Determination of Trace Aluminum in Natural Waters by Ion Exchanger Fluorometry

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Morin (2',3,4',5,7-pentahydroxyflavone) has been used as a ligand in the fluorometric microdetermination of aluminum at the sub-µg l^{-1} level. A method has been developed which is based on ion exchanger fluorometry (IEF). The 1:1 aluminum-morin complex is fixed on a dextran-type cationic exchanger, and the fluorescence of the gel, packed on a 1-mm quartz cell, is measured directly using a solid-surface attachment. The concentration for the method ranges between 0.4 and 1.6 µg l^{-1}, although this can be diminished by increasing the sample volume. The method has been successfully applied to the determination of aluminum in natural water and offers several advantages in comparison with solution methods.

Keywords　Ion-exchanger fluorometry, aluminum determination, natural waters

Aluminum determination by fluorescence measurements have been widely studied, and numerous methods have been proposed.[1] One of the best known involves morin as a reagent.[2,3] This method yields a sensitive and relatively selective procedure, though there are several disadvantages regarding practical applications. The most important items are: a high blank value, the interference of several common species and a dependence of the analytical signal on the temperature.[4]

Some of the above-mentioned problems may be partially solved by using the so-called ion exchanger fluorometry (IEF) technique.[5-8] Other related techniques are methods involving conventional fluorescence on a solid surface, widely used in the assay of organic substances directly on solid surfaces[9] and the ion-exchager photometry devised by Yoshimura in 1976.[10] The IEF methodology involves measuring of the diffuse, transmitted fluorescence of a solid, usually an ion-exchanger resin, trapping the preconcentrated analyte, and producing a fluorescent by the use of an appropriate reagent.

The fixation of the morin-aluminum complex on a cationic ion exchanger is discussed here. It allows for the application of IEF as a basis for an improvement of the method in solution. By using this technique, higher sensitivity, a lower detection limit and a smaller interference level than in solution are obtained.

Experimental

Reagents

Ion exchanger: Sephadex SP C-25 cation-exchange gel in the sodium form, with no previous treatment to avoid possible contamination.

Morin (2',3,4',5,7-pentahydroxyflavone) stock solutions, 0.02% w/v in absolute ethanol: The working solutions were prepared by diluting with the same solvent. The morin was purified following a procedure described by Laitinen and Kivalo.[11] Morin working solutions were freshly prepared every day and the stock solutions weekly.

An aluminum(III) stock solution at 0.1 g dm^{-3} in Al(III) was prepared by dissolving $Al(NO_3)_3 \cdot 9H_2O$ in 6.5×10^{-2} mol dm^{-3} HNO_3 and complexometrically standardized with EDTA using Xylenol Orange as an indicator. Aluminum working solutions were made *in situ* from this same solution by dilution with doubly-distilled water.

Buffer solutions of required pH were prepared from 0.1 mol dm^{-3} CH_3COOH and 0.1 mol dm^{-3} CH_3COONa.

Unless otherwise stated, all reagents were of analytical grade.

Apparatus

All fluorometric measurements were performed using an LS-5 Perkin Elmer spectrofluorometer, equipped with a xenon discharge lamp (9.9 W) pulsed at the line frequency, F/3 Monk-Gillieron monochromators, a quantic Rodamine 101 counter to correct the excitation spectra, a Hamamatsu R928 photomultiplier, a (model Omnigraphic) X-Y Houston recorder, a variable-angle solid-surface accessory (designed and constructed by us), and a Braun Melsungen Thermomix 1441 thermostat. In order to compare all of the fluorometric measurements and to ensure reproducible experimental

conditions, the LS-5 luminescence spectrometer was checked daily. A polymer fluorescence standard of p-terphenyl (10^{-7} mol dm^{-3}) gives a relative fluorescence intensity of 90% at λ_{em}=340 nm, λ_{ex}=295 nm, slit widths 2.5/2.5 nm and a sensitivity factor of 0.594. Furthermore, we used a Crison 501 digital pH-meter equipped with a calomel and glass electrodes and an Agitaser-2000 rotating bottle agitator.

