



ELSEVIER

Journal of Chromatography A, 739 (1996) 241–248

JOURNAL OF
CHROMATOGRAPHY A

Analysis of fluoride in rain water Comparison of capillary electrophoresis with ion chromatography and ion-selective electrode potentiometry

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Abstract

Fluoride concentrations in Dutch rain water samples were determined by three different analytical techniques, i.e., (i) capillary electrophoresis (CE), (ii) ion chromatography (IC) and (iii) ion-selective electrode potentiometry (ISE). Performance characteristics in terms of precision, limit of detection and run time have been obtained for the three applied methods using standard solutions in the range of 0.5 to 10.0 $\mu\text{mol l}^{-1}$. Limits of detection were found to be similar for IC and ISE (0.2 and 0.3 $\mu\text{mol l}^{-1}$, respectively) and somewhat higher for CE (0.6 $\mu\text{mol l}^{-1}$). Statistical analysis of the fluoride concentrations in rain water samples as obtained by CE, IC and ISE indicated that there was no evidence for systematic differences between CE and ISE, whereas the fluoride concentrations obtained by IC were significantly higher. The observed differences are most likely due to the presence of aluminium cations.

Keywords: Water analysis; Environmental analysis; Fluoride

1. Introduction

Fluoride is emitted into the environment by various industrial processes, such as phosphate fertilizer production, aluminium reduction and metal smelting. Although fluoride concentrations in air have fallen in the Netherlands during the 1980s, the atmospheric concentrations are such that damage to ecosystems, agricultural and livestock farming cannot be excluded [1]. For this reason, determination of fluoride in rain water samples was included in the Dutch national monitoring program, which is carried out at our institute.

From an analytical point of view various methods have been reported for the determination of fluoride

in aqueous solutions, such as colorimetric, conductometric, complexometric and potentiometric methods [2]. From this series, potentiometry has been widely used for quite some time due to its simplicity and short analysis time. However, the selectivity is rather limited, especially if chemically similar ions are present in the sample. For natural samples other serious limitations arise. In general, the limit of detection is not far below $10^{-6} \text{ mol l}^{-1}$ and conditioning of the electrode surface is frequently time consuming. Finally, the poor precision of potentiometry reduces its applicability under conditions where accurate measurements are required. Recent developments in separation techniques have led to an improvement in the determination of fluoride in terms of selectivity (qualitative) and sensitivity (quantitative) [3–5]. IC is increasingly used for the

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determination of various ions, especially anions, in one single run. As a result, IC has become a favourite measurement technique for the determinations of anions, including fluoride, in aqueous samples. Even more recent is the introduction of capillary electrophoresis as a new separation technique for inorganic compounds [6–8]. CE appears to be very suitable for the analysis of inorganic anions due to short run times, large separation power, simplicity, low costs and low production of laboratory waste [9].

One of the major problems in the analysis of total fluoride concentrations in natural samples is the impact of metal ions like iron, calcium and aluminium on the analytical response. Due to binding of fluoride with these cations, only a fraction of the total fluoride concentration is determined in most cases. Elimination of this type of interference may be achieved by addition of metal complexing agents such as 1,2-cyclohexylenedinitrilotetraacetic acid (CDTA) [4,10], sodium 1,2-dihydroxybenzene-3,5-disulfonate (Tiron) [11,12] or citrate [13].

The aim of the present paper is to compare the results of fluoride determination in rain water samples as obtained by different experimental methods, i.e., capillary electrophoresis, ion chromatography and ion-selective electrode potentiometry. The comparative evaluation includes (i) performance characteristics, such as precision and limit of detection, as obtained for standard solutions and (ii) interference of aluminium on the response.

