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Fast spectrophotometric determination of fluoride in ground waters by flow injection using partial least-squares calibration

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Abstract

The presence of sulphate constitutes a serious interference in the usual zirconium lake-based spectrophotometric method for the determination of fluoride in water. In this report, full spectral data have been recorded for the zirconium lake of 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonate (SPADNS) in the simultaneous presence of fluoride and sulphate, as obtained with a flow injection system with a diode-array detector. The information has been processed with partial least-squares (PLS) multivariate calibration. Adequate modeling using a sixteen-sample calibration set allows fluoride to be determined in ground waters by the automated flow injection method, even in the presence of sulphate in concentrations up to 1000 mg l^{-1}. In the calibration range 0–1.50 mg l^{-1} for fluoride, the limit of detection is 0.1 mg l^{-1}. The fluoride contents in real samples, as determined with the present method, were satisfactorily compared with those provided by ion selective potentiometry.

Keywords: Flow injection analysis; Partial least-squares regression; Fluoride analysis; Ground waters; Sulphate interference

1. Introduction

Fluoride plays a central role in the prevention of dental caries [1,2], and is regularly employed for this purpose in drinking water. Although in some cases ground water contains naturally occurring fluoride, in many cases it is externally added in water plants, with optimal fluoride levels varying from 0.6 to 1.1 mg l^{-1}. A continuous monitoring of the fluoride levels is needed, since its excess may produce fluorosis and renal, gastrointestinal and immunological toxicity [3]. Furthermore, it is known that hemodialyzed patients consuming fluoride-rich water face the risk of hyperkalemia [4].

The usual reference method for the determination of fluoride in waters is based on the effect of the latter on the absorbance of the lake formed by Zr ion and 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonate (SPADNS) [5–7]. Several other techniques have been reported for the determination of fluoride in drinking water, such as potentiometry with fluoride ion selective electrodes (ISE) [8–10], ion chromatography [11], inductively coupled plasma-mass spectrometry [12], capillary electrophoresis [13], solvent-extraction coupled to fluorimetry [14], polarography [15] and spectrophotometric techniques based on dyes different than SPADNS [16–18]. Methods based on flow injection analysis (FIA) have also been reported, using different detection methodologies [19–21]. Nevertheless, the Zr–SPADNS spectrophotometric method remains as a simple, low-cost, reliable and rapid alternative, which is also amenable to automation [22] and to field analytical uses [23]. The method involves the measurement of the absorbance changes brought about by fluoride on an acid solution of the zirconium complex. At 570 nm, the absorbance decrease is proportional to the fluoride concentration, although the presence of sulphate constitutes a serious interference in this determination [24]. Consequently,

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the Zr–SPADNS-based spectrophotometric method cannot be applied to subterranean water sources, which usually contain high sulphate levels.

The present investigation was prompted by the needs of a regional water supplier, where the Zr–SPADNS method is regularly employed, unless the sample is of subterranean origin and contains significant sulphate concentration to constitute an interference, in which case the ion selective electrode has to be used. An alternative was to explore the Zr–SPADNS method incorporating full spectral measurements and a suitable multivariate calibration methodology. Partial least-squares (PLS) regression appeared to be the candidate of choice, due to the quality of its predictive models, the availability of software and the ease of its implementation [25]. An additional objective was to combine the above strategy with flow injection analysis, in order to develop an automated method for routine fluoride monitoring.

In this report, we show that an appropriately trained multivariate calibration model based on PLS regression of Zr–SPADNS visible spectra in the presence of F^- and SO_4^{2-} is able to exploit this information for the determination of fluoride, with the accuracy and precision required for routine water analysis in subterranean samples. The flow injection system provides simplicity, feasibility and high sampling frequency. By coupling the FIA system to a diode-array spectrophotometric detector it is possible to obtain the spectra from the recorded FIA peaks. Leave-one-out cross-validation was employed to construct an adequate PLS model [26], which was subsequently validated using a set of randomly designed binary mixtures. Several real samples have been studied using the proposed methodology, and the results compare favorably well with those provided by ion selective potentiometry.

2. Experimental

2.1. Reagents

Analytical-reagent grade chemical were employed in all experiments. SPADNS and potassium fluoride standards were obtained from Merck (Darmstadt, Germany), while zirconium oxide chloride octahydrate and sodium sulphate were obtained from Mallinckrodt (St. Louis, USA). Doubly distilled water was used.