Fluorescence measurements

The measured relative fluorescence intensity (RFI) of the gel beads, containing the fluorescence complex and packed into a 1-mm quartz cell, was the diffuse transmitted fluorescence emitted from the gel. The optimal angle formed between the cell plane and the excitation beam was 45° in all cases.[7]

Procedures

General procedure. A 500 ml water sample containing 0.4–1.6 µg dm^{-3} of Al(III) was transferred to a 1-dm^3 polyethylene bottle and 2 cm^3 of 6.2×10^{-3}% ethanolic morin solution, 10 cm^3 of 0.1 mol dm^{-3} acetate buffer solution (pH 5.30) and 60 mg of Sephadex SP C-25 ion exchanger were added. The mixture was shaken mechanically for 15 min. The gel beads were then collected by filtration under suction and, with the aid of a pipette, were packed into a 1-mm cell together with a small volume of the filtrate. A blank solution containing all reagents, except aluminum, was prepared and treated in the same way as the sample. The fluorescence intensity (20.0±0.5°C) for both the sample and the blank was measured at a λ_{em}=496 nm, for a λ_{ex}=426 nm. A calibration curve was constructed in the same way, using an Al(III) solution of known concentration.

Procedure for natural waters. The above-mentioned reagents were added to a volume of natural water sample containing an adequate amount of Al(III), levelled off at 500-cm^3 with doubly-distilled water and placed into a 1-dm^3 polyethylene bottle, in the same manner as described in the general procedure. Both calibration curve and standard addition methods were used for calibration purposes.

Reference method. A determination of aluminum by AAS with a dinitrogen oxide–acetylene flame after extraction with 8-quinolinol (oxine)–4-methyl-2-pentanone (MIBK) was used as a reference method.[12]

Treatment of the sample. Natural water was filtered through 0.45-µm membrane filter paper (Millipore), treated with conc. HNO$_3$ (0.25 cm^3/1000 cm^3) and collected in a polyethylene container, which had previously been washed with nitric acid.[12]

Results and Discussion

Excitation and emission spectra in both gel and solution

The fixation of morin in a supporting gel principally occurs either by ion exchange or by adsorption. The

spectral features of fixed morin depend on the mechanism followed. In the ion exchanger dextrane gels used, the adsorption of morin was negligible (less of 2% under experimental conditions).

Morin in solution reacts with Al(III) while developing a well-known green fluorescent complex in a moderately acid medium.[13] In the presence of a Sephadex cation exchanger, the complex, which is probably cationic, is fixed on the gel. The complex is not, however, fixed on an anionic gel. We chose an SP C-25 dextran-type gel based on the fact that there is originally less background fluorescence and a higher affinity to the complex, as compared to other similar ion exchangers.

The peak wavelengths in the emission spectra of the morin-Al(III) system are different for solution (512 nm) and gel (496 nm) (Fig. 1). The maxima of the excitation spectra of the two systems are located at 431 nm in solution, and at 426 nm in the gel phase. The changes effected in the environment surrounding the complex in the gel with respect to solution most probably determine the fluorescence spectra features. The most noticeable outstanding difference between the fluorescence spectra is the narrower peak width which characterizes the solution spectrum. A similar effect is observed in the Be(II)-morin system fixed on Sephadex QAE.[8]

From a study of the half-life time (τ) of the excited state of the complex in the gel phase at different temperatures, we infer that the luminescence process is most probably fluorescence ($\tau < 5 \times 10^{-6}$ s).
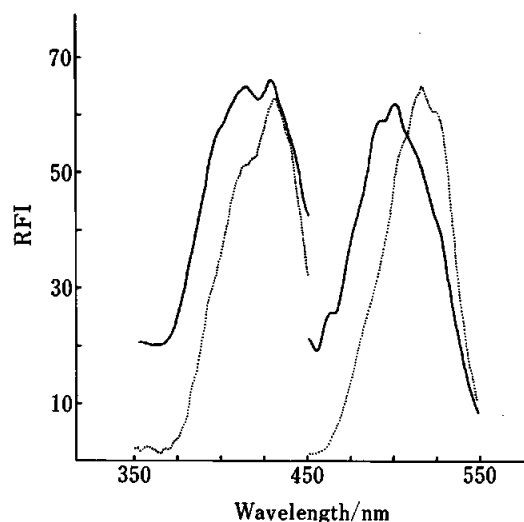

