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Ion chromatographic determination of fluoride in welding fumes with elimination of high contents of iron by solid-phase extraction

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Abstract

An ion chromatography (IC) procedure was developed for the determination of fluoride in fumes from arc-electric welding of steels with basic electrodes. The interference of metal ions was eliminated by passing the sample solution through an on-line pre-column of a strong cation-exchange resin. Both a strong acid (H^+ form) resin and a strong chelating (Na^+ form) resin were experimented for this purpose. Linear response was obtained from 0.02 to 1 mg of fluoride (in a 50- μ l loop), which corresponds to a concentration range from 0.15 to 7.5 mg/m³ air (6 to 300% of the threshold limit value-time weighted average), for the experimental conditions used (2-h sampling periods, air flow-rate 17 l/cm²·h, through a 1.2- μ m pore size cellulose nitrate filter, from which a 1-cm diameter disk was attacked and analysed). The short-term (within 30 min) precision of the IC determination was <3% (7 determinations). The accuracy of the procedure was evaluated by analysing both synthetic solutions and real samples. When several mixed standard solutions of fluoride, iron(III) and aluminium(III), covering the ranges and ratios of concentration levels in real samples, were analysed, practically quantitative fluoride recovery (97–101%) was found. When 13 samples with 0.6–18 mg/l of fluoride were determined in parallel by IC (0.03–0.9 μ g injected) and a well established ion-selective electrode (ISE) procedure, no bias was found: a linear regression $[IC] = 0.99 (\pm 0.12) [ISE] + 0.9 (\pm 1.4)$ (confidence limits at 95% confidence level in parentheses) was obtained.

1. Introduction

Fluoride has been identified as an important pollutant in arc-electric manual welding with basic electrodes, whose coating includes a large amount (20–40%, w/w) of salts of this anion, e.g., calcium fluoride and sodium fluoride [1–3]. In a programme developed in this Department [4,5] for studying the occupational atmosphere of a large welding plant, a large number of samples

of fumes had to be analysed and procedures to expedite the fluoride determinations were considered. Until recently, ion-selective electrode (ISE) potentiometry was the main technique used for this purpose [6–11]. In such measurements, the interferences of metal ions, of which iron(III) and aluminium(III) are usually the most important, are easily eliminated by complexation with 1,2-cyclohexylenedinitrilotetraacetic acid (CDTA), or a similar complexant included in a “total ionic strength buffer” (TISAB) [6] added to the solution. Ion chroma-

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tography (IC) with conductivity detection is a sensitive technique of increasing relevance for ionic quantification in environmental samples. It has been applied to the determination of fluoride in several types of samples including air filtrates [10–13], and can be advantageous for determinations on welding fumes provided interferences of metal ions are avoided. The same type of interferences occurs in IC with spectroscopic detection (UV–Vis, after post-column reaction [14], or fluorescence, in AlF^{2+} form [15]).

In the present case, the most frequent process in the plant was manual welding of mild steel with basic electrodes, which produces a large quantity of iron and some aluminium. Unless their interference is eliminated, those metals would provoke low results for fluoride, due to the formation of stable metal ion complexes. When IC with conductivity detection was applied to airborne particulate matter from aluminium smelters [11], no marked interference of aluminium was noted and the interference of iron was not considered. Therefore, no procedure to eliminate interferences was included in the analytical method. IC was also applied to welding fumes [10], but the procedure used to eliminate interferences was not explicitly mentioned. On the other hand, complexation of iron(III) with cyanide, used to avoid the precipitation of iron hydroxides in IC determination of anions in natural waters [16], is not convenient for IC since the large affinity of the hexacyanoferrate(III) for the resins may provoke deterioration of the columns. In addition, complexants like CDTA used in TISAB can provoke poisoning of the columns by accumulation, probably due to the high charge of the ion.

