# Indirect determination of trace amounts of fluoride in natural waters by ion chromatography: a comparison of on-line post-column fluorimetry and ICP-MS detectors

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An alternative method for the determination of trace levels of fluoride in drinking and sea-water samples is presented. It is based on the formation of the aluminium monofluoride complex in excess of $Al^{3+}$ and separation of the two species formed ($AlF^{2+}$ and $Al^{3+}$) in a small (5 cm long, CG2) ion exchange guard column. The final determination is accomplished by both ICP-MS specific detection and post column derivatisation with fluorimetric detection. Fundamental studies on the formation kinetics of the complex, ion chromatographic separation and optimum aluminium concentration were carried out using spectrofluorimetric detection by post-column reaction of the species with 8-hydroxyquinoline-5-sulfonic acid in a micellar medium of cetyltrimethylammonium bromide. Fluorimetric detection showed good detection limits, but interferences from cations such as $Mg^{2+}$ and $Zn^{2+}$ required the use of the longer CS2 ion exchange column. Iron interfered in relatively large amounts but adding EDTA to the sample solution eliminated the interference. A similar separation methodology was applied using ICP-MS detection for the indirect determination of fluoride, by monitoring aluminium at mass 27. In this case, a detection limit of 0.1 ng $ml^{-1}$ was obtained using 0.45 M $HNO_3$ as eluent and no interference caused by high concentrations of iron was observed. The proposed method was applied to the determination of very low levels of fluoride in natural waters.

## Introduction

During the last decade, the majority of fluoride determinations have been performed using techniques such as potentiometry with fluoride ion selective electrodes (ISE),[1,2] ion-exchange chromatography with conductivity detection,[3–4] spectrophotometry[5] and most recently capillary electrophoresis.[6,7] The use of ISEs has been the preferred technique for this determination, but their sensitivity is insufficient to measure fluoride at ng $ml^{-1}$ levels. A spectrophotometric method using SPADNS has been applied to drinking waters.[5] In the case of ion chromatography, the weak binding affinity of fluoride to the ion exchangers used to perform the separation process causes its early elution from the column, too close to the so-called injection peak, containing non-retained compounds and also the sample solvent. Most interferences in fluoride determination come from the presence of high levels of iron or aluminium in the sample. In these cases distillation of fluoride as HF can be performed.[8]

Atomic spectrometric techniques have not been used so far for direct fluoride determinations. The high excitation and ionisation potentials presented by this halogen resulted in poor sensitivity for atomic emission spectrometric (AES) detection even using powerful spectrochemical sources such as helium-based plasmas (*e.g.*, He MIP or He ICP). In this respect, good detection limits have been achieved for other halogens such as chloride or bromide,[9,10] but no results have been reported so far on fluoride determinations by AES. One interesting and recently developed alternative involves fluoride determination by electrospray mass spectrometry, with promising results.[11]

Several groups have investigated indirect fluoride determination. Marco *et al.*[12] determined fluoride by measuring the molecular absorption of the $AlF^{2+}$ complex in a graphite tube using a Pt hollow cathode lamp. The chromatographic separation of Al–fluoride species was first described by Bertsch and Anderson,[13] who determined the stability constants of the several possible $AlF_x$ species. Later, Jones[14] determined fluoride as $AlF^{2+}$ after chromatographic separation from the excess of $Al^{3+}$ using indirect fluorimetric detection with 8-hydroxyquinoline-5-sulfonic acid, obtaining detection limits in the low ppb range.

Previous work in our laboratory[15] showed that aluminium could be better detected in the presence of cationic micelles of cetyltrimethylammonium bromide (CTAB) and it was also observed that the aluminium monofluoride complex could be detected by this fluorimetric reaction after ion chromatographic separation from $Al^{3+}$.[16, 17] Here, the optimum conditions for the formation of the $AlF^{2+}$ complex were studied using ion chromatography and post-column fluorimetric detection. Two types of elution conditions were evaluated, using $K_2SO_4$[14,16] and $HNO_3$ as eluents. The analytical characteristics using fluorimetric detection were compared with ICP-MS as a specific detection method monitoring aluminium at *m/z* 27. Examples of the application of the proposed method are presented for the determination of low fluoride levels in drinking and sea-water samples.