Fig. 1 Fluorescence spectra of Morin-Al(III) complex. (——) gel phase: [Morin], 7.3×10^{-7} mol dm^{-3}; [Al(III)], 5.9×10^{-8} mol dm^{-3}; pH, 5.30 (acetate buffer solution); 60 mg SP Sephadex C-25; 500 cm^3 sample; stirring time, 15 min; λ_{ex}, 426 nm, λ_{em}, 496 nm; f_s, 0.25; slit$_{ex}$=slit$_{em}$, 2.5 nm; T, 20.0±0.5°C. (···) solution: [Morin], 1.4×10^{-5} mol dm^{-3}; [Al(III)], 3.0×10^{-7} mol dm^{-3}; pH, 5.30 (acetate buffer solution); λ_{ex}, 431 nm, λ_{em}, 512 nm; f_s, 6.0; slit$_{ex}$=slit$_{em}$, 2.5 nm; T, 20.0±0.5°C; % ethanol, 0.4.
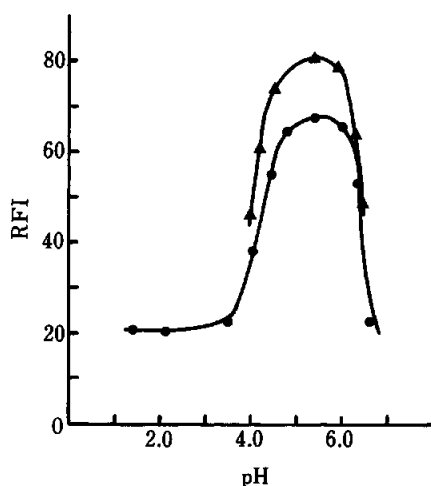
Fig. 2 Influence of pH. (●), HCl and NaOH; (▲), acetate buffer solution; [Morin], 2.4×10^{-6} mol dm^{-3}; [Al(III)], 7.4×10^{-8} mol dm^{-3}; pH, 5.30 (acetate buffer solution); 100 mg SP Sephadex C-25; 500 cm^3 sample; stirring time, 15 min; λ_{ex}, 426 nm, λ_{em}, 496 nm; f_s, 0.25; slit$_{ex}$=slit$_{em}$, 2.5 nm; T, 20.0±0.5° C.

Fig. 3 Effect of morin concentration on RFl. [Morin] from 0.2×10^{-6} mol dm^{-3} to 4.7×10^{-6} mol dm^{-3}; [Al(III)], 7.4×10^{-8} mol dm^{-3}; pH, 5.30 (acetate buffer solution); 60 mg SP Sephadex C-25; 500 cm^3 sample; stirring time, 15 min; λ_{ex}, 426 nm, λ_{em}, 496 nm; f_s, 0.5; slit$_{ex}$=slit$_{em}$, 2.5 nm; T, 20.0±0.5° C.

Optimization of variables

pH dependence. The optimum pH for the formation and fixation of the species is found within the 4.7-6.0 range. For pH values less than 3.5 or more than 6.6, the complex is not formed and/or fixed on the ion exchanger (Fig. 2).

Different buffer solutions (acetate, hydrogen phthalate, monochloroacetate and hydrochloric acid) were tested. Acetic acid/acetate (pH=5.30) was found to give the best results. It should be pointed out that optimum pH in the gel phase is higher than in solution (pH=3-4).[10,14,15]

Relative fluorescence intensity (RFI) (regulated with NaClO$_4$) does not depend on the ionic strength, up to concentrations of 4×10^{-3} mol dm^{-3}. For higher values, fluorescence decreases according to the equation RFI= $2.71 \times \mu^{-1/3}$ (μ, ionic strength). This effect may be attributed to the competition of other ions in the ion exchange equilibrium.

Morin concentration. RFI increases with the morin concentration up to 1.8×10^{-6} mol dm^{-3}, *i.e.*, 6.10×10^{-5}%, remaining constant at higher concentrations (Fig. 3). This behavior (absence of quenching) is attributed to the anionic nature of morin at the working pH and, consequently, to a morin exclusion from the gel by the Donnan effect. These results differ from those obtained by systems in which the ligand is fixed in the ion exchanger, which leads to a ligand concentration in the ion exchanger and, hence, to a concentration-induced quenching effect. This effect has been observed for the Be(II)-morin system fixed in an anionic Sephadex QAE gel.[8] The working morin concentration in the standard procedure was 2.5×10^{-5}% (7.3×10^{-7} mol dm^{-3}). This value is lower than that proposed by Will (3.0×10^{-3} mol
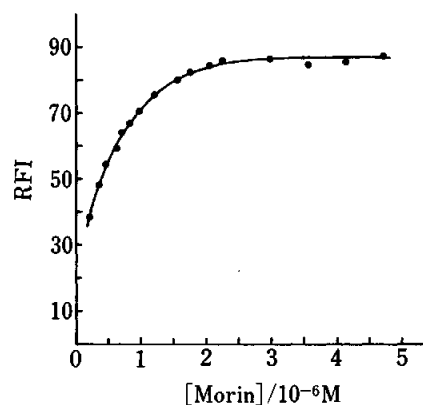
dm^{-3}).[16]

As an increase in the ethanol percentage increase the fluorescence intensity, 0.4% has been chosen as the optimum value.