2.2. Apparatus

Spectrophotometric measurements were performed on a Hewlett Packard 8452A diode-array spectrophotometer equipped with a Hellma 178-712-QS flow cell with an inner volume of 8 μl and 10 mm light path. The propulsion system consisted of a Gilson Minipuls 3 peristaltic pump. A Rheodyne 5041 injection valve was employed. All the reaction coils were made of PTEF tubing (i.d. 0.5 mm). Spectra were read in the range 560–640 nm each 2 nm (41 data points per spectrum).

Ion selective potentiometric measurements were carried out using a WTW PMX3000 pH/ion meter and an Orion 9609 BN ion selective electrode, under the conditions described in the official literature [27].

2.3. PLS calibration set

A calibration set of 16 samples was prepared, using a full factorial design in which four levels were considered for both F^- and SO_4^{2-} ions. The levels corresponded to four equally spaced values in the range 0–1.50 mg l^{-1} for F^- and 0–1000 mg l^{-1} for SO_4^{2-}. They were prepared by measuring appropriate aliquots of the standard solutions, and mixing them in 100.00 ml volumetric flasks in order to obtain the desired design concentrations (completion to the mark was achieved with doubly distilled water). The training samples were injected, in random order, into the FIA system described below, and the visible spectra were read in the range 560–640 nm each 2 nm (41 data points per spectrum).

2.4. PLS test set

A 12 sample test set was prepared with F^- and SO_4^{2-} concentrations different than those employed for calibration, following a random design, but keeping all values between the corresponding calibration ranges for each analyte. This set was used for validating the PLS model. All samples were prepared and analyzed in triplicate, in order to estimate prediction errors for applying accuracy tests. Injection into the FIA system was made in random order and in different days as compared to the calibration samples.

2.5. Real samples

Seven natural samples, known to contain between 0.6 and 0.9 mg l^{-1} of naturally occurring fluoride, were obtained from Aguas Provinciales de Santa Fe, the major regional water supplier. All samples were of subterranean origin, and contained sulphate ion in the range 350–550 mg l^{-1}, as determined by turbidimetry based on the precipitation of barium sulphate [28]. Fluoride content in these samples was determined by injection into the FIA system and data processing with PLS and also by ISE, in both cases in triplicate, in order to compare the results. The content of other sample components was provided by the company (see below).

3. Theory

3.1. PLS

Multivariate calibration methods such as PLS involve a calibration step in which the relation between spectra and component concentrations is estimated from a set of reference samples, and a prediction step in which the

results of the calibration are used to estimate the component concentrations in an unknown sample spectrum [25]. The PLS-1 version employed here is optimized for the determination of a single analyte of interest.

The optimum number of PLS loading vectors is selected in order to avoid overfitting. We applied the leave-one-out cross-validation method described by Haaland and Thomas [26]: the technique is well known, and details on its implementation are easily available [25,26]. Usually, both spectral and concentration data are mean centered, in order to remove constant background effects. During cross-validation, mean centering is applied each time a sample is left out, employing data for each of the calibration subset of samples.

Realistic sample-specific standard deviations for the PLS predicted concentrations can be estimated with the aid of the following equation [29]:

$$s = [(I^{-1} + h)(s_c^2 + ||\boldsymbol{b}_k||^2 s_R^2) + ||\boldsymbol{b}_k||^2 s_R^2]^{1/2} \quad (1)$$

where s is the standard deviation in the concentration of a given analyte k in a multicomponent mixture, I the number of calibration samples (16 in our case), s_c and s_R the standard deviations in calibration concentrations and instrumental signals, $\boldsymbol{b}_k$ the vector of regression coefficients for analyte k provided by the model (|| || indicates Euclidean norm), and h is the so-called sample leverage. Values of s_c and s_R are usually available to experienced analysts from calibration measurements and instrumental blank replication.

The limit of detection for analyte k (LOD_k) can be estimated as:

$$LOD_k = 3 s_R ||\boldsymbol{b}_k|| \quad (2)$$

where the parameter $||\boldsymbol{b}_k||$ plays the role of the inverse sensitivity in univariate calibration.

3.2. Software

PLS was implemented with an in-house Matlab 6.0 routine [30], based on the well-known algorithm [26]. The routine employs user interface controls, and provides an easy environment for performing different multivariate calibration tasks [31].

