores (<1 μm diameter) and cracks (1–3 μm long, <1 μm wide), which appeared to be homogeneously distributed.

(iii) Gelman Teflon supported membranes (Gelman Scientific Inc.). The Teflon 200 and 450 with the polypropylene screen, had pore diameters of 0.2 and 0.45 μm, respectively, and a thickness of 0.18 mm (including the thickness of the webbing). Membrane discs were cut to size for use in the spiral gas diffusion Modules III and IV. Electron microscopy scans showed a network fibrous microstructure rather than distinct pores of clearly defined diameters; however, the spacings between the fibres in the microstructure were consistent with the claimed 0.45 and 0.2 μm pores.

(iv) Millipore (type FA). One micron pore Teflon membrane, cut to size for use in diffusion Module III.

(v) Teflon gas seal tape (Dupont™ A.G.A. Approval No. 3228). This yellow tape is used to prevent gas leakages; thickness, approx. 0.11 mm; specific gravity, 1.6 g/cm^3. Electron microscopy revealed a microstructure of irregular cracks, 1–2 μm long and about 0.2 μm wide.

Reagents and their storage

The zirconyl chloride ($1.1 \times 10^{-3}M$) in $0.20M$ $H_2SO_4/0.55M$ HCl solution was prepared as in our previous paper.[7] The alizarin red S solution ($2.30 \times 10^{-3}M$) was prepared as recommended by Meyling and Meyling.[8] The hexamethyldisilaxane (HMDSA, Aldrich) solution was prepared fresh daily by measuring out a volume of the acid solution (H_2SO_4 or mixed H_2SO_4/H_3PO_4) in a flask, adding the appropriate volume of the HMDSA and stirring for about 5 min. The above solutions were stored in glassware which had been cleaned with Teepol before soaking for 24 hr in 20% H_2SO_4 and rinsing with deionized water.

The sodium hydroxide solutions used as the acceptor and donor streams were dispensed from polyethylene containers fitted with soda-lime guard tubes to exclude carbon dioxide. All fluoride standard solutions were stored in screw top polyethylene bottles which had been washed with Teepol, soaked in 20% H_2SO_4 for 24 hr and washed with copious amounts of deionized water before use.

RESULTS AND DISCUSSION

On-line preconcentration

The flow injection system constructed using the Tecator FIAstar 5020 analyzer and a four-channel peristaltic pump is shown schematically in Fig. 1. The upper half of the manifold is based on the spectrophotometric detection of fluoride at 520 nm using the zirconium/alizarin sulfonate complex. The reddish-violet complex ion is formed in acid conditions and it reacts with fluoride to release the yellow alizarin sulfonate ion (ALIZ-) and the colorless hexafluorozirconate anion:[8]

$$[Zr(ALIZ)_2]^{2+} + 6F^- \rightleftharpoons [ZrF_6]^{2-} + 2ALIZ^-.$$

Although the optimal parameters and reagent concentrations for this method have been established previously,[7] it was necessary to use a NaOH solution as the carrier and match its composition with that of the acceptor stream to improve the reproducibility of the results by avoiding matrix effects. In the lower half of the manifold, the Gilson pump is used to deliver the sample (S), the acid stream (D) containing HMDSA and the acceptor stream (AC) to the gas diffusion module. The acceptor stream of the gas diffusion unit constitutes the sample loop of the injection valve in the upper half of the manifold.

While the acceptor stream is stationary, the sample and acidic HMSDA streams are pumped simultaneously and merge within a Y-piece. The acidified sample is heated while passing through a long reaction coil RC2 immersed in a thermostatted water bath, where the following reaction takes place to generate trimethylfluorosilane:[5]

$$2[(CH_3)_3Si]_2NH + 4HF + H_2SO_4 \rightarrow 4(CH_3)_3SiF + (NH_4)_2SO_4.$$

The liberated fluoride compound diffuses through the permeable membrane to be absorbed in the stationary acceptor stream enclosed in the sample loop of the injection valve, where it is preconcentrated. The absorption step in alkaline solution is

$$2(CH_3)_3SiF + 2NaOH \rightarrow [(CH_3)_3Si]_2O + 2NaF + H_2O.$$

Once the preconcentration period is over, the flow of the acidic sample stream is halted, the injection valve is activated, the carrier passes through the sample loop and flushes out the fluoride for its spectrophotometric determination in the upper half of the manifold.