In the present study, alternative procedures for elimination of the iron(III) interference in the determination were considered. There is currently much interest in using solid-phase extraction as a preparative technique for IC when cleaning up samples prior to analysis is required and dilution or filtration are unsuitable, like in the present case, where interferences and analyte are both soluble [17,18]. In consequence, it was decided to study the use of on-line solid-phase extraction for elimination of the interfer-

ence. This paper reports the results of an evaluation study of an IC procedure, for the determination of fluoride in welding fumes, which includes elimination of iron(III) [and aluminium(III)] by solid-phase extraction. In the evaluation, IC and ISE potentiometry were used in parallel for comparison.

2. Experimental

2.1. Instrumentation and operative conditions

Cassella AFC 123 personal samplers (with flow-rates ca. $17 \text{ l/cm}^2 \cdot \text{h}$ or 2 l/min) were used to collect fumes at the breathing zone of welders on cellulose nitrate filters (Millipore RAWP 047 00, $1.2 \mu\text{m}$ pore size).

IC determinations were carried out in a Dionex 4000i ion chromatograph with a conductivity detector, equipped with a HPIC AG4A pre-column to screen foreign matter from the sample, a HPIC AS4A anion separator column and an AMMS anion micromembrane suppressor. The chromatograms were recorded and manipulated in a Spectra-Physics SP4290 integrator (paper rate 0.5 cm/min).

A $50\text{-}\mu\text{l}$ injection loop was used. The eluent was a $0.15 \text{ mM NaHCO}_3/2.0 \text{ mM Na}_2\text{CO}_3$ solution, at a flow-rate of 2 ml/min . The suppressor regeneration reservoir was pressurized with nitrogen at 0.5 atm ($1 \text{ atm} = 101\,325 \text{ Pa}$) to maintain constant flow (ca. 5 ml/min) of regenerant ($12.5 \text{ mM H}_2\text{SO}_4$). Measurements were made on the $100 \mu\text{S/cm}$ scale.

The solutions were injected with polyethylene syringes through a cellulose acetate filter (Schleicher & Schuell FP030/3, $0.2 \mu\text{m}$ pore size) and a cation-exchange pre-column (see below), both disposable (at high levels of interferent two pre-columns were used, see below).

For ISE determinations, a fluoride ISE, a double-junction Ag/AgCl electrode (Orion 94-09-00 and 90-02-00, respectively) and a Sargent Welch 6050 pH meter were used. Measurements were carried out in a polyethylene cell, at $25.0 \pm 0.2^\circ\text{C}$, with magnetic stirring. To control the pH

of the solution, a Philips GAH110 glass electrode was used.

2.2. Solutions

All chemicals were of analytical-reagent grade, unless otherwise stated, and all solutions were prepared with deionised water of resistivity $> 14 \text{ M}\Omega \text{ cm}$.

2.3. Procedures

Filter extracts

For comparison purposes, the following four different pre-treatments of the filter discs were used: (a) ultrasonic extraction with eluent during ca. 30 min; (b) extraction with water at ca. 70°C for 2 h, with magnetic stirring; (c) similar to (b) but with TISAB (pH 5.5) as extractor, at room temperature; (d) attack with concentrated HNO_3 at ca. 80°C (the destruction of the piece of filter was complete in 10 min), the acidity of the solution was neutralized with 300 ml of 5 M sodium hydroxide and, after cooling, the flask was filled with TISAB, the final pH of the solution being 5.2. In all cases calibrated flasks of 5 ml (the minimum volume necessary for a single ISE determination) were used for wet digestion.

Procedures a and b were followed in IC and procedures c and d in ISE determinations. Extraction and analysis were carried out on the same day.

Ion chromatography

Calibrations. From a 1 g/l F^- standard stock solution prepared from NaF dried at 110°C , five or six F^- standards in the range 0.2–20 mg/l were prepared daily in eluent (or in pure water, depending on the medium used for the F^- extraction from the filters).