## Experimental

### Instrumentation

The chromatographic system used consisted of a Pharmacia (Uppsala, Sweden) Model P-500 medium pressure pump and an Model 5M PA inert valve from Pharmacia fitted with a 100 μl sample loop and a 5 cm long Dionex (Camberley, UK) Ion Pac

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HPIC-CG2 ion exchange column. For the experiments using the $K_2SO_4$ as eluent, the column was immersed in a water-bath at 50 °C.

The spectrofluorimetric detector was a Shimadzu (Kyoto, Japan) R-F5000 equipped with a 12 μl flow cell. The excitation and emission wavelengths were 390 and 500 nm, respectively, and the chromatograms obtained were recorded using a Shimadzu Chromatopac C-R3A integrator. The post-column reagent was pumped using a Scharlau (Barcelona, Spain) HP4 peristaltic pump.

Al-specific ICP-MS detection was carried out using an HP 4500 instrument (Hewlett-Packard, Yokogawa Analytical Systems, Tokyo, Japan) fitted with a concentric nebuliser and a Peltier cooled (2 °C) spray chamber. All chromatograms were obtained monitoring aluminium at *m/z* 27 using time resolved analysis.

Fig. 1 shows the instrumental set-up of the system using alternatively fluorimetric or ICP-MS detection. Neither detection system could be used on-line because of incompatibility of the eluents and post-column reaction. For fluorimetric detection, the eluent from the column was mixed with the post-column reagent using a T-piece and a 2 m × 0.5 mm id PTFE reaction coil. For ICP-MS detection, the eluent leaving the column was connected directly to the nebuliser.

### Reagents

All chemicals were of analytical-reagent grade unless stated otherwise and water obtained from a Milli-Q system (Millipore, Molsheim, France) was used to prepare stock standard solutions of all the reagents. Aluminium standard solution (1000 μg $ml^{-1}$) was obtained from Merck (Darmstadt, Germany). Stock standard solutions of $F^-$ (1000 and 1 μg $ml^{-1}$) were prepared by dissolving solid NaF (Merck) in water.

For fluorimetric detection, $K_2SO_4$ (Merck) was used to prepare the mobile phase. The post-column reagents, 8-hydroxyquinoline-5-sulfonic acid (HQS) and CTAB, were obtained from Sigma Aldrich, (St. Louis, MO, USA). The pH of the post-column reagent was adjusted using acetic acid–sodium acetate buffer (Merck). To prevent interferences from other metals present in the sample such as Fe, a standard solution of EDTA (Sigma Aldrich) was also used.

For ICP-MS determination, no post-column reagent was necessary and the mobile phase used was prepared from 65% $HNO_3$ (Suprapur, Merck) and diluted with Milli-Q water.

### Preparation of $AlF^{2+}$ complex

Samples and standard solutions were adjusted to pH 3 with nitric acid and spiked with $Al^{3+}$, at least a five-fold mass excess of Al to fluoride being required to ensure that only $AlF^{2+}$ was formed. The samples were diluted by volume (fluorimetric detection) or mass (ICP-MS detection), transferred into 10 ml polypropylene test-tubes and immersed in a water-bath at 50 °C for 60 min. This ensured quantitative formation of the $AlF^{2+}$ complex. For natural water samples and fluorimetric detection, EDTA was added at $1.6 \times 10^{-5}$ M.

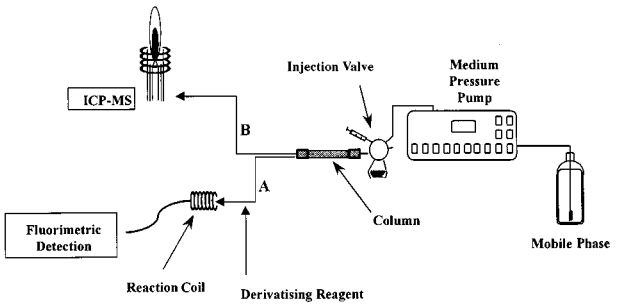


**Fig. 1** Instrumental set-up of the system using (a) fluorimetric and (b) ICP-MS detection.

### Chromatographic separation

For fluorimetric detection, the mobile phase was 0.1 M $K_2SO_4$ in water adjusted to pH 3 with nitric acid. A flow rate of 1 ml $min^{-1}$ was used. The CG2 HPLC column was immersed in a water-bath at 50 °C following the recommendations of Jones *et al.*[18] For ICP-MS detection, the mobile phase was 0.45 M $HNO_3$ at a flow rate of 0.5 ml $min^{-1}$ and the column was kept at room temperature.