Modifications to the injector

Two serious problems were encountered in preliminary experiments using the system and conditions in Fig. 1. Firstly, a large negative peak was consistently observed just prior to the

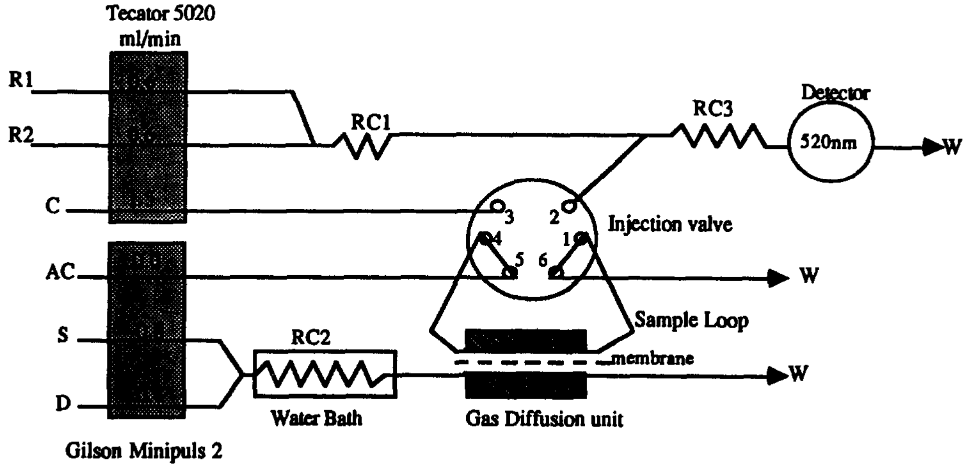

Fig. 1. Schematic diagram of the gas diffusion flow injection system in the preconcentration mode where the acceptor portion of the gas diffusion module constitutes the injector sample loop. R1, 2.3 × $10^{-3}M$ alizarin red S solution; R2, 1.1 × $10^{-3}M$ zirconyl chloride in $0.2M$ $H_2SO_4/0.55M$ HCl; C, $0.1M$ NaOH solution; AC, $0.1M$ NaOH solution; D, 1.25% HMDSA in $1M$ H_2SO_4; S, sample stream; flow rates as specified in the diagram; RC1 and RC3, reaction coils of 30 and 60 cm, respectively; RC2, 330 cm coil in a thermostatted (88–90°C) bath; gas diffusion Module I and Teflon gas tape; W, waste lines. Flow rates at the end of the preconcentration period; AC, 1.5 ml/min; S and D, 0.0 ml/min.

Table 1. Comparison of different Teflon membranes (mean ($n = 3$) peak heights (mV))*

Fluoride Conc. (*mg/l*)	Gelman (0.20 μm)	RSD (%)	Gelman (0.45 μm)	RSD (%)	Millipore (1.0 μm)	RSD (%)	Unasco (Tape)	RSD (%)	Gas (Tape)	RSD (%)
0.3	147	3.0	161	4.0	126	2.8	85	4.2	122	4.8
0.5	209	1.5	211	2.5	176	2.8	166	1.3	168	15.5
1.0	407	0.6	366	1.9	321	2.0	330	1.5	298	2.0
2.0	722	0.4	667	0.5	—	—	617	0.9	590	3.7

*With the manifold in Fig. 1, the following conditions were used.