2. Experimental

2.1. Reagents

All solutions were prepared using water purified with a Milli-Q system (Millipore, Bedford, MA, USA). HCl, acetic acid, aluminium nitrate, 1,2-cyclohexylenediaminetetraacetic acid, NaOH, triethanolamine (TEA) and ethylene diamine were of pro analysis quality, 1,2,4,5-benzenetetracarboxylic acid (also known as pyromellitic acid, PMA) was of pro synthesis quality and NaF was of supra pure quality. For Tiron the quality was not provided by the manufacturer. All chemicals were obtained from Merck (Darmstadt, Germany), except for hexane-

1,6-bis[trimethyl]ammonium bromide (HMBR), which was purchased from Sigma (St. Louis, MO, USA).

2.2. Samples

For the Dutch rain water monitoring program, which is carried out at our institute, rain water samples are collected monthly at 14 different sampling stations. For the present study, samples obtained in May, June and July 1995 were used. All samples were filtered over a 450 μm sieve in the field. Additional filtering over a 250 μm sieve was carried out at the laboratory. Sieves were obtained from Stokvis/Smit (IJmuiden, The Netherlands).

2.3. Capillary electrophoresis

The presently applied CE procedure is based on Dionex Application Note 68 and has been described in detail elsewhere [14]. Briefly, electropherograms were obtained using a Waters Quanta 4000 CE system equipped with a UV detector, a negative power supply and an automatic sample changer. For data acquisition an NEC Powermate 433 PC was connected to the CE system via an SAT/IN interface. Data were acquired using the 5 Hz data acquisition rate. Millennium 2010 (Version 2.10, Millipore) software was used for data collection and treatment. Separations were carried out using an AccuSep (Waters) fused-silica capillary (60 cm \times 75 μm I.D., effective length 52 cm) at a voltage of 30 kV. Injection was performed hydrostatically by elevating the sample at 10 cm for 240 s at the cathodic side of the capillary. Indirect UV detection at 254 nm was used. The time constant of the UV detector was 0.3 s.

Prior to use the capillary was pretreated daily with 1 mol l⁻¹ NaOH for 5 min, then rinsed with deionized water for 2 min. In order to obtain stable electropherograms in terms of baseline noise, the capillary was rinsed successively with 0.1 mol l⁻¹ HCl (0.2 min), deionized water (0.3 min) and carrier electrolyte (1.4 min) before each sample injection.

The carrier electrolyte was prepared from a stock solution containing 22.5 mmol l⁻¹ PMA and 16 mmol l⁻¹ TEA. This solution was sonicated in an ultrasonic bath in order to dissolve the PMA com-

pletely. To a 20-fold dilution of the carrier stock solution, an electro-osmotic flow modifier solution containing HMBr was added using an OnGuard-A cartridge (Dionex) in order to remove ionic bromide. The resulting working carrier solution contained 1.13 mmol l⁻¹ PMA, 0.8 mmol l⁻¹ TEA and 2.13 mmol l⁻¹ HMOH (pH 7.7).

In order to decomplex possible fluoride–metal complexes, Tiron [11,12] (0.1 mol l⁻¹) was added to each sample in such a quantity that the final concentration equalled 10⁻⁴ mol Tiron l⁻¹ sample.

2.4. Ion chromatography

For the analysis of fluoride in rain water samples, we followed the procedure described in Ref. [15]. In short, IC determinations were carried out in a Dionex 4500i ion chromatograph with a pulsed electrochemical detector in conductivity mode. Sample and eluent were lead via a Dionex AG10 anion guard column through a Dionex AS10 separator column and a Dionex ASRS-1 anion micromembrane suppressor using a Dionex GPM-2 pump. The IC system was automated in terms of (i) sample introduction by means of a Dionex ASM-II sample changer and (ii) data processing using Dionex AI-450 software (Release 3.3). To that end the detector was connected with an Olivetti M380 PC using a Dionex ACI interface.