4. Results and discussion

4.1. Optimization of the FIA system

The employed FIA manifold for the chemometric-assisted spectrophotometric determination of fluoride in water involves a water flow, a flow of Zr–SPADNS–HCl, both driven by a peristaltic pump, a valve for injecting the sample, a reactor and a diode-array spectrophotometric detector. The simplicity of this FIA system allows it to be used as a routine laboratory technique for determining fluoride in water samples with a significant sulphate content. The sample throughput was 40 h^{-1}.

A sample volume was injected in the carrier stream (doubly distilled water) which merged with the reagent stream (Zr–SPANDS complex) into the reactor, where the chemical reaction took place. For optimization, FIA signals were recorded at 570 nm. This wavelength corresponds to the maximum absorption of the Zr–SPANDS complex, which was used as baseline. When a sample water volume was injected, a negative FIA peak was recorded owing to the presence of fluoride.

The chemical and FIA variables were studied and optimized by the univariate method. For this purpose, a sample standard solution with a fixed concentration of fluoride was used.

The concentrations of the reagents (keeping in mind that an excess of SPADNS should exist over Zr), the acidity (in terms of HCl concentration), the sample volume, the reactor length, and the flow rates of both streams were considered as variables. The analyzed ranges and optimum values are shown in Table 1, which led to obtaining the largest signal, compatible with a good reproducibility.

4.2. Spectra

Fig. 1A shows the spectra of the sixteen training samples in the region 560–640 nm, obtained after injection into the FIA system. The latter region is the most useful for F^- determination: below 560 nm the spectra are dominated by high-absorbance peaks of free SPADNS, and above 640 nm no significant signal is obtained. Fig. 1B, in turn, collects results for the calibration solutions which contain either fluoride or sulphate. As can be appreciated, increasing fluoride concentrations causes a linear decrease of the absorbance as compared with the spectrum in the absence of fluoride, which is the basis for the univariate Zr–SPADNS determination employed when the sulphate content is low. Sulphate does also produce an absorbance decrease, although it is smaller than that brought about by fluoride, and is seemingly nonlinear in nature (Fig. 1B). The decrease is explained by the fact that Zr forms colorless species of general composition ZrF_n^{4-n} with fluoride [32] and $Zr(SO_4)_n^{4-2n}$ with sulphate [33], with sulphate complexes being less stable than fluoride containing ones.

Table 1
Optimization of the chemical and FIA variables for the determination of fluoride in ground waters using the Zr–SPADNS lake

Variable	Studied range	Optimum value
SPADNS concentration (mol l^{-1})	1×10^{-4} to 1.6×10^{-3}	1.22×10^{-3}
Zr concentration (mol l^{-1})	5×10^{-5} to 4.5×10^{-4}	1.5×10^{-4}
HCl concentration (mol l^{-1})	0.1–0.82	0.82
Sample volume (μl)	100–500	400
Reactor length (mm)	100–1000	600
Water flow rate (ml min^{-1})	0.5–2.1	1.5
Zr–SPADNS lake flow rate (ml min^{-1})	0.5–2.1	1.0