Spiral gas diffusion Module III; D, 1.25% (v/v) HMDSA in $1M$ H_2SO_4; flow rates of D and S streams, 0.88 ml/min during the preconcentration step; C, $0.05M$ NaOH; AC, $0.05M$ NaOH; RC2, 350 cm, 0.5 mm i.d; preconcentration time, 3 min, sample consumption, 2.6 ml; water bath, 98 ± 1°C.

absorbance peak of interest. This peak was reasonably reproducible for each run and was only observed in runs which involved stopping and starting of the acceptor and donor streams through the gas diffusion module. Secondly, air bubbles were produced in the acceptor stream during the preconcentration period. As the Perspex separation module was transparent, it was observed that the flow of the lower donor stream resulted in a peristaltic effect on the upper acceptor stream resulting in the breaking up of the continuity of the acceptor stream, *i.e.* creating gaps/bubbles within the upper channel, as it was pushed along slowly by the flow of the donor stream. This peristaltic effect led to NaOH acceptor solution flowing very slowly out of the waste line although the compression lever for this channel on the pump had been released to arrest the flow of the acceptor stream. A coil (300 x 0.3 mm) inserted on the waste line of the injector reduced the bubble formation but it failed to halt the slow forward flow of the acceptor stream.

It appeared that the only way to prevent this peristaltic effect on the acceptor stream was to close the injection loop at both the inlet and outlet ends so that there was resistance to flow in either direction during the preconcentration period. The immediate solution was the introduction of two-way Hamilton valves (or tubing clamps), one just before the pump and the other after the injection valve, and these were closed during the preconcentration step. Results obtained using this manual system are satisfactory as indicated by tabulated data elsewhere in this paper.

Choice of membrane

The permeability of the volatile fluoride product (TMFS) through several kinds of Teflon membranes and the durability of the membranes were studied. The highest permeability was shown by the two Gelman membranes which also demonstrated good precision, as shown in Table 1. The lower permeability of the Unasco tape was probably due to its greater thickness; Schulze *et al.*[9] investigated the influence of membrane thickness on diffusion rate across a membrane and found that transfer efficiency decreased linearly with increasing thickness as expected from Fick's Law. The life times of the Gelman filters and the Unasco tape in the gas diffusion module varied from 3 to 14 days. On the other hand, the yellow gas seal tape was not able to withstand the pressure required to seal the two Teflon blocks together in the clamp; coupled with the high temperature of the reaction, the tape soon softened giving rise to mixing between the upper and lower streams. In subsequent experiments, the 0.45 μm or 0.2 μm Gelman membrane filters and the Unasco tape were used; more often the latter was chosen as this had the advantage of being more readily available and it was very much cheaper. For all the membranes tested, a recalibration is recommended with every change of the membrane, although the variation in the observed signal on changing a Gelman membrane in the gas diffusion module is less than that observed after changing the Unasco tape. This can be justified by the fact that the Gelman membranes have more standardized chemical and physical characteristics.

Temperature effects

Figure 2 demonstrates the effect of the water bath temperature on the peak height for fluoride concentrations in the range 0.2–1.0 mg/l. As can be seen, there is a significant increase in the peak height and sensitivity on elevation of the temperature to 98 ± 1°C. The enhancement in signal may be due to acceleration in production of the volatile compound as well as an increase in gas transference across the membrane as a result of an increase in partial pressure in the donor stream and the temperature dependence of the diffusion coefficient.[9]

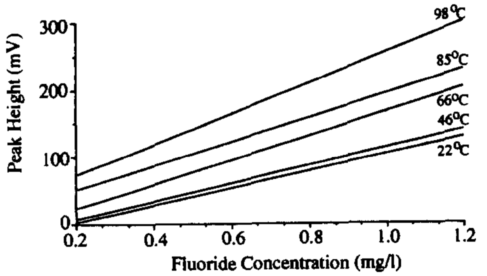

Fig. 2. Effect of temperature on the diffusion process. Gelman 0.2 μm membrane; preconcentration time, 2 min; other conditions as in Table 1.