### Spectrofluorimetric detection

The post-column reagent contained HQS and CTAB at optimum concentrations of $1 \times 10^{-3}$ and $2 \times 10^{-3}$ M, respectively and the optimum pH of 6 was adjusted with 0.25 M acetic acid–sodium acetate buffer. The optimum flow rate was 0.43 ml $min^{-1}$. The excitation and emission wavelengths selected were 390 and 500 nm respectively, providing the highest analytical signals for $AlF^{2+}$ determination. The excitation and emission slits were both 5 nm.

### ICP-MS detection

The ICP-MS operating conditions are summarised in Table 1. The output from the column was fed directly to the inlet of the concentric nebuliser and the *m/z* value monitored was 27 using the time resolved analysis mode, a 0.5 s integration time and 1 point per mass unit.

## Results and discussion

### Kinetic studies

The initial aim of this work was to obtain chromatographic conditions that allowed the separation and detection of the $AlF^{2+}$ complex from the excess $Al^{3+}$, to provide a sensitive method for indirect fluoride determination. First, some studies on the formation kinetics were performed and the determination

**Table 1** Typical operating conditions

| | |
|---|---|
| Instrument | HP 4500 |
| Rf power | 1300 W |
| Nebuliser | Meinhard |
| Spray chamber | Scott type, double pass, cooled at 2 °C |
| Sampling depth | 5.7 mm |
| *Gas flow rates*— | |
| External | 15 l $min^{-1}$ |
| Intermediate | 1 l $min^{-1}$ |
| Carrier | 1.17 l $min^{-1}$ |
| *Ion lens settings*— | |
| Extract 1 | −221 V |
| Extract 2 | −106 V |
| Einzel 1, 3 | −144V |
| Einzel 2 | 39.3V |
| Omega bias | −48V |
| Omega (+) | 6 V |
| Omega (−) | −7 V |
| QP focus | 8 V |
| Ion deflector | 39 V |
| Oxide level ($CeO^+/Ce^+$) | < 0.5% |
| Double charged level ($Ce^{2+}/Ce^+$) | < 1% |

of the complex was carried out using spectrofluorimetric detection.

In aqueous acidic solution, aluminium ions are present as $[Al(H_2O)_6]^{3+}$, which can react with $F^-$ to form the $AlF^{2+}$ complex. It has been demonstrated[1] that in a highly acidic medium, $F^-$ reacts with $H^+$ to form HF, leading to a decrease in the rate of complexation of $Al^{3+}$ with $F^-$. At pH > 3.0, the hydrolysis reaction of $Al^{3+}$ can take place with the formation of $Al(OH)_i^{(3-i)+}$, which reduces free aluminium and therefore the concentration of the complex. The optimum pH for the complex formation seems to be between 2 and 4,[1,14] and therefore in this work the pH selected was 2.6–3, where the complex $AlF^{2+}$ proved to be stable.

Under these conditions, several parameters were evaluated in order to determine the formation kinetics of the complex, such as temperature and excess of aluminium necessary to obtain the quantitative formation of the $AlF^{2+}$.

Fig. 2 shows the fluorimetric peak heights obtained for the $AlF^{2+}$ complex as a function of solution temperature (15, 22 and 50 °C with solutions containing 100 ng ml$^{-1}$ fluoride and 1 μg ml$^{-1}$ aluminium) and complexation time. As can be appreciated, on heating the solution containing fluoride and aluminium at 50 °C, the formation of the complex can be considered quantitative after 50 min. At room temperature, more than 5 h are necessary to obtain stable signals for the complex. The slow reaction kinetics of the $AlF^{2+}$ complex formed at room temperature could allow its separation from the excess of $Al^{3+}$ without any decomposition or formation of alternative species during passage through the chromatographic column.