A 0.32 ml injection loop was used. The eluent was a 13 mmol l⁻¹ NaOH solution, to which ethylenediamine (0.375%, v/v) was added in order to reduce possible accumulation of metal ions in the columns. To remove sulfate and nitrate from the column, the system was rinsed between successive runs with a 200 mmol l⁻¹ NaOH solution containing ethylenediamine (1.25%, v/v) for 8 min. Prior to the next injection, equilibration of the system was

achieved by rinsing with the diluted eluent (13 mmol l⁻¹ NaOH; 0.375% (v/v) ethylenediamine) for 9 min.

2.5. Ion-selective electrode potentiometry

For ISE determinations, an automated flow system was constructed containing a fluoride ISE (Orion 9409), an Ag/AgCl reference electrode and a Philips PW 9421 pH meter. 1,2-cyclohexylenediaminetetraacetic acid was added to the sample in order to decomplex fluoride–metal complexes, which might be present in the rain water samples. The method is described in detail in a standard operating procedure [16].

3. Results and discussion

3.1. Performance characteristics

Performance characteristics in terms of precision and detection limits of the analytical response were obtained from reproducibility experiments. On nine different days various fluoride calibration solutions were measured using capillary electrophoresis, ion chromatography and ion-selective electrode potentiometry as described in Section 2. Usually, experiments were carried out by different analysts. In Table 1 the standard deviation (SD) of the response is summarized for each fluoride standard solution. The corresponding limit of detection (LOD) is defined as 3-times the S.D. in the intercept of the calibration curve, which can be obtained mathematically according to the procedure described below [17]. The starting point is the assumption that the response is linearly related to the fluoride concentration:

Table 1
Precision of standard solutions in terms of S.D. (in $\mu\text{mol l}^{-1}$) for the applied ISE, IC and CE procedures

| Technique | [F] ($\mu\text{mol l}^{-1}$) | | | | | | | | | |
|-----------|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 4.0 | 6.0 | 8.0 | 10.0 |
| ISE | 0.086 | 0.115 | 0.132 | 0.166 | 0.181 | 0.259 | 0.290 | n.d. | n.d. | n.d. |
| IC | n.d. | 0.041 | n.d. | 0.083 | n.d. | n.d. | 0.149 | 0.148 | 0.253 | 0.245 |
| CE | 0.220 | 0.080 | n.d. | 0.190 | n.d. | n.d. | 0.320 | 0.210 | 0.160 | 0.330 |

n=9; n.d., not determined.

$$y = a + bc \quad (1)$$

where a and b denote the intercept and slope of the calibration curve, respectively; y is the response and c is the fluoride concentration. The physical concept of the mathematical procedure is that with maintenance of linearity, variations in response are related to (i) variations in the value of the intercept and (ii) variations in the slope of the calibration curve. Only the second contribution is dependent on the concentration of the analyte. Summation of both effects is simply expressed by the summation of the corresponding variances. Values for the variation in intercept (SD_a) and for the variation in slope (SD_b) are obtained by fitting the measured standard deviation as a function of the concentration, according to:

$$SD_{\text{fit}}^2 = SD_a^2 + (SD_b \cdot c)^2 \quad (2)$$

Eq. 2 reflects the tendency of dispersion being constant at the lower end and being proportional to the concentration at the higher end of the measurement range. The coefficients SD_a and SD_b in Eq. 2 are obtained by linear regression analysis. If one considers that the measured values for S.D. for each concentration of analyte may be not normal distributed, the present mathematical model is an approach which seems quite acceptable, considering the uncertainty in SD_{fit} obtained with a limited number of standard solutions. Only at a high number of measurement pairs it may be worthwhile to introduce three terms in the variance function [17].