The IC system was calibrated at the beginning of each run with a blank (matrix of the standards) and the standards. To control within-run sensitivity changes, the highest concentrated standard was analysed after each group of five samples (i.e., after ca. 30 min) and the system was re-calibrated (one-point calibration). F

concentrations were obtained automatically from calibration graphs based on peak height. Each determination took about 6 min (because samples also contain NO_3^- and SO_4^{2-} , see Fig. 1).

Metal ion interferences. The metal ion interferences were eliminated by passing the sample solution through on-line pre-columns of styrene-based resin in strong acid H^+ form, with 1.8–2 mequiv. of cation exchange capacity (Dionex "On Guard H"). One unit was found to be enough up to ca. 10 mg/l of iron(III) [in the present case the aluminium(III) concentration is low enough to be ignored], but two serial units were necessary to obtain quantitative fluoride recovery for higher levels of interferent (see discussion below). Alternatively, an on-line pre-column of styrene–divinylbenzene-based chelating resin in Na^+ form (Chelex-100, Bio-Rad) was used. One column with a bed (0.3–0.5 g) equal to an On Guard H (0.18–0.3 mequiv. of cation-exchange capacity) was enough in all situations.

To check the precision and the accuracy of the results, mixed standard solutions of fluoride, iron(III) and aluminium(III), with concentrations in the ranges of 0.5–20 mg/l, 0.5–20 mg/l, and 0.5 mg/l, respectively, were analysed.

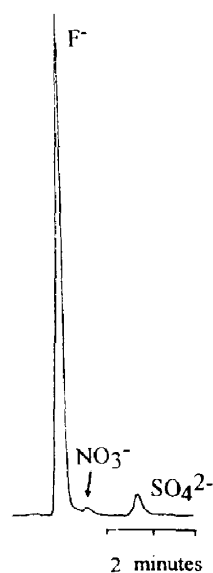


Fig. 1. A real-sample chromatogram obtained for 17.4 mg/l F^- in welding fumes by IC.

ISE potentiometry

For ISE determinations a literature procedure [6–10] was followed.

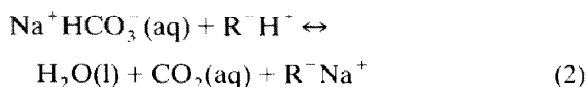
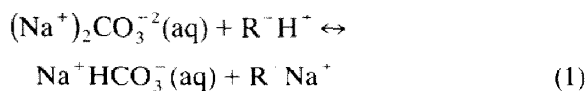
Calibrations. Five standards covering the range of 0.2–200 mg/l were prepared as above but in TISAB. The TISAB was prepared as described in the literature [6] but with 5 g/l of CDTA. The adjustment by linear regression analysis showed no bias and a near theoretical slope down to 0.2 mg/l, with high correlation coefficient ($R > 0.9999$). This value was considered as the practical detection limit for measurements. The F^- electrode was calibrated at the beginning of each working day.

3. Results and discussion

3.1. Baseline perturbation

When the eluent was injected through a on-line On Guard H pre-column (H^+ form), a small baseline perturbation at the beginning of the chromatogram was observed, which may overlap the peak of F^- for low concentrations of the analyte. However, the injection of eluent through a sodium-saturated On Guard H pre-column gave no baseline perturbation.

These results suggest that when the eluent passes through the On Guard H pre-column, hydrogen ion is displaced out of the resin (R^-) by the sodium ion from the eluent, which makes the solution acid (pH 4.5 at the exit of the On Guard H pre-column),



The loss of cations in the acid form of the eluent makes it a comparatively poor conductor, and this is the cause of the negative peak, similar to that found for water injection.