In order to optimise the aluminium concentration to be added for complete formation of the complex, solutions containing 200 ng ml$^{-1}$ fluoride were tested. Increasing amounts of aluminium were added to each sample and the solutions were heated at 50 °C for 1 h. The results obtained are shown in Fig. 3 and were measured fluorimetrically as peak height. As can be observed, a plateau was reached when using an aluminium concentration of 1 μg ml$^{-1}$ or higher. In order to increase the linear range as much as possible, a concentration of 10 μg g$^{-1}$ of aluminium was used in subsequent studies using fluorimetric detection.

### Ion exchange separation: study of the mobile phase

Fig. 4 shows the typical chromatograms obtained for the separation of $AlF^{2+}$ and $Al^{3+}$ using 0.1 M $K_2SO_4$ as eluent and increasing amounts of fluoride from 0 to 400 ng ml$^{-1}$. As can be observed, using 0.1 M $K_2SO_4$ the $AlF^{2+}$ peak increases with increase in fluoride concentration and the excess $Al^{3+}$ elutes after 2.5 min. In order to optimise the concentration of $K_2SO_4$ in the eluent, several concentrations were evaluated and Fig. 5 shows the standard representation of the logarithm of the capacity factor (log $k'$) *versus* the negative logarithm of potassium concentration (−log [$K^+$]).[19] As can be observed, the slopes of the lines are 1.90 and 3.12 for $AlF^{2+}$ and $Al^{3+}$, respectively, and therefore it seems clear that the charge of the compounds is +2 and +3, respectively, and the structure of the complex is the one proposed.

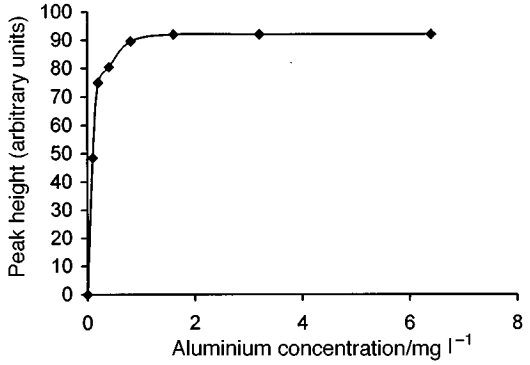


**Fig. 3** Optimisation of the aluminium concentration required for complete formation of the $AlF^{2+}$ complex in a solution containing 200 ng ml$^{-1}$ fluoride.

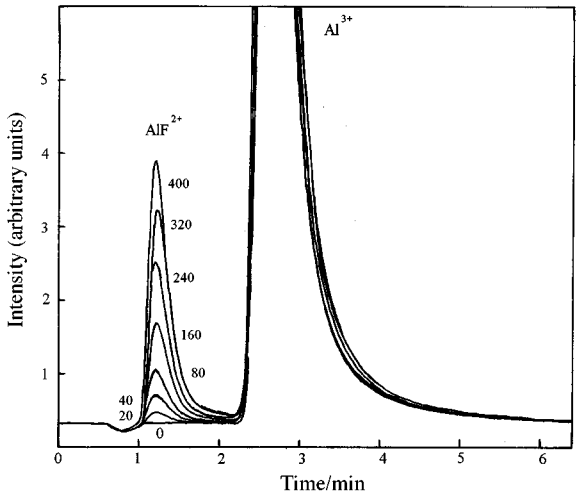


**Fig. 4** Typical chromatograms obtained for the separation of $AlF^{2+}$ and $Al^{3+}$ using 0.1 M $K_2SO_4$ as eluent and increasing amounts of fluoride from 0 to 400 ng ml$^{-1}$.