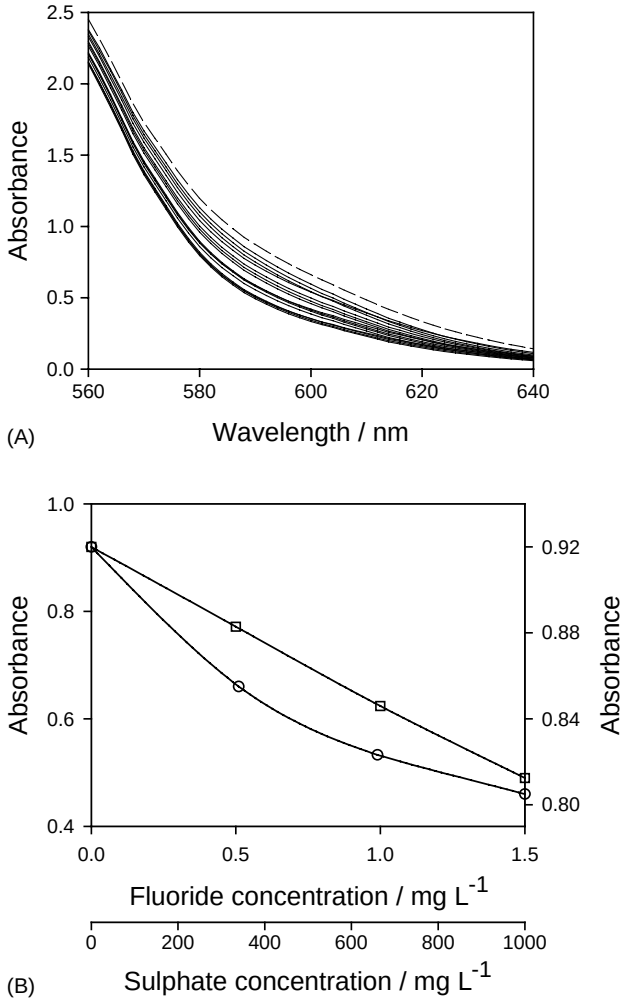

Fig. 1. (A) Absorption spectra obtained after injection into the FIA system of the sixteen sulphate/fluoride binary mixtures employed for calibration of the PLS model. The dashed line corresponds to the sample without fluoride or sulphate added. (B) Effect of fluoride and sulphate on the absorbance at 570 nm: squares, values for the solutions containing only fluoride; circles, values for the solutions containing only sulphate. The solid lines are for the eye guide.

It should be noticed that if only these binary species were formed in the presence of F^- and SO_4^{2-}, no multivariate technique would be able to discriminate the effect of fluoride on the absorbance decrease from that of sulphate. However, Zr ion shows a tendency to form ternary complexes with dyes and either fluoride [34–37] or sulphate [38,39]. The formation of these complexes would lead to the existence of spectral variations across a given spectral range which will differ for each analyte. The successful PLS results discussed below are indeed supportive of the latter possibility.

4.3. PLS calibration and validation

In order to build a multivariate calibration model for fluoride determination, FIA signals were recorded after the injection of each calibration sample. The spectral data were obtained at the maximum of the corresponding FIA peak, which is possible owing to the use of a diode-array spectrophotometer as a detector. Thus, sixteen spectra in the range 560–640 nm were obtained. Using the spectra of the calibration samples, partial least-squares at the PLS-1 level coupled to leave-one-out cross-validation was then performed in order to estimate the number of optimum latent variables. This analysis led to the conclusion that the latter number is two, in accordance with the sources of variability which are expected to be present in the studied system, namely the concentrations of fluoride and sulphate. Two latent factors allow PLS to explain more than 99% of the observed variance in the calibration data.

Table 2 shows the prediction results for the test set, using data registered in the above mentioned spectral range with two latent factors, also after FIA injection, and Fig. 2A shows the plot of predicted versus nominal concentrations. Acceptable results were obtained for samples with SO_4^{2-} concentration ranging from 260 to 1000 mg l^{-1}, which