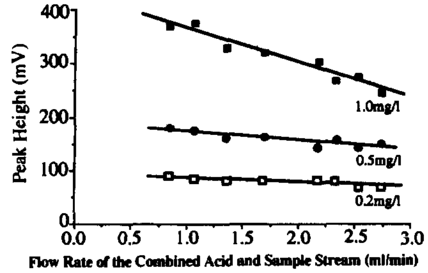

Fig. 3. Effect of the flow rate of the combined acid/sample stream on the FIA peak height. Conditions as in Table 2 with RC2 = 350 cm; flow rates of individual S and D streams are identical during the preconcentration step.

Optimization of conditions for gas diffusion

The length of reaction coil RC2 is important as it determines the reaction time between the HMDSA-acid solution and the fluoride sample and subsequently the amount of volatile product produced. Initial experiments above indicate that the reaction to produce the volatile product is slow and it is necessary to use a relatively long reaction coil to provide efficient mixing and give a detectable response at low concentrations of fluoride. The results obtained for reaction coil lengths in the range 90–555 cm are tabulated in Table 2. The effect of the reaction coil length on the reproducibility of the detector response was insignificant, however, the detector response reached a maximum for a coil length of about 350 cm at fluoride levels of 1 mg/l or below so this coil length was used for the remaining experiments.

The flow rate of the combined acid-sample stream through RC2 can affect the reaction time between the acidic HMDSA and fluoride as well as the residence time in the gas diffusion module, thus influencing the efficiency of transfer of the gas. From Fig. 3, it is evident that as the flow rate is increased, a decrease in the signal is observed and this is more pronounced at higher concentrations. A combined flow rate in the region 1.5–2.0 ml/min seems to be a reasonable compromise between sensitivity considerations, signal stability and sample throughput. In these experiments, the flow rates of the acid and the sample streams were about equal before they merged at the confluence T. Tests were carried out in which the flow rate of the sample stream was faster than the flow rate of the acid stream and vice versa, however, the most sensitive results were obtained using equal flow rates of the acid and sample streams.

Table 2. Dependence of peak height on length of RC2*

	Reaction coil length(*cm*)					
Fluoride Conc.	90	150	235	350	435	555
(*mg*/*l*)	Peak height (*mV*)					
0.3	89	116	130	147	143	142
0.5	122	192	203	209	203	187
1.0	231	295	373	416	403	289
2.0	512	594	684	765	835	549

*With the manifold in Fig. 1, the following conditions were used. Gas diffusion Module III; D, 1.5% (v/v) HMDSA in 1*M* H_2SO_4; Gelman 0.2 μm membrane; all other conditions as in Table 1. Peak heights are the mean of three determinations.

The concentration of the alkaline acceptor solution has been claimed to influence several factors in the diffusion process; these include the absorption capacity of the acceptor stream and thus the transfer process in the diffusion module, the reaction of the volatile species after it permeates the membrane and possibly the kinetics of the spectrophotometric reaction.[10] The relevance of these claims in the system under study was tested for fluoride standards in the range 0.2–2.0 mg/l by varying the concentration of the acceptor solution between 0.025 and 0.25*M* NaOH; throughout this investigation, the NaOH concentration of the acceptor and carrier streams were identical. It was observed that the signal decreased as the concentration of sodium hydroxide increased and that baseline noise increased substantially above 0.1*M* NaOH. A concentration of 0.05*M* was considered to be optimal for further studies although there was little difference in the responses and precision for acceptor solutions of 0.05*M* and 0.025*M* NaOH.

Acidic conditions are required to convert the fluoride to the volatile product.[5] The acid concentration of the donor stream was varied to determine its effect on sensitivity and it was concluded that there was no advantage in using concentrations of acid above 1*M*. It was found that the efficiency of the diffusion process and thus the sensitivity was more dependent on the concentration of HMDSA in the acid medium; this confirms the findings of Taves[11] that the key factor in the diffusion process is the formation of the hydrophobic volatile product. To test this claim, the concentration of HMDSA in 1*M* H_2SO_4 was varied between 0.25 and 2.5% (v/v) and it was found that the sensitivity increased as the concentration of HMDSA increased and then stabilized above 0.9%. In further studies, a concentration of HMDSA of 1.5% in 1*M* H_2SO_4 gave reliable results.