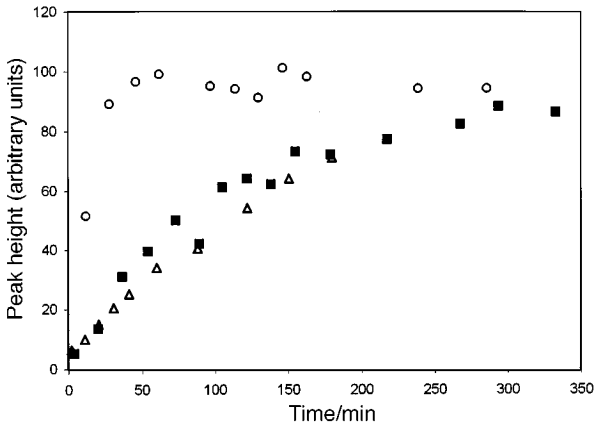


**Fig. 2** Fluorimetric peaks heights obtained for the $AlF^{2+}$ complex as a function of solution temperature (Δ, 15; ■, 22; and ○, 50 °C) containing 100 ng ml$^{-1}$ fluoride and 1 μg ml$^{-1}$ aluminium.

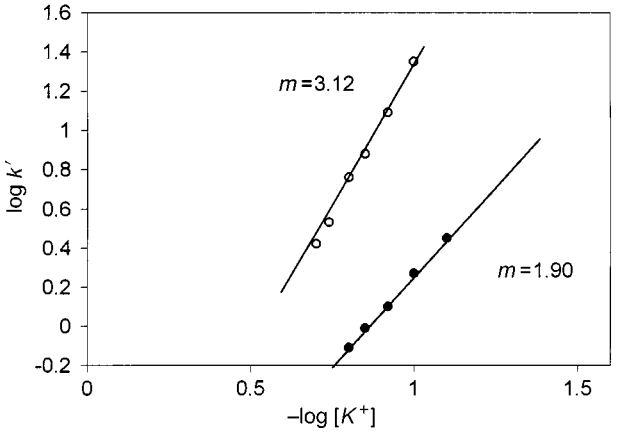


**Fig. 5** Representation of the logarithm of the capacity factor (log $k'$) obtained both for $AlF^{2+}$ and $Al^{3+}$ using different $K_2SO_4$ eluents. The slope of the log–log plot provides the charge of the species.[19]

Because saline solutions, such as $K_2SO_4$, are not recommended in ICP-MS (possible clogging of the central channel of the torch and deposits on the cones), alternative mobile phases were tested. $HNO_3$ was found to be a good eluent for the separation of $AlF^{2+}$ and $Al^{3+}$ and detection by ICP-MS. Different concentrations of nitric acid, from 0.15 to 0.75 M, were tested for the above mentioned separation. The conditions chosen for subsequent studies were 0.45 M nitric acid at a flow rate of 0.5 ml $min^{-1}$ and detection at $m/z$ = 27. The chromatogram obtained under these conditions for 20 ng $g^{-1}$ $F^-$ in the presence of 100 ng $g^{-1}$ of Al is shown in Fig. 6. As can be observed, two aluminium containing peaks are detected. The first peak could be ascribed to the $AlF^{2+}$ complex as its peak height/area was found to be proportional to the concentration of fluoride in the sample.

## Analytical performance characteristics

Analytical performance characteristics for both detection modes are summarised in Table 2. The linear dynamic range for fluoride determination depends on the excess of aluminium added to the sample. It was observed with both detection modes that, for a given aluminium concentration, the upper linear limit for fluoride determinations was about one fifth of the total aluminium concentration. For ICP-MS, aluminium concentrations higher than 500 ng $g^{-1}$ were not tested. Using fluorimetric detection, linear upper limits up to 2000 ng ml $F^-$ were obtained (using 10 μg $ml^{-1}$ excess $Al^{3+}$).

The detection limits obtained were 0.6 ng $ml^{-1}$and 0.1 ng $g^{-1}$ for fluorimetry and ICP-MS, respectively, calculated as three times the standard deviation of the blank divided by the slope of the linear calibration graph between 0 and 5 ng $g^{-1}$. The detection limit using ICP-MS detection is one of the lowest ever reported for the determination of fluoride.