These results showed that when an on-line On Guard H pre-column is included in the system to remove metal ion interferences in the determination of anions, the use of the eluent matrix does not completely prevent the occurrence of a baseline perturbation at the beginning of the chromatogram, which disturbs the F^- peak. Therefore, the influence of this perturbation on the limit of detection of the procedure was investigated. For this purpose, calibrations (blank and six standards in the range 0.2–20 mg/l) without (C1 calibration) and with blank correction (i.e., with the chromatogram of the blank deducted from each standard chromatogram) (C2 calibration) were carried out. The relative errors associated to each standard peak height (h) in C1 calibration were calculated by the equation

$$(h_{C2} - h_{C1}) \cdot 100/h_{C2} \quad (3)$$

It was found (Table 1) that the C1 procedure introduced an error of 43% for the lower standard. The error decreased progressively for the more concentrated standards, and lost significance ($< 2.5\%$) for F^- concentrations higher than 10 mg/l. Therefore, a blank correction is required for F^- concentrations lower than 10 mg/L. In the present work, the C2 procedure was used instead of C1.

When the eluent was injected through a on-line Chelex-100 pre-column, no baseline perturbation at the beginning of the chromatogram was observed. This was expected because the resin was in Na^+ form. A typical real-sample chromatogram obtained under these experimental conditions is presented in Fig. 1.

Table 1
Relative errors associated with peak height in calibration without blank corrections (C1 procedure)

Standard (mg/l)	0.2	1.0	2.0	5.0	10	20
Error (%)	43	18	8.8	3.5	2.5	0.7

3.2. Metal interferences

The efficiency of On Guard H and Chelex-100 pre-columns to avoid metal interferences in F^- determinations was evaluated by measurements of the anion concentrations in mixed standard solutions of F^- , Fe(III) and Al(III), in which the concentrations of interferent ions (magnitudes and interferent/ F^- ratios) were similar to or higher than those expected in welding fume samples.

Recovery percentages (Table 2) between 97 and 101% were found for the whole fluoride working concentration range, if a single Chelex-100 pre-column or two On Guard H pre-columns in series were used. A single On Guard H pre-column provided complete recovery only up to 10 mg/l of both F^- and Fe(III) and 0.5 mg/l Al(III). The results also suggest that a Chelex-100 pre-column allows better recovery (98–99%) than two On Guard H pre-columns for the higher levels of concentrations.

3.3. Calibration behaviour and limit of detection

It has been demonstrated [19–22] that careful calibration over a wide range of concentration (\geq two orders of magnitude) in anionic IC with conductivity detection involving background suppression of a weakly basic eluent, reveals that the signal may be not a perfect linear function of the sample concentration (or, more precisely, of

the injected mass of analyte). Deviations from linearity occur caused by the hydrogen ions in the sample band passing the detector. These hydrogen ions will influence the dissociation equilibrium of the carbonic acid. Therefore, the conductance of the baseline during sample elution will be lower than the background level corresponding to the eluent alone. Therefore, reliable results require calibrations and measurements in a narrow range of analyte concentration. However, as environmental samples often show concentration levels dispersed in quite broad ranges, calibration in a narrow range reduces the practical interest of the method.

In the present work, linear regression was applied to a seven-point (six standards and blank) calibration in the range 0.2–20 mg/l of F^- , and perfect linearity was obtained. Therefore, none of the procedures suggested by Midgley and Parker [21] in order to reduce errors was applied to the calibration data. From the intercept and standard deviation of a typical calibration curve, peak height = 40.1 (± 0.8) [F^-] – 3.5 (± 6.8) (95% confidence limits in parentheses), the detection limit of the procedure was calculated [23]. A value of 0.4 mg/l or 0.02 $\mu g F^-$ was found, which corresponds to 4 μg for each filter disc (or 0.15 $\mu g/m^3$ air, for a 2-h sample).

The range of concentrations 0.4–20 mg/l F^- was found to be satisfactory for the majority of samples. When samples with higher F^- concen-

Table 2
Mean percentage of fluoride recovery obtained with and without interferents (6 measurements in 30 min)