Temperature dependence. The temperature dependence was studied in two phases: during the ion exchange process and, later, during fluorescence emission. The dependence of the ion exchange process on temperature, measuring RFI at 20°C (Fig. 4), behaves much in the same way as the Be(II)-morin system fixed onto a Sephadex QAE ion exchanger.[8] Moreover, RFI decreases when the temperature of the system increases. The fixation of the species, in this case, was carried out at 20.0±0.5°C.

The decrease of RFI with temperature measurement was totally irreversible, an opposite effect to that observed in the morin alone and the Be(II)-morin system mentioned above. This may be attributed to the nature of the species fixed in the ion exchanger. Only the cationic morin-Al(III) complex is present in Sephadex SP, and probably bound through the Al(III) ion, while an excess of ligand together with the anionic morin-Be(II) complex is fixed in Sephadex QAE, which prevents the decrease of the fluorescence through decomposition of the reagent. A previous fixation of the morin seems to stabilize the complex. This agrees with the variation of RFI with temperature for morin alone on QAE gel (Fig. 4).

The two temperature influences on the ion exchange and the fluorescence process studied are considered to cause the same phenomena (hydrolysis of the morin heterocyclic ring and condensation or oxidation of the open-ring structure formed[17]). This instability of the morin-Al(III) complex has been tested many times in solution, although the data is often contradictory.[13,15,16,18] *Other experimental conditions.* The optimum stirring time depended on the sample volume. Stirring times of
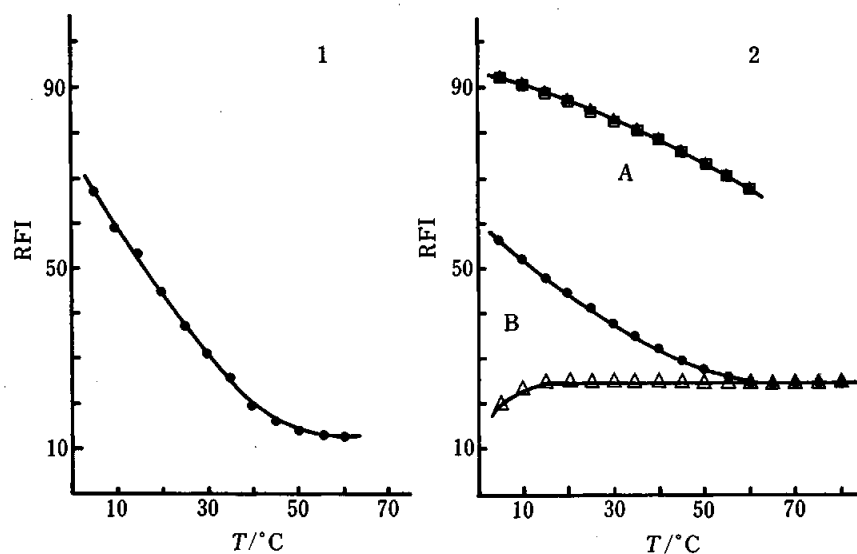
Fig. 4   Influence of the temperature. 1: On ion exchange process (RFI measured at 20°C). [Morin], 4.4×10^{-7} mol dm^{-3}; [Al(III)], 1.5×10^{-8} mol dm^{-3}; pH, 5.30 (acetate buffer solution); 60 mg SP Sephadex C-25; 500 cm^3 sample; stirring time, 15 min; λ_{ex}, 426 nm, λ_{em}, 496 nm; f_s, 0.1; slit$_{ex}$=slit$_{em}$, 2.5 nm.   2: On RFI measurement.   A. Morin: (□) heating; (▲) cooling; [Morin], 2.9×10^{-7} mol dm^{-3}; pH, 11.50 (HPO$_4^{2-}$/PO$_4^{3-}$ buffer solution); 80 mg QAE Sephadex A-25; 500 cm^3 sample; stirring time, 10 min; λ_{ex}, 445 nm, λ_{em}, 562 nm; f_s, 0.1; slit$_{ex}$=slit$_{em}$, 2.5 nm.   B. Morin-Al system: (●) heating; (△) cooling; [Morin], 5.9×10^{-7} mol dm^{-3}; [Al(III)], 2.2×10^{-8} mol dm^{-3}; pH, 5.30 (acetate buffer solution); 60 mg SP Sephadex C-25; 500 cm^3 sample; stirring time, 15 min; λ_{ex}, 426 nm, λ_{em}, 496 nm; f_s, 0.2; slit$_{ex}$=slit$_{em}$, 2.5 nm.