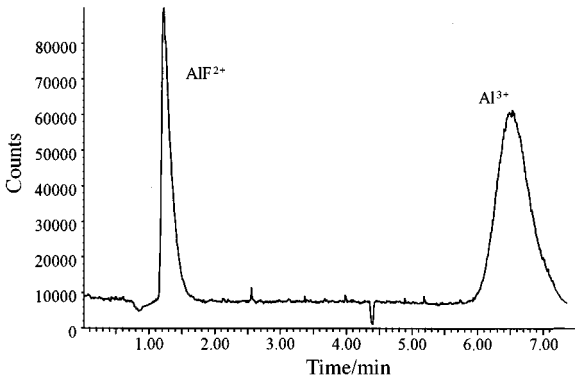


**Fig. 6** Chromatogram obtained for 20 ng $g^{-1}$ of fluoride in the presence of 100 ng $g^{-1}$ of aluminium using ICP-MS detection. Eluent, 0.45 M nitric acid.

**Table 2** Comparative analytical performance characteristics of spectrofluorimetric and ICP-MS detection

| Analytical characteristics | Spectrofluorimetric detection | ICP-MS detection |
|---|---|---|
| Detection limit | 0.6 ng $ml^{-1}$ | 0.1 ng $g^{-1}$ |
| Precision | 2.3%[a] | 4%[b] |
| Linear range | Up to 2000[c] ng $ml^{-1}$ | Up to 100[d] ng $g^{-1}$ |
| Regression coefficient ($r$) ($n$ = 7 points) | 0.9995 | 0.9993 |

[a] For five injections of 20 ng $ml^{-1}$ fluoride. [b] For five injections of 20 ng $g^{-1}$ fluoride. [c] Using 10 μg $g^{-1}$ aluminium. [d] Using 500 ng $g^{-1}$ aluminium.

## Interference studies

An exhaustive study of possible interferences from other anions and cations was carried out first using spectrofluorimetric detection. The results are summarised in Table 3. As can be observed, typical anions present in natural waters such as $HCO_3^-$ and $Cl^-$ do not interfere at the maximum concentration tested (200 μg $ml^{-1}$). Other anions such as $H_2PO_4^-$ and $BO_3^{3-}$ can be present at 100 and 200 μg $ml^{-1}$, respectively, without causing interference.

The main interferences were observed from trace metals, which can be present in natural waters. $Fe^{3+}$ at concentrations higher than 0.5 μg $ml^{-1}$ decreased considerably the peak height from the $AlF^{2+}$ peak owing to competition with $Al^{3+}$ for fluoride or quenching of the fluorimetric reaction. However, in the presence of $1.6 \times 10^{-5}$ M EDTA this interference was eliminated. $Ca^{2+}$ and $Sr^{2+}$ up to 100 and 50 μg $ml^{-1}$, respectively, did not show any interference effect. $Cu^{2+}$ and $Pb^{2+}$ at concentrations higher than those in Table 3 produced a small decrease in the fluorimetric signal of $AlF^{2+}$, which can be ascribed to co-elution with $AlF^{2+}$ and the formation of competing chelates with the post-column reagent. On the other hand, $Zn^{2+}$ and $Mg^{2+}$ formed fluorescent chelates with the post-column reagent and co-eluted with $AlF^{2+}$ using the 5 cm CG2 column. The use of a 25 cm CS2 column and a lower eluent concentration of 0.05 M $K_2SO_4$ resulted in the separation of the $AlF^{2+}$ peak from $Mg^{2+}$ and $Zn^{2+}$. However, in this case the retention time for $Al^{3+}$ increased to 30 min, as shown in Fig. 7 for a real water sample.

Using ICP-MS aluminium specific detection, no effect on detection from co-eluting divalent cations should be expected. The only possible interference could be with the formation and retention of $AlF^{2+}$ complex. No effect of $Fe^{3+}$ on the height or area of the $AlF^{2+}$ peak was obtained for $Fe^{3+}$ concentrations up to 100 ng $g^{-1}$ at the same aluminium concentration and 20 ng $g^{-1}$ of fluoride. Also, when monitoring at $m/z$ 57,