For the three applied techniques (CE, IC and ISE), the fitted SD curves are presented in Fig. 1. At low fluoride concentrations, the standard deviation appears to be smaller for ISE and IC compared to CE, resulting in lower detection limits for ISE and IC (see Table 2). For ISE, the standard deviation increases rapidly with increasing fluoride concentration due to the logarithmic response characteristic. For the investigated calibration range (0.5–10.0 $\mu\text{mol l}^{-1}$), the precision appears the highest for IC. For CE, the precision is less compared to ISE at low fluoride concentrations (<3 $\mu\text{mol l}^{-1}$), but improves significantly at higher concentrations. The mathematical procedure works quite well for ISE and IC, indicated by the quality of the fit, which is indicatively expressed by the correlation coefficient (r) and appears to be 0.973 and 0.926 for ISE and IC,

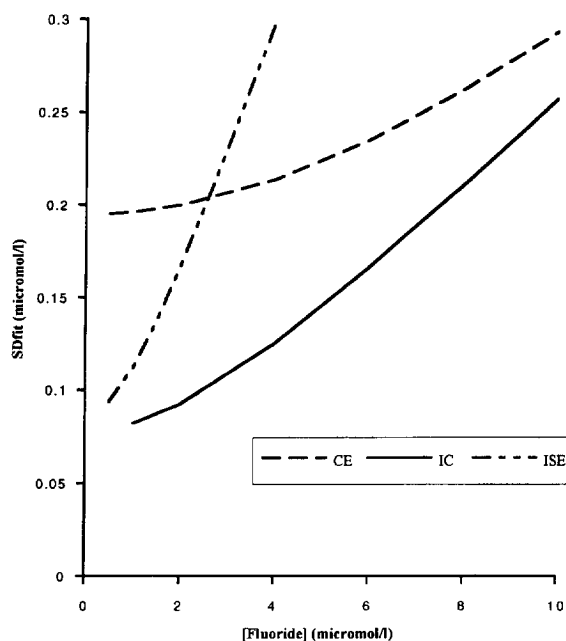


Fig. 1. Fitted SD curves as a function of the fluoride concentration in calibration standards for CE, IC and ISE. For details, see the text.

respectively. In the case of CE, there is much more scatter of experimental points about the fitted curve ($r=0.473$).

Retention and migration times of fluoride calibration solutions were found to be 6.86 min and 4.03 min for IC and CE, respectively. The corresponding RSD values in both retention and migration time appeared to be lower than 2%. The total run time includes sample introduction, purging/washing time and run time, whereas the time needed for pretreatment of the sample and to calculate the corre-

Table 2
Performance characteristics of applied techniques

| | CE | IC | ISE |
|--|------|------|---------|
| Calibration range ($\mu\text{mol l}^{-1}$) | 1–10 | 1–10 | 0.5–4.0 |
| Detection limit ($\mu\text{mol l}^{-1}$) | 0.6 | 0.2 | 0.3 |
| Retention /migration time (min) | 4.03 | 6.86 | – |
| RSD retention /migration time (%) | 0.8 | 1.8 | – |
| Run time (min) ^a | 10 | 30 | 2.5 |

^a Run time including purging and sample introduction; excluding sample preparation and calculation.

sponding concentration are not taken into account. These latter contributions are estimated to be approximately equal for the three experimental methods. The total run time was found to increase in the order $ISE < CE < IC$.

3.2. Analysis of rain water samples

Fig. 2a and b show the chromatogram and the electropherogram, respectively, of a rain water sample collected at Beek. In the case of IC, beside the fluoride peak ($t=6.93$ min) a neighbouring peak appears in the chromatogram due to the presence of acetate at $t=8.00$ min. The shape of the electropherogram is quite different from that of the chromatogram. The number of peaks in the electropherogram is larger than in the chromatogram indicating the presence of a variety of compounds in the rain water sample. Fast anions, like chloride, sulfate and nitrate, appear at the beginning of the electropherogram ($t=3.1$ – 3.6 min), whereas less mobile ions, such as phosphate and hydrogen carbonate can be found at later migration times ($t=5.4$ – 6.0 min). Using IC, these type of anions are more retained on the AS10 column compared to fluoride and, hence, their response would appear later in the chromatogram. Fig. 2a and b illustrate the strength of CE as compared to IC, i.e., the large separation power, which makes it possible to determine a variety of anions within a short run time under the presently employed experimental conditions.