10, 15 and 40 min were necessary for 250, 500 and 1000 cm^3, respectively.   At stirring times exceeding 10 min over the optimum time, luminescence decreased in all cases due to complex decomposition. The order in which reagents were added was found to be irrelevant.   The order followed in these experiments, however, was aluminum-morin-buffer-ion exchanger. For all measurements, 60 mg of resin was used as the optimum amount to fill the cell and facilitate handling. RFI measurements remained stable for at least 1 h at temperature below 20.0°C, and later diminished (14% at 120 min).   At higher temperatures, the stability plateau was smaller.   A temperature of 20.0±0.5°C with a measuring time under 1 h was therefore chosen for the experiments.

Effect of the volume on sensitivity.   One of the main advantages in IEF is the potential increase in sensitivity with an increase of the sample volume taken for analysis. This magnifying effect can be calculated by measuring the RFI of Sephadex equilibrated with different volumes of solutions containing the same concentration of Al(III) and a proportional amount of the other reagents (Fig. 5).   The behavior of the experimental data, *i.e.,* RFI becomes independent at higher sample volumes, similarly to those shown by the beryllium-morin system fixed on Sephadex QAE[8], suggest an exponential dependence.
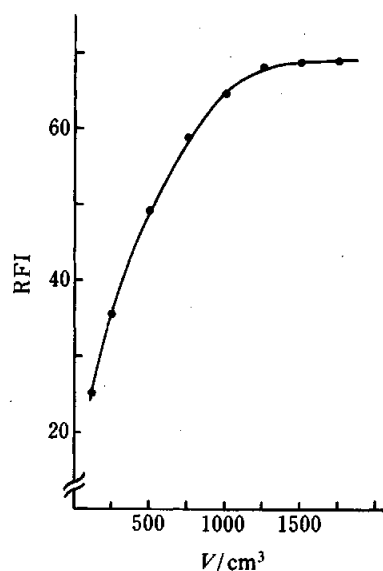

Fig. 5   Influence of the sample volume on RFI.   [Morin], 5.9×10^{-7} mol dm^{-3}; [Al(III)], 2.2×10^{-8} mol dm^{-3}; pH, 5.30 (acetate buffer solution); 60 mg SP Sephadex C-25; volume sample, from 100 to 1750 cm^3; stirring time, 15 min; λ_{ex}, 426 nm, λ_{em}, 496 nm; f_s, 0.12; slit$_{ex}$=slit$_{em}$, 2.5 nm; T, 20.0±0.5°C.

Stoichiometry of the complex fixed on the ion exchanger gel

Two possible stoichiometries have been proposed in water–alcohol mixtures: $1:1$[18] and the $1:3$[13], although the latter is disputable, given the steric hindrance.[18] The stoichiometry of the fixed morin-Al(III) complex on Sephadex was established using the equilibrium shift as well as the Bent and French methods. Results indicate that a $1:1$ cationic complex is fixed on the resin.

These results agree with those found in the study of the $1:1:4$ aluminum mixed-ligand cationic complex, morin-antipyrine, extracted as an ion-pair with perchlorate in $CHCl_3$ and MIBK.[19] Moreover, Saarl and Seltz suggest the formation of a $1:1$ aluminum complex with the morin immobilized on powdered cellulose.[14]

The slope of $\log D$ plot vs. pH ($D=RFI/RFI_{max}-RFI$) plot, obtained by using the ascendent branch of the RFI–pH graph, was 1.00. This suggests the loss of a morin proton (probably the 3-OH proton) through complexation and agrees with the morin pK_a values [$pK_1=-1$; $pK_2=4.8$; $pK_3=7$; $pK_4=9$; $pK_5=13$].[17]

The aluminum ion is bonded to morin through carbonylic oxygen and the previously de-protonated 3-OH, creating the $1:1$ cationic complex.[2,20] While considering that at the working pH the morin is mono-dissociated ($pK_2=4.8$) and the Donnan exclusion prevents the uptake of morin by the Sephadex SP gel, we suggest that the mechanism of fixation requires the previous reaction of Al(III) with morin in a solution involving the displacement of a hydrogen ion, and back-fixation of the cationic complex on the gel.