**Table 3** Effect of foreign ions on the determination of fluoride with spectrofluorimetric detection (200 ppb $F^-$, 10 ppm $Al^{3+}$)

| Interference | Maximum concentration allowed/μg $ml^{-1}$ (recovery 100 ± 5%) |
|---|---|
| $Fe^{3+}$ | 0.5 (10, in the presence of $1.6 \times 10^{-5}$ M EDTA) |
| $Zn^{2+}$ | Interferes |
| $Mg^{2+}$ | 10 |
| $Cu^{2+}$ | 1.6 |
| $Ca^{2+}$ | 100[a] |
| $Sr^{2+}$ | 50[a] |
| $Pb^{2+}$ | 2 |
| $HCO^-$ (as $NaHCO_3$) | 200[a] |
| $Cl^-$ (as KCl) | 200[a] |
| $H_2PO_4^-$ (as $NH_4H_2PO_4$) | 100[a] |
| $BO_3^{3-}$ (as $Na_3BO_3$) | 200[a] |

[a] Maximum concentration tested.

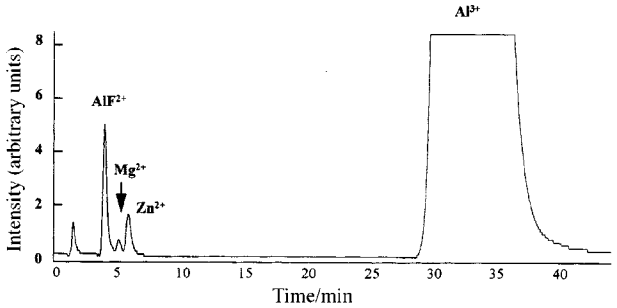


**Fig. 7** Chromatogram obtained for a real water sample using the CS2 column (25 cm long) and 0.05 M $K_2SO_4$ as eluent with fluorimetric detection.

representing a minor iron isotope, no elution of Fe from the column could be detected owing to insufficient sensitivity. Wang *et al.*[1] have reported that the formation of the Fe–fluoride complex is strongly pH dependent. The optimum pH for iron–fluoride complex formation is 1.5 but at pH 2.5 complex formation decreased significantly.[1] Our results on pH effects agreed well with such observations.

### Determination of fluoride in fresh and sea-water samples

**Fluorimetric detection.** Natural water samples may contain a large range of fluoride concentration from a few ng ml$^{-1}$ to several μg ml$^{-1}$. The concentrations of interfering compounds should be well below those indicated in Table 3 except, perhaps, for Fe, Mg and Zn in some samples. The chromatogram of a mineral water sample diluted 1 + 9 with Milli-Q water and containing 3.1 μg ml$^{-1}$ of fluoride determined by ISE is shown in Fig. 7; 0.05 M $H_2SO_4$ as eluent and the CS2 column were used. As can be observed, the $AlF^{2+}$ peak is well separated from $Mg^{2+}$ and $Zn^{2+}$. The concentration found in this sample by reference to a calibration graph was 3.1 ± 0.1 μg ml$^{-1}$ ($n$ = 5) and the recovery for spiked fluoride was 97%. Unfortunately, under these conditions the retention time for $Al^{3+}$ was > 30 min, increasing dramatically the time required for each measurement as $Al^{3+}$ must be eluted from the column before the next injection.

**ICP-MS detection.** Under the optimum separation conditions using $HNO_3$ for elution, the retention time for $Al^{3+}$ is < 8 min, allowing a sampling rate of 6–7 h$^{-1}$, and the detection is much more selective. Therefore, the proposed ICP-MS method was applied to the determination of fluoride in natural and drinking waters from a variety of sources and with different saline concentrations. As no stable aqueous fluoride reference material was available, it was decided to compare the proposed methodology with the fluoride ion selective electrode (FISE) and spiking the samples with fluoride to calculate the recoveries.

In order to minimise aluminium addition to the samples and contamination of the ICP-MS system, up to 200-fold dilution of some drinking and sea-water samples was necessary. The results obtained are summarised in Table 4. As some of the concentrations found were around 150 ng g$^{-1}$, and sometimes lower, the determination using FISE was adequate in only a few cases. As can be observed, the results obtained were in good agreement with the values found by FISE, when this determination was possible. In the other cases tested, recoveries of 100 ± 10% were obtained, showing the applicability of the proposed methodology to perform fluoride determinations at extremely low levels.