A comparison of the results for the determination of fluoride in Dutch rain water samples ($n=42$) using CE and ISE, and using CE and IC are shown in Fig. 3a and b, respectively. In the present set of rain water samples, the concentration of fluoride varies from approximately 0.3 to $3.5 \mu\text{mol l}^{-1}$. Only for CE, a few samples ($n=6$) appeared to have fluoride concentrations below the limit of detection, i.e. $0.6 \mu\text{mol l}^{-1}$. In Fig. 3a and b, the dotted line represents the function $x=y$. Results obtained by CE and ISE scatter equably about the $x=y$ function, indicating that both techniques result in comparable fluoride concentrations. In the case of CE/IC comparison (Fig. 3b), the pattern of scattering is rather different. Most data points are found below the $x=y$ function, indicating that application of IC leads to higher results for fluoride concentrations as compared to

CE. These qualitative observations are confirmed by the results of statistical analysis according to Student's t -test, showing that there is no significant difference between the results obtained with ISE and CE, whereas there is certainly a significant difference in the case of IC and CE (see Table 3). The general observation is that application of the IC procedure to the present set of rain water samples leads to the highest fluoride concentration. CE and ISE give approximately equal results, but definitely lower concentrations than using the IC measurement method.

The observed differences in fluoride concentration in rain water samples as obtained by different measurement methods can most likely be explained by considering possible interference with aluminium. Typical concentrations of aluminium in Dutch rain water were found to be in the range of 2 to $6 \mu\text{mol l}^{-1}$, the same as the fluoride concentrations obtained in the present study. Considering stability constants of aluminium fluoride complexes [18], it is expected that part of the fluoride in the original sample will be bound by aluminium. Obviously, the added decomplexing agents Tiron and 1,2-cyclohexylenediaminetetraacetic acid are not able to fully decomplex fluoride bound by metals. This hypothesis was validated by adding aluminium nitrate to fluoride calibration standards. For CE, where aluminium was added in 10 times excess over fluoride ($[\text{F}^-]=10 \mu\text{mol l}^{-1}$), the resulting response decreased by approximately 25% compared to the aluminium free solution. A 90% decrease in response was observed using ISE ($[\text{F}^-]=3 \mu\text{mol l}^{-1}$; $[\text{Al}^{3+}]=500 \mu\text{mol l}^{-1}$), while no significant decrease in response was observed for IC up to aluminium concentrations of 4 mmol l^{-1} with $[\text{F}^-]=3 \mu\text{mol l}^{-1}$. This means that the decomplexing agents applied are not able to decomplex fluoride completely from its aluminium complex form. Thus, for natural samples which contain aluminium, measured fluoride concentrations as obtained by using the ISE or CE measurement methods as described in Section 2 are a fraction of the total fluoride concentration. It is well known that without manipulation of the sample solution the potentiometric response is related to the activity of the free ion in solution. A peak in the electropherogram is a priori related to ions with the same mobility, which depends on the size and charge of the ion.