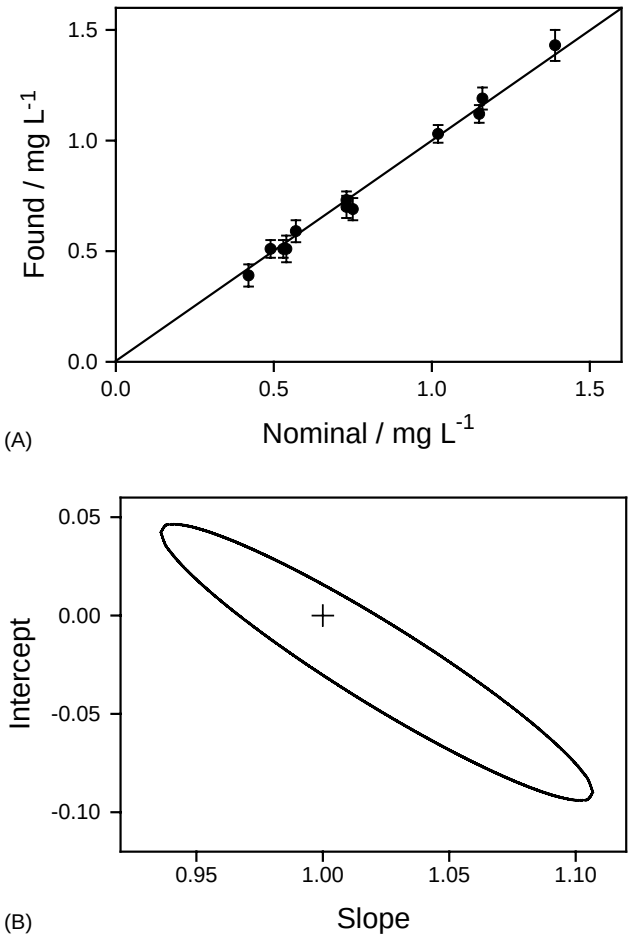

Fig. 2. (A) Plot of the fluoride concentrations predicted by the FIA/PLS method in the test set, as a function of the nominal values. Error bars indicate the standard deviations of the triplicate sample analysis (see Table 2). The solid line is the perfect fit. (B) Elliptical joint region (at 95% confidence level) for the slope and intercept of the weighted least-squares regression of the data shown in plot (A). The plus symbol marks the theoretical (1, 0) point.

Table 2
Prediction results for the fluoride content in the test set, using the FIA/PLS methodology

Nominal sulphate ($mg\,l^{-1}$)	Nominal fluoride ($mg\,l^{-1}$)	Found fluoride ($mg\,l^{-1}$)	s	
			Calculated[a]	Experimental[b]
460	0.42	0.39	0.05	0.05
1000	0.49	0.51	0.05	0.04
300	0.53	0.51	0.05	0.04
580	0.54	0.51	0.05	0.06
200	0.57	0.59	0.05	0.05
840	0.73	0.70	0.05	0.05
500	0.73	0.73	0.05	0.04
440	0.75	0.69	0.04	0.05
860	1.02	1.03	0.04	0.04
500	1.15	1.12	0.04	0.04
720	1.16	1.19	0.05	0.05
260	1.39	1.43	0.05	0.07

Statistical analysis: RMSE ($mg\,l^{-1}$) = 0.03 (RMSE $= \left[1/(I-1)\sum_1^I (c_{act}-c_{pred})^2\right]^{1/2}$ where $I = 12$) and REP (%) = 4.2 (REP% $= 100 \times$ RMSE/$\bar{c}$ where $\bar{c}$ is the mean calibration concentration ($0.75\,mg\,l^{-1}$)).

[a] Calculated s from Eq. (1), using $s_c = 0.01\,mg\,l^{-1}$ and $s_R = 0.002$ absorbance units.

[b] Experimental s from triplicate sample analysis.

would constitute a serious interference for the univariate official method. Table 2 also reports the standard deviations computed for the triplicate sample analysis, and those estimated with the aid of Eq. (1), leading to reasonable agreement between them. This confirms that Eq. (1) provides realistic estimations of prediction errors.

Other figures of merit provided by the model are the absolute and relative root mean square errors for the test set ($0.03\,mg\,l^{-1}$ and 4.2%, see Table 2), and the limit of detection, calculated according to Eq. (2) as $0.1\,mg\,l^{-1}$.

In analyzing the results presented in Table 2 and Fig. 2A for the twelve sample validation set, weighted least-squares linear regression is the preferred technique, the weights being the variances of each experimental determination. The linear fit yields: slope = 1.02(3), intercept = –0.02(2). Although individually considered these latter results indicate that the slope and intercept are not statistically different than 1 and 0, respectively, it is preferable to examine the joint confidence region for the slope and intercept [40]. The latter is shown in Fig. 2B, which includes the theoretically expected value of (1, 0), indicating that the proposed methodology is accurate.

An important point which should be taken into account is the calibration maintenance. A sensible recommendation for end users of methods such as the presently described one is that a set of freshly prepared calibration samples should be run on a monthly basis, in order to check whether the model is preserved.

Finally, full validation by carrying out inter-laboratory comparisons is under way.