[F^-] (mg/l)	Recovery \pm S.D. (%; $n = 6$)			
	On Guard H		Chelex 100	
	1 pre-column, [Fe^{3+}] = [Al^{3+}] = 0	1 pre-column, [Fe^{3+}] = [F^-], [Al^{3+}] = 0.5 mg/l	2 pre-columns, [Fe^{3+}] = [F^-], [Al^{3+}] = 0.5 mg/l	1 pre-column, [Fe^{3+}] = [F^-], [Al^{3+}] = 0.5 mg/l
0.5	99.2 \pm 1.12	101 \pm 1.44		
5.0	101 \pm 0.68	99.2 \pm 1.31		
10.0	101 \pm 0.17	97.6 \pm 1.20	97.2 \pm 0.41	98.7 \pm 0.19
15.0	99.9 \pm 0.41	93.6 \pm 2.26	97.0 \pm 2.56	97.6 \pm 0.46
20.0	106 \pm 0.35	95.8 \pm 0.80	96.7 \pm 5.63	99.4 \pm 0.33

trations were measured, accuracy was preserved by dilution of the sample solution. For lower F^- concentrations a more sensitive conductivity scale can be employed in the detector (see below).

The chromatographic system must be re-calibrated periodically during the working day, because the precision usually diminishes along the run, as discussed below. For this purpose, to save time, one-point (blank and one standard) calibrations are recommended [24]. In this work the highest standard (20 mg/l F^-) was used for these one-point re-calibrations. To ensure that this procedure preserved the response characteristics of the system, the reference factor, $F_r = \text{peak height}/[F^-] = 39.5 \text{ mS} \cdot \text{l}/\text{mg}$, was compared with the slope of the calibration curve ($40.1 \pm 0.8 \text{ mS} \cdot \text{l}/\text{mg}$). As both values were identical at 95% confidence level, the one-point calibration was considered acceptable.

3.4. Precision

Homogeneity of fume deposition on the filter

As found in a previous work [5], the homogeneity of particle deposition on the filters allows determination on discs of 1 cm diameter.

Analytical signal

The precision of the chromatographic response was evaluated by repeated measurements (six measurements in 30 min) on mixed standard solutions, at different levels of F^- and interferences. The results (Table 2) show that the precision was generally less than 3% when On Guard H pre-columns were used and up to 0.5% for a Chelex-100 pre-column.

3.5. Accuracy

Filter blanks

To check whether the filters used for sampling contributed with F^- , twelve discs cut at random from several blank filters were treated by procedure (a) and measured by IC. For this purpose, a more expanded conductivity scale, 10 $\mu\text{S}/\text{cm}$, and calibrations in the range 0.05–1.0 mg/l F^- concentrations were used. For these experimental conditions, the practical detection

limit [23] was 0.03 mg/l (or 1.5 ng) of F^- . Levels of F^- in the range 0.03–0.09 mg/l, with mean $0.06 \pm 0.02 \text{ mg}/\text{l}$ (or $0.6 \pm 0.2 \mu\text{g}$ for each filter disc), were obtained. These values correspond to 15% of the detection limit value and 0.3% of the maximum concentration determined by the present procedure. Similar studies were carried out for both ISE procedures, but in consequence of the relatively higher detection limit of the ISE technique, ca. 0.2 mg/l, F^- was not found. It was concluded that the contribution to F^- from filters was negligible.

Comparison of procedures

As the sample pre-treatment depended on the analytical technique used for measurement, the final results could depend on both stages of the procedure, and therefore it was decided to investigate them separately.

Extractions. To extract welding fumes from filters, HCl solutions have been recommended for ISE determination of F^- [9]. However, acid solutions are unacceptable for IC determination of F^- , because the eluent is alkaline. Besides, with HCl as extractor [9], a large Cl^- peak would occur overlapping the F^- peak, because their retention times are similar.

To evaluate the influence of wet digestion on the amount of fluoride extracted, pairs of discs cut from six filters were treated in parallel by procedures a and b (see above) and measured by IC. The same procedure was applied to compare the fraction of fluoride extracted by procedures c and d for ISE determinations, but sixteen samples were used. The fluoride concentrations in solution were in the ranges 1.1–20 mg/l (IC) or 0.6–23 mg/l (ISE). Linear least-squares adjustment of each set of results yielded the following equations (95% confidence limits in parentheses [25]), [(a)IC] = $0.938(\pm 0.092) \cdot [(b)IC] + 0.41(\pm 0.93)$, $R = 0.998$, and [(c)ISE] = $1.067(\pm 0.093) \cdot [(d)ISE] - 0.3(\pm 1.3)$, $R = 0.989$. These results show no evidence of relative or fixed bias in the measured range, which means that the two extraction procedures used for each type of determination yielded the same fraction of fluoride.