Macdonald and Wu[2] added a surfactant (ICI Ethylan) to the acid solution, claiming that it improved the diffusion characteristics at the Teflon membrane by allowing better contact. In the present study, addition of this surfactant led to wetting of the membrane and subsequent permeation of donor into the acceptor solution which was manifested by large positive peaks for blanks. In classical diffusion studies, diffusion was enhanced by the addition of ethanol to the acid solution[12] but this approach led to lower responses for fluoride at or below 1.0 mg/l and poor reproducibility.

Gas diffusion module

The influence of the geometrical design of the gas manifold unit has been studied by several researchers[9–10,13–15] and it was agreed that several parameters influence the diffusion processes.

A large surface area to volume ratio is required thereby allowing a greater mass transfer of gas between the two streams. This condition can be achieved practically by employing as wide a channel as possible without permitting the membrane to collapse into one channel or the other and a long channel to increase the contact surface area between the sample solution and the membrane. The latter will also increase the time in which the donor stream is in contact with the membrane. The depth of the channel also influences the efficiency of the diffusion process. The donor stream has been discussed in terms of three different layers:[14] (i) the bulk solution itself, (ii) the few-molecules-thick layer against the membrane, and (iii) the gas in the membrane layer. In the molecular diffusion process, only the second and third layers influence the efficiency of the physical diffusion process. Thus, it is claimed[14] that lessening the depth of the channel decreases the ratio between the bulk solution and the second layer.

Residence time is another parameter which can affect the gas transfer efficiency.[9,14] The residence time can be increased to allow more time for the diffusion process to occur by several means, *e.g.* by decreasing the flow rate of the donor stream, using the stopped-flow mode (*i.e.* stopping the acceptor stream but not the donor stream; stopping both channels offers no real advantage since mixing is poor in the stagnant state and the second layer is not replenished[14]) or by increasing the length of the gas diffusion channel.

Spiral, serpentine and channels with right angle bends have been recommended in preference to straight grooves.[13,14] It has been suggested that the bends/curves in these designs improve the mixing in the sample plug, thereby replenishing the second layer.

In the present study, four gas diffusion modules were used; the dimensions of the modules are given in the Experimental section. Module IV gave the highest transference of the volatile product, in particular, at lower concentrations (Table 3). The superiority of this module is perhaps a consequence of the spiral shape of the groove and the longer channel. With respect to Module I, on the basis of theory (*i.e.* large surface area to volume ratio, shallow groove, *etc.*) one would expect an efficiency of diffusion similar to that for Module IV; this is the case for high concentrations of fluoride but the efficiency is lower for low concentrations. One possible explanation for this is the presence of a negative peak which is observed before the peak of interest, the negative peak being relatively larger at low concentrations. It is possible that the positive peak is not totally resolved from the negative peak, so a lower than expected result is obtained.

Interference study

Murty *et al.*[16] and Shell[17] used mixtures of sulfuric (or perchloric acid) and phosphoric acids to effectively break down fluoride complexes of polyvalent cations such as aluminium

Table 3. Dependence of peak height on choice of module*

Fluoride Conc. (*mg/l*)	Gas diffusion module I	II	III	IV
	Mean peak height (*mV*)			
0.3	142	175	137	214
0.5	239	258	233	349
1.0	540	479	379	658
2.0	1238	933	689	1290
3.0	1828	1420	1053	1853
5.0	2585	2257	1654	2575

*Conditions as in Table 2 with Unasco tape used as the membrane. Values are the mean of 3–4 measurements.