4.4. Analysis of real samples and comparison with ISE

A series of real ground water samples was analyzed by means of the proposed method. These natural water samples not only contain fluoride and sulphate, but also other components. As can be seen in Table 3, the average composition indicates that only sulphate constitutes a serious interference for the determination of fluoride using spectrophotometric data. In any case, multivariate calibration techniques such as PLS provide users with several resources which aid in detecting possible unmodeled interferents in unknown samples. One of them is the consideration of the size of the variance of the spectral residuals for a new spectrum:

$$\mathrm{var}(\boldsymbol{r}) = \frac{\sum_{j=1}^{J}(r_j - \hat{r}_j)^2}{J-1} \quad (3)$$

where $\boldsymbol{r}$ is the unknown sample spectrum, J the number of digitized wavelengths, r_j the spectral intensity at wavelength j for the unknown sample, and $\hat{r}_j$ is the value estimated by the regression model. Samples are regarded as outliers if the

Table 3
Average composition of the real samples studied, and tolerated concentrations for the univariate Zr–SPADNS method

Component	Average concentration[a] ($mg\,l^{-1}$)	Tolerance[b] ($mg\,l^{-1}$)
$CaCO_3$ (alkalinity)	600	2000
Al^{3+}	<0.01	0.06
Ca^{2+}	60	1000
Fe^{3+}	0.05	1
Mg^{2+}	40	600
SO_4^{2-}	455	12
PO_4^{3-}	<0.1	1

[a] Data provided by the water supplying company.

[b] According to [22]; the tolerance quoted is the component concentration which produces a bias of $\pm 0.1\,mg\,l^{-1}$ in the predicted fluoride concentration.

Table 4
Comparison of the fluoride content for samples of different ground waters, as determined by the FIA/PLS methodology and by ISE potentiometry

Sample	Sulphate content[a] ($mg\,l^{-1}$)	Fluoride content[b] ($mg\,l^{-1}$)		$t(P)$[c]
		FIA/PLS	ISE	
1	370	0.87(1)	0.90(1)	3.7 (0.02)
2	570	0.80(2)	0.79(1)	0.8 (0.47)
3	350	0.79(1)	0.79(1)	0.0 (0.50)
4	500	0.82(1)	0.85(1)	3.7 (0.02)
5	550	0.76(1)	0.77(1)	1.2 (0.30)
6	450	0.62(1)	0.62(1)	0.0 (0.50)
7	400	0.70(1)	0.69(1)	1.2 (0.30)

[a] Determined by the turbidimetric method described in [28].
[b] Standard deviation in parenthesis, as calculated for triplicate measurements in both cases.
[c] Calculated according to [41] (4d.f.): t, experimental Student coefficient and P, associated probability.

following ratio exceeds a critical value:

$$F = \frac{I\sum_{j=1}^{J}(r_j - \hat{r}_j)^2}{\sum_{i=1}^{I}\sum_{j=1}^{J}(r_{j,\mathrm{cal}} - \hat{r}_{j,\mathrm{cal}})^2} \quad (4)$$

where $r_{j,\mathrm{cal}}$ is the spectral intensity for sample i at wavelength j, and $\hat{r}_{j,\mathrm{cal}}$ is the corresponding value as estimated by the regression model with A factors. The critical F parameter is estimated with $[(J-A)/2]$ and $[(J-A)((I-A-1)/2]$ degrees of freedom (d.f.) at a certain confidence level [26]. If the sample is indeed an outlier, a judicious analysis of the distribution of spectral residuals may provide an indication of the kind of interference present, allowing to select appropriate spectral windows where the interference is minimal. However, in all samples studied with the presently developed approach the ratio given by Eq. (4) was smaller than the critical value, pointing to the absence of serious interferences, other than the sulphate modeled by the calibration set.

The specific results pertaining to the real samples studied are collected in Table 4, where they are compared with triplicate analyses made by potentiometric measurements with an ion selective electrode, which is known to provide accurate results even in the presence of sulphate. Statistical analysis indicates no significant differences between the obtained means (the probability P values quoted in Table 4, associated to the relevant Student coefficients, are all larger than 0.01 with 4d.f., i.e., all t values are smaller than the critical one at 99% confidence level).

5. Conclusions

Flow injection analysis combined with multivariate calibration of absorption spectra appears to be an excellent analytical resource for the determination of fluoride in water samples with significant sulphate content, for which regular univariate spectrophotometric methodologies cannot be applied. The proposed method is fast, amenable to automation and of low-cost. The importance of the use of a diode-array spectrophotometer as a detector lies in the recording of the spectral data from the FIA peak, allowing the multivariate calibration model to be rapidly built, by only recording the corresponding FIA peak of each calibration solution. This leads to simplicity and fast analysis, which are very important characteristics for routine work. The comparison between the obtained results by using the proposed method and those obtained with an ion selective electrode showed a good agreement.

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