This mechanism is different from that proposed for the fixation of the Be(II)-morin complex, where the ligand is immobilized in the supporting gel and Be(II), consequently, becomes preconcentrated.[8]

Calibration and precision

The calibration graphs for the samples treated with

the procedure described above are linear for the concentration range 0.4 to $1.6 \, \mu g \, dm^{-3}$ for 250 and $500 \, cm^3$ and 0.2 to 1.2 for $1000 \, cm^3$ samples. The analytical parameters are summarized in Table 1.

Reproducibility was established for the proposed method by measuring the aluminum concentration of $0.4 \, \mu g \, dm^{-3}$ and 10 independent determinations. The relative standard deviation (RSD, %) found was 2.9, 2.0 and 2.7% for 250, 500 and $1000\text{-}cm^3$ sample methods, respectively. Moreover, the precision (RSD, %) of the packing operation, calculated on the basis of 10 measurements, was 1.7% for ion exchanger gel with the complex fixed, 1.7% for gel blank (ion exchanger with morin and buffer) and 1.0% for gel only. It therefore appears that one of the main contributions to the reproducibility comes from the packing of the ion exchanger. The precision of the fluorescence measurement (noise) was approximately 0.5%.

Sensitivity and detection limits

The increase in sensitivity with an increase in sample volume in the analytical procedures proposed here may be calculated in practice from the slope of the calibration graphs. The calculated sensitivity ratio for the samples analyzed are $S_{1000/250}=3.20$ and $S_{500/250}=2.38$.

The increase in sensitivity is perticularly noticeable in relation to the morin method in solution. In order to compare this increase, the calibration graph for the determination of Al(III) with morin is solution was established, i.e. the Will method.[16] Under our experimental conditions, the equation for the calibration graph was $RFI=0.01+0.14C$ ($r=0.995$), where the slope ratio was 256.

Table 1   Analytical parameters for IEF aluminum determination

| | Volume of sample system | | |
	$250 \, cm^3$	$500 \, cm^3$	$1000 \, cm^3$
Intercept	-1.24	-0.08	1.94
Slope	15.10	35.90	48.35
Linear dynamic range/ $\mu g \, dm^{-3}$	$0.4-1.6$	$0.4-1.6$	$0.2-1.2$
Correlation coefficient	0.991	0.999	0.997
Detection limit/ $\mu g \, dm^{-3}$	0.05	0.04	0.03
Determination limit/ $\mu g \, dm^{-3}$	0.18	0.12	0.07
RSD, %	2.9	2.0	2.7
Analytical sensitivity/ $\mu g \, dm^{-3}$	0.035	0.012	0.013

Table 2   Methods for the fluorometric determination of Al(III)

Reagent	Detection limit[a]/$\mu g \, l^{-1}$	Reference
2,2'-Dihydroxyazobenzene	0.5	22
8-Hydroxyquinoline-5-sulfonic acid[b]	0.4	23
o-(Salicylideneamino)-2-hydroxybenzenesulfonic acid	0.4	24
Salicylidene-o-aminophenol	0.27	25
Morin	0.27	16
6-(4-Methylsalicylideneamino)-m-cresol	0.2	26
N-Salicylidene-2-hydroxy-4-carboxyaniline	0.2	27
Morin[c]	0.1	28
2,4-Dihydroxybenzaldehyde semicarbazone	0.08	29
N-Salicylidene-2-hydroxy-5-sufoaniline	0.08	27
Morin-IEF	0.02	this paper

a. Or minimum concentration used for calibration.
b. Kinetics.
c. Extraction procedure.

Table 3   Aluminum content in natural waters

Water	Aluminum content/$\mu g \, l^{-1}$				
	AAS[a]	Direct calibration[a]	RSD, %	Standard-addition[a]	RSD, %
Tap water (city of Granada)	157	158 (0.6%)	2.9	151 (3.8%)	5.4
Raw water (Quentar dam)	18.4	—	—	19.7 (7.1%)	6.7
Mineral water (Ortigosa del Monte)	14.5	14.2 (2.1%)	2.9	16.4 (13.1%)	5.2
Mineral water (Lanjaron)	5.0	4.5 (10.0%)	3.1	—	—

a. Data is based on the average obtained from three determinations.