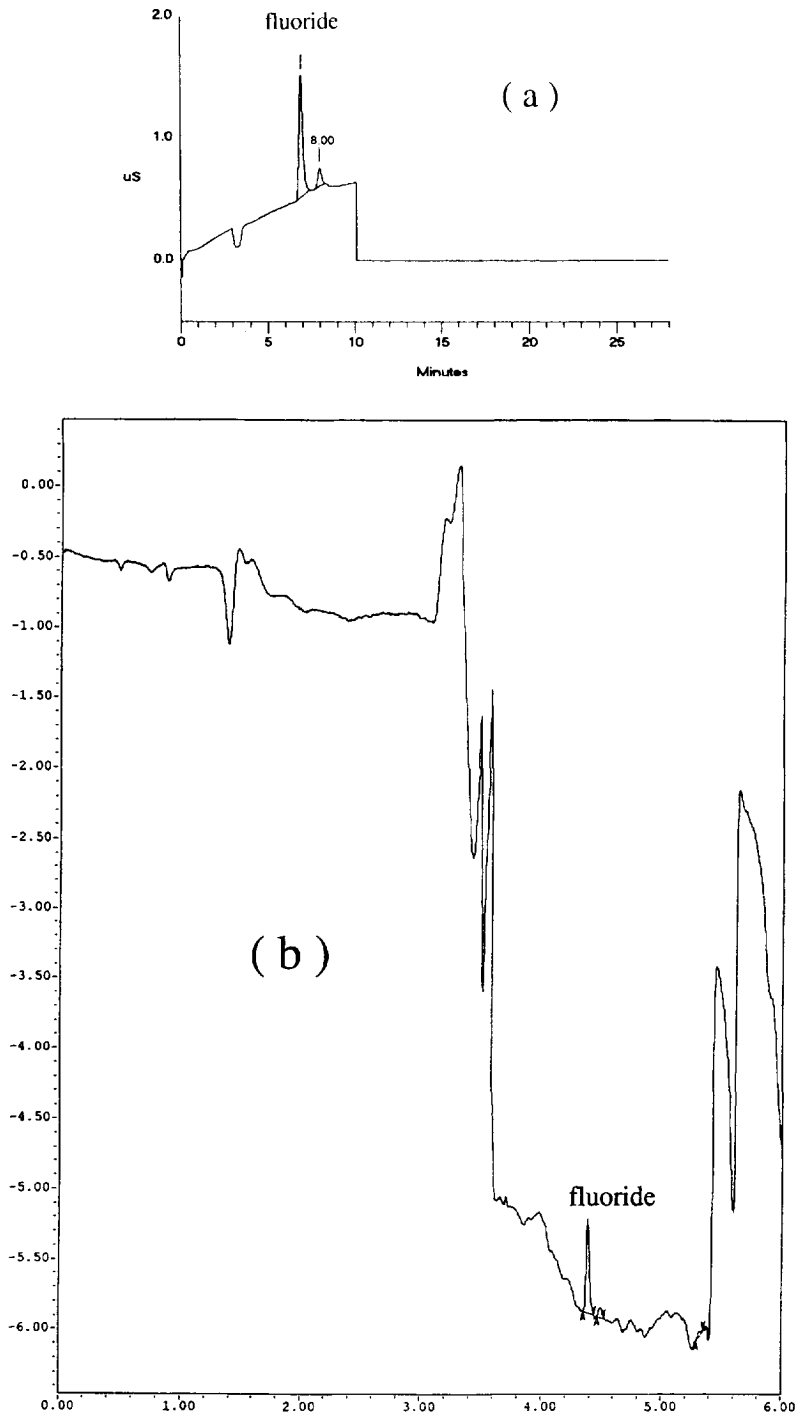


Fig. 2. Chromatogram (a) and electropherogram (b) of a rain water sample collected at Beek. For experimental details, see Section 2.