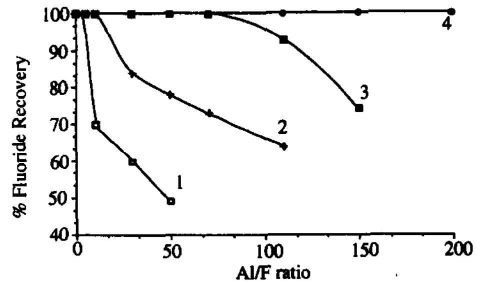

Fig. 4. Effect of aluminium on the detection of fluoride at various acid stream compositions. Flow rates of donor (D) and sample (S) streams, 0.85 ml/min during the preconcentration step; acid stream compositions: 1, 1*M* H_2SO_4; 2, 1*M* H_2SO_4/1*M* H_3PO_4; 3, 1*M* H_2SO_4/2*M* H_3PO_4; 4, 1*M* H_2SO_4/3*M* H_3PO_4; other conditions as in Fig. 3.

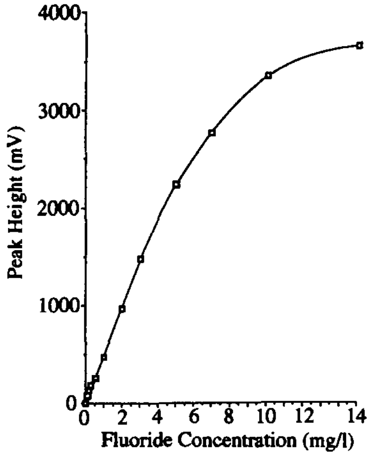

Fig. 5. Calibration curve for fluoride. Gas diffusion Module IV; Unasco tape as membrane; D, 1.5% HMDSA in 1*M* H_2SO_4/3*M* H_3PO_4; other conditions as in Fig. 3. Curve equation is $y = 3.4 + 544x^2 - 20.8x^2$.

and iron in the distillation of fluoride. Later, in a diffusion procedure, Yoshida *et al.*[6] was able to mask aluminum at 500 times the concentration of the fluoride in a standard sample by the addition of phosphoric acid to the sulfuric acid/HMDS mixture.

In the present Flow Injection method, donor streams containing a fixed concentration of HMDSA (1.5%) in solutions of various sulfuric/phosporic acid ratios were tested to ascertain the mixture that would eliminate the aluminium interference or at least increase the tolerance limit of the ion. The data in Fig. 4 indicate that aluminum up to 200 times the fluoride concentration can be tolerated using an acid mixture which is 1*M* in H_2SO_4 and 3*M* in H_3PO_4. On the other hand, the interference from ferric ion at 500 times the fluoride concentration is eliminated by employing a donor stream which contains only H_2SO_4 (1*M*) and HMDSA. Phosphate does not interfere in this method.

The mixed acid donor stream containing HMDSA was employed with aqueous fluoride standards in the concentration range 0–15 mg/l. The calibration plot is shown in Fig. 5 and is essentially linear in the range 0.1–4 mg/l fluoride. The limit of detection (LOD) was calculated to be 0.055 mg/l and the limit of quantification (LOQ) was 0.18 mg/l. A sample throughput of 17/hr was possible under the optimized conditions, with r.s.d. values around 3% at concentrations below 3 mg/l and better precision at higher fluoride concentrations (r.s.d. = 1%).

Determination of fluoride in water samples

To establish the viability of this new method, it was applied to the determination of fluoride in water samples collected from bores, a drainage farm, reservoirs and reticulation sites by the Rural Water Commission (Victoria, Australia). The FIA results obtained in this laboratory were compared to results obtained

Table 4. Determination of fluoride in water samples by the GD–FIA and fluoride–ISE methods, including data for aluminium, iron and phosphate*

	Fluoride conc. (*mg/l*)				
Sample ID	GD–FIA	Fluoride–ISE	Al (AAS)	Fe (AAS)	Phosphate (color)
USEPA†	0.96	1.00	ND‡	ND	ND
1455/1	0.73	0.81	ND	0.41	0.01
0872	0.49	0.46	ND	ND	ND
0962/1	0.34	0.35	ND	ND	ND
28071	0.23	0.22	<0.5	0.07	0.013
28072	0.25	0.25	0.6	0.04	<0.003
28073	0.44	0.42	<0.5	0.03	0.012
28074	0.48	0.49	<0.5	0.02	0.01
28075	0.21	0.20	4.9	0.13	0.98
28077	1.18	1.20	<0.5	0.03	0.014

*Conditions as in Fig 5.
†Specified as 1.00 mg/l by USEPA – 95% confidence interval, 0.89–1.09 mg/l.
‡ND = Not determined.