The fluctuation in the background fluorescence measured for the blank, from and average of 10 determinations and noted as SD units is 0.27, 0.44 and 0.37 for 250, 500 and 1000-cm³ sample system, respectively. The IUPAC detection limit ($K=3$), the quantification limit ($K=10$), and the estimated analytical sensitivity[21] are shown in Table 1.

This method is compared (Table 2) with the chelate-formation methods described in the literature for a fluorometric determination of aluminum. For comparison purposes, we have chosen those methods which, in our opinion, may be considered among the most sensitive devised to date.

Effect of foreign ions.   A systematic study of the effect of foreign ions on the determination of Al(III), at the $0.4 \, \mu g \, dm^{-3}$ level, was conducted. A $4000 \, \mu g \, dm^{-3}$ of potentially interfering ions were first tested and, if interference occurred, the ratio was progressively reduced until interference ceased. Higher ratios were not tested. Tolerance is defined as the amount of foreign ions that produce an error equal to $\pm 5\%$ in the determination of the analyte. The results found were: CO_3^{2-} and NO_3^{-} up to at least a 10000-fold ratio; Cl^{-} up to a 2000-fold ratio; Mg(II) up to a 1250-fold ratio; Ca(II) up to a 1000-fold ratio; SO_4^{2-} up to a 500-fold ratio; PO_4^{3-} up to a 125-fold ratio, Cu(II) up to a 25-fold ratio and F^{-} and Fe(III) up to a 2.5-fold ratio. The interference was positive for Ca(II) and Mg(II) and negative for other species.

It is important to note that the interference level can be reduced by sample dilution. Taking the concentration range for the proposed methods and the average level of aluminum in water into account a minimum of a 100 to 200-fold dilution is required.

Determination of aluminum in tap and natural waters

The method was applied to a determination of aluminum in water samples. Tap water and raw water from Granada City Supplies (Spain) were selected as representative samples together with mineral water from the Lanjaron (Granada) and Ortigosa del Monte (Segovia) springs. The sample volume depended on the aluminum content: 3 cm³ tap water, 10 cm³ raw water

Table 4   Study of aluminum recovery in water samples

Water	Amount added/ $\mu g \, dm^{-3}$	Amount found[a]/ $\mu g \, dm^{-3}$	% Recovery
Mineral water	—	0.57	—
(Ortigosa	0.20	0.80	113.4
del Monte)	0.40	0.98	101.7
	0.60	1.20	105.0
Tap water	—	0.95	—
(city of	0.10	0.95	56.7
Granada)	0.30	1.20	104.4
	0.50	1.38	98.7

a. Data is based on the average obtained from three determinations.

and 20 cm³ for mineral water. Hence, an adequate volume of natural water, whose concentration after dilution to 500 cm³ with doubly-distilled water, falls within the calibration range. The analysis was conducted using a calibration curve and the standard addition method.

The loss of sensitivity by a matrix effect can be evaluated by the slope's ratio between the standard calibration graph and the standard-additions calibration graph. The ratio found was to be 0.9 for tap water, 0.6 for raw water, 2.0 for Lanjaron water and 1.1 for Ortigosa del Monte water.

The average aluminum content (based on three determinations) in the samples studied is shown in Table 3. AAS prior extraction by oxine was used as a reference method.

Moreover, the results obtained through the application of the IEF method were comparable to those obtained by atomic absorption spectrometry (AAS). The relative errors with respect to the AAS method (in brackets in Table 3) was less than 7%, except for mineral water from Ortigosa del Monte, for which the difference was 13.1%.

The precision (expressed as RSD) for the IEF method varies between 2.9 and 6.7%. The average precision for the four water samples analyzed was 4.4%. The AAS method is generally more precise, and in our spe-

cific study RSD average was shown to be 7%.

Taking into account these results, we concluded that there is no important interference in the water analyzed by the proposed IEF method; in fact, the dilution of the sample necessary for the Al content to be within the linear range of the method avoids any possible interference.

To check the accuracy of the proposed method, we conducted a recovery study using two different water samples. To do so, a different amount of Al(III) was added to 500 cm³ of diluted water, obtaining a recovery percentage acceptable for the established standard conditions (Table 4).

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