IC vs. ISE. The F^- contents of the thirteen samples, in the range 0.6–18 mg/l, were de-

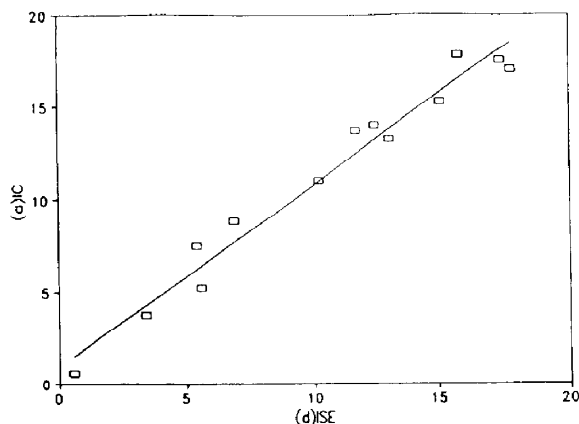


Fig. 2. Comparison of (a)IC vs. (d)ISE methods for F⁻ determination from welding fumes (see details in the text). Values along axes in mg/l.

terminated in parallel by the (d)ISE procedure (attack with HNO₃) and by the (a)IC method (eluent extraction). A linear regression of IC vs. ISE results (Fig. 2) yielded the equation (95% confidence limits in parentheses) [(a)IC] = 0.99(±0.12) · [(d)ISE] + 0.9(±1.4), with *R* = 0.983. These results show no relative or fixed bias at the measured concentration level. Therefore, the proposed IC procedure is considered to be acceptable for determination of F⁻ from welding fumes of the present type.

Moreover, these last results together with those obtained in the comparison of the extraction procedures, which showed that (a)IC and (b)IC as well as (c)ISE and (d)ISE were equivalent, show that the fraction of F⁻ extracted from the filter was independent of pH and of the composition of the solution. These results show that no significant losses of volatile HF occurred during the digestion with HNO₃. They also suggest that all the F⁻ in the welding fumes under monitoring was water soluble.

4. Conclusions

The present results show that interferences of metal ions in the IC determination of F⁻ in welding fumes can be effectively avoided by passing sample solutions through On Guard H or Chelex-100 in Na⁺ form on-line pre-columns. The latter seems more convenient since it allows

better precision and accuracy and does not cause any baseline perturbation when samples with eluent as matrix are injected. It was shown that the fraction of F⁻ extracted was not affected by pH variation over a broad range (< 0–10.5) and that mild extraction conditions to aqueous solutions required by IC are adequate.

IC is preferred to ISE when maximum sensitivity and/or speed is required. IC is also more versatile as a measurement technique. Although the ISE technique can be used in a large range of fluoride concentration (0.2–200 mg/l), this range cannot be modified by altering experimental conditions, since both the filter area and dilution volume were fixed. In contrast, IC has a narrower range of linear response (0.4–20 mg/l F⁻ in the proposed procedure), but the operational range can be moved to higher or lower concentration levels by changing operational parameters, e.g. loop capacity, eluent concentration, the sensitivity of the detector, etc. For instance, a detection limit for the IC procedure one or two orders of magnitude lower than for ISE potentiometry can be obtained, which is particularly suitable for determinations at low concentrations of fluoride in air or for short periods of sampling (grab samples). These are useful for measurement of concentration fluctuations during the working day.

In conclusion, the IC approach provides a sensitive procedure of measuring F⁻ from welding fumes. Moreover, the technique has considerable potential for the simultaneous measurement of other of inorganic anions in the sample.

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