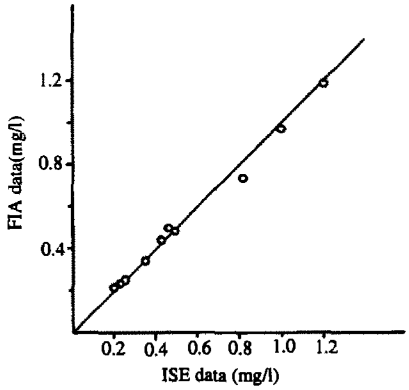

Fig. 6. Correlation plot of FIA and fluoride–ISE data for several water samples.

independently by the above organization using a fluoride ion-selective electrode method, and the results are presented in Table 4, together with analytical data for aluminum, iron and phosphate. The USEPA Environmental Monitoring and Support Laboratory state that the true concentration of their standard is 1 mg/l with a 95% confidence interval of 0.89–1.09 mg/l. Other constituents of the USEPA sample, at mg/l levels are: Cl^-, 52; SO_4^{2-}, 20; Na^+, 20; Ca^{2+}, 20; data for Al, Fe and phosphate were not reported. The only sample found with a high Al/F ratio was Sample 28075, and the FIA result gave excellent agreement with the fluoride-ISE analysis.

Figure 6 shows that the results obtained in this laboratory by the FIA method correlate well with those obtained by the fluoride-ISE method. The FIA method gives a slightly lower concentration than that obtained by the ISE method (slope of regression line = 0.94) with a correlation coefficient of 0.9970.

CONCLUSIONS

The gas-diffusion method for on-line pretreatment of fluoride samples prior to spectrophotometric detection in FIA has been found to be reliable with good precision and at this stage, with a detection limit comparable with other batch and continuous fluoride colorimetric detection methods. The interference problems typically associated with fluoride colorimetric detection methods have been eliminated or decreased; in the case of PO_4^{3-}, the interference has been eliminated and the tolerance levels of Fe^{3+} and Al^{3+} have been increased to at least 500 and 200 times the fluoride concentration, respectively. The lower detection limit of the present method can be varied by changing the preconcentration time. The accuracy and precision of the method for real water samples has proven to be comparable with the fluoride-ISE batch method for the samples tested.

Some recent papers which deal with the use of the fluoride ion-selective electrode in FIA comment on the influence of several cations including Fe^{3+} and Al^{3+} on the signal and response time of the electrode in the presence of several TISAB buffer mixtures. It is agreed that Al^{3+} is the most serious of the interferents, and that the TISAB should be premixed with the sample for a considerable time (Nicholson and Duff[18] suggest a minimum decomplexing time of 20 min for TISAB III; however, for samples containing high Al^{3+} levels 24 hr is more suitable) to allow for decomplexation prior to analysis in the continuous flow system. Davey *et al.*[19] investigated the in-stream masking ability of several buffer systems. In the procedure, the sample was allowed to come in contact with the TISAB solution for defined periods of time. Tiron-based buffers were recommended for fast release of fluoride (>90% in 16 sec) at equimolar amounts of Al and F but citrate-based buffers were preferred at higher Al/F ratios although fluoride release was slower. Frequent calibration of the electrode is essential when analysing real samples, as contamination of the electrode surface from dirty samples can affect the signal and response time. On the basis of this information, it is concluded that the newly developed GD–FIA system is superior in this regard and it offers a reliable alternative to the use of the fluoride–ISE in the analysis of fluoride samples in FIA, particularly in the presence of aluminium.

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