**Table 4** Results obtained for the determination of fluoride in water samples using ICP-MS after dilution of the samples

| Water sample (dilution factor) | Concentration found ($n$ = 3) by ICP-MS/ng g$^{-1}$ | Concentration found by FISE/ng g$^{-1}$ | Spiked amount/ng g$^{-1}$ | Recovery (%) |
|---|---|---|---|---|
| Fontecelta (200) | 8050 ± 80 | 7700 | 4300 | 104 |
| Font-Vella (10) | 182 ± 2 | — | 205 | 97.8 |
| Tap water (10) | 161 ± 1 | — | 210 | 90 |
| Sea-water[a] (100) | 1030 ± 60 | 1080 | 1080 | 97.5 |

[a] Collected at Gijon, Asturias, Spain.

## Conclusions

The formation of the $AlF^{2+}$ complex in excess of $Al^{3+}$ can be considered quantitative after thermal treatment of the sample for 1 h at 50 °C. Once formed, the complex is stable and can be separated from the excess of aluminium by cation exchange chromatography without decomposition even using highly acidic eluents (0.45 M $HNO_3$).

The detection of aluminium can be accomplished either by a post-column fluorimetric reaction, with interferences from other cations such as $Fe^{3+}$, $Zn^{2+}$ and $Mg^{2+}$, or by ICP-MS. The latter detection method proved to be extremely sensitive, with a detection limit of 0.1 ng g$^{-1}$ of $F^-$, and free from interferences from other cations and anions in natural water samples.

In comparison with the fluoride ISE, the proposed indirect ICP-MS method is at least two orders of magnitude more sensitive, it is not affected by interferences from aluminium and iron (in fact, the formation of the $AlF^{2+}$ complex is the basis of the method) and it can be applied without modification to a large range of water samples of different salinity.

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## References

1 H. Wang, Z. Zhang, A. Sun, D. Liu and R. Liu, *Talanta*, 1996, **43**, 2067.
2 R. W. Kahama, J. J. M. Damen and J. M. ten Cate, *Analyst*, 1997, **122**, 855.
3 T. A. Biemer, N. Asral and A. Sippy, *J. Chromatogr. A*, 1997, **771**, 355.
4 J. M. Talmage and T. A. Biemer, *J. Chromatogr. A*, 1987, **410**, 494.
5 S. A. Sen, K. Kesava Rao, M. A. Frizzell and G. Rao, *Field Anal. Chem. Technol*., 1998, **2**(1), 51.
6 P. Wang, S. F. Y. Li and H. K. Lee, *J. Chromatogr. A.,* 1997, **765**, 353.
7 S. A. Shamsi and N. D. Danielson, *Anal. Chem*., 1995, **37**, 1845.
8 *Standard Methods for the Examination of Water and Waste Water*, American Public Health Association, New York, 15th edn., 1980, p. 337.
9 F. Camuña, J. E. Sánchez-Uría and A. Sanz-Medel, *Spectrochim. Acta, Part B*, 1993, **48**, 1115.
10 A. H. Mohammed, J. T. Creed, T. M. Davidson and J. A. Caruso, *Appl. Spectrosc*., 1989, **43**, 1127.
11 D. A. Barnett and G. Horlick, *J. Anal. At. Spectrom*., 1997, **12**, 497.
12 V. Marco, F. Carrillo, C. Pérez-Conde and C. Cámara, *Anal. Chim. Acta*, 1993, **283**, 489.
13 P. M. Bertsch and M. A. Anderson, *Anal. Chem*., 1989, **339**, 535.
14 P. Jones, *Anal. Chim. Acta*., 1992, **258**, 123.
15 J. I. Garcia Alonso, A. López García, E. Blanco González and A. Sanz-Medel, *Anal. Chim. Acta,* 1989, **225**, 339.
16 J. I. Garcia Alonso, A. Rodriguez Garcia and A. Sanz-Medel, paper presented at Euroanalysis VII, Vienna, 1990.
17 A. Rodriguez Garcia, Master's Degree, Faculty of Chemistry, University of Oviedo (1991).
18 P. Jones, L. Ebdon and T. Williams, *Analyst,* 1988, **113**, 641.
19 R. Rosset, H. Conde and A. Jordy, *Manuel Pratique de Chromatographie en Phase Liquide*, Masson, Paris, 2nd edn., 1982.

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