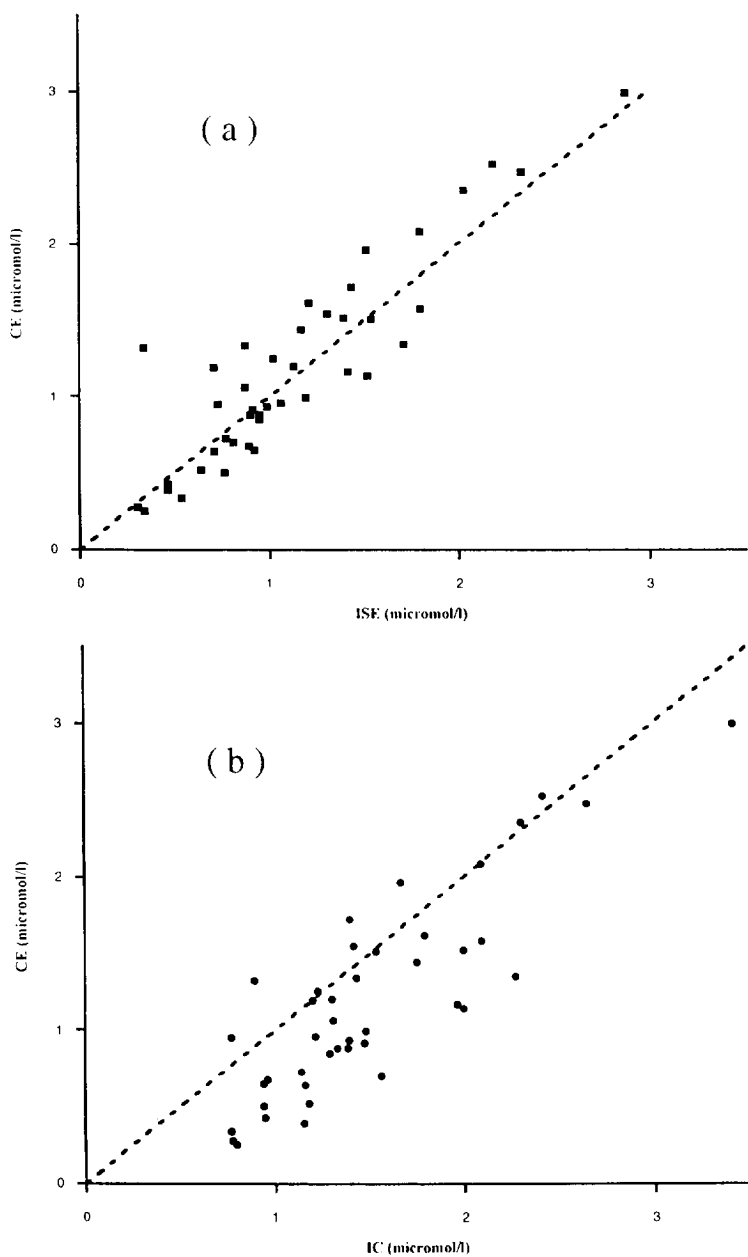


Fig. 3. Comparison of the results for the determination of fluoride in Dutch rain water samples ($n=42$) using CE and ISE (a) and CE and IC (b). The dotted line represents the $x=y$ function.

Considering the presence of different aluminium fluoride complexes, like AlF_2^{2+} and AlF_2^+ , having different molecular sizes and (opposite) charges, the

observed CE response is also related to the concentration of free fluoride ions as obtained under the presently employed experimental conditions.

Table 3

Statistical analysis results of the correlation between fluoride concentrations in rain waters obtained by ISE and CE, by IC and CE, and by ISE and IC

| | Intercept | Slope | r^2 | t | $t_{critical}$ |
|------------|------------|-----------|-------|-------|----------------|
| ISE vs. CE | 0.19±0.16 | 0.80±0.12 | 0.821 | -1.29 | 2.02 |
| IC vs. CE | 0.60±0.20 | 0.76±0.15 | 0.731 | -5.97 | 2.02 |
| ISE vs. IC | -0.27±0.09 | 0.93±0.05 | 0.879 | -11.7 | 2.02 |

Confidence limits, ±95%; two-tail; $n=42$.

4. Conclusions

CE, IC and ISE were used for the determination of fluoride concentrations in rain water samples. Fluoride concentrations obtained by IC were significantly higher than using CE or ISE. Comparable concentrations were found with CE and ISE. The observed difference can be explained by considering the presence of aluminium in the natural samples. The applied decomplexing agents in the CE and ISE methods were not able to totally decomplex all fluoride bound by aluminium. Here, the response is more related to free fluoride concentrations than total concentrations.

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