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Reverse flow-injection manifold for spectrofluorimetric determination of aluminum in drinking water

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Abstract

A simple reverse flow-injection (rFIA) manifold for the direct determination of aluminum in drinking water is proposed. This rapid and sensitive method is based on the formation of an Al^{3+} complex with salicylaldehyde picolinoylhydrazone (SAPH), which shows a maximum blue-green fluorescence ($\lambda_{ex} = 384$ nm, $\lambda_{em} = 468$ nm) at pH 5.4. Operative conditions both for batch and rFIA procedures were investigated including reagent concentration, buffer solutions, injection loop, reacting coil and wavelengths used for the fluorimetric detection. The tolerance limits of foreign ions have been also evaluated, before and after the addition of masking agents. The reverse flow-injection procedure allows determination of Al^{3+} at ppb level (LOD: 1.9 μg l^{-1}) within a working range of 5–30 μg l^{-1}. The proposed method was successfully employed for the determination of Al^{3+} in several commercial drinking, soft drinking (as certified reference material), and tap water samples.

Keywords: Aluminum; Fluorimetry; water; Reverse flow-injection analysis

1. Introduction

Although aluminum is present at low levels (μg l^{-1}) in natural waters, significant amounts are added to certain water supplies as a flocculating agent during potabilization process, increasing in many cases its final concentration. Elevated aluminum concentrations correlate well with anthropogenic acidification of natural waters [1]. High concentrations of aluminium imply latent toxicity and negative influence on the central nervous system [2]. Increased attention is paid to the determination of aluminum at present because of the harmful effects caused to human beings when ingested in excess. Analytical techniques for bulk aluminum determinations at trace-levels are: neutron activation, inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), direct current plasma-atomic emission spectrometry (DCP-AES), graphite furnace atomizers and atomic absorption spectrometry (GFAAS) or fluorimetry [2]. Fluorimetric methods are generally

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very sensitive; several methods have been described for the fluorimetric determination of aluminum based on the formation of metal complexes [3–11].

Currently, ‘in situ’ or real time determinations of metal elements dissolved in water are often required. For this purpose, aluminum determinations by flow techniques have employed ICP-AES [12–14], FAAS [15], GFAAS [16,17], amperometry [18,19], ion-selective electrode (ISE) potentiometry [20], colorimetry [21–24] and fluorimetry [25–32] for detection.

In this work, a simple reverse flow-injection analysis (rFIA) procedure for the direct determination of Al^{3+} in drinking water was developed. It is based on a reagent–buffer injection into the flowing sample solution, where Al(III) forms a complex with SAPH in the reacting coil. Al–SAPH complex has been previously applied to the batch determination of aluminum in different environmental samples, such as soil [5] or seawater [8]. This chelate shows a blue–green fluorescence (λ_{ex} 384 nm, λ_{em} 468 nm), which is used as an analytical signal [5]. Operative conditions both for batch and rFIA procedures were investigated, including reagent concentration, buffer solutions, injection loop, reacting coil and wavelengths used for the fluorimetric detection.

2. Experimental

2.1. Reagents and solutions

The salicylaldehyde picolinoylhydrazone (SAPH) was prepared by condensation of equimolar amounts of the salicylaldehyde (SA) and picolinoylhydrazide (PH) as other related aroylhydrazones [33]. The reagent PH was prepared according to Grammaticakis [34], through an addition reaction between picolinic acid ethyl ester and hydrazine compounds. Ethanol absolute (Merck GR) was used as a solvent, and all the solutions were prepared used high purity deionized water (Milli Q, Millipore, USA). A commercial stock solution of 1000 μg l^{-1} of Al^{3+} was purchased from Merck (Darmastadt, Germany). Further dilutions were made daily as required. The acetate buffer solutions were prepared by using acetic acid and sodium acetate of Suprapur quality reagent, Merck (Daarmstadt, Germany). All other reagents used in this work were also of analytical grade Merck (Daarmstadt, Germany). As aluminum is very rapidly released from glassware all reagent and sample bottles and reactions flasks were of polyethylene or PVC material.

2.2. rFIA: apparatus and procedure

A rFIA manifold has been developed for direct analysis of aluminum (Fig. 1). We used a four-channel peristaltic pump Perimax (Spetec, Germany), equipped with Tygon tubing and a six-port low presure injection valve (Rheodyne, USA) was used to control the flows of reagent and sample solutions. The transport lines and reaction coil were made using 0.8 mm i.d. teflon tubing. Connections were made of polypropylene (Omnifit, UK). A Perkin–Elmer LS-5B (Perkin–Elmer, USA) spectrofluorimeter was used with a flow quartz cell, with 1-cm optical pathlength and 20 μl inner volume (Hellma, Germany). Slit widths were 5 and 10 nm, respectively, for excitation and emission. The rFIA procedure is based on a reagent–buffer (mixture) injection into the flowing sample solution, where aluminum ions form a complex with reagent in the reacting coil; the chelate shows a fluorescence, which is used as an analytical signal.

2.3. Atomic absorption: apparatus and procedure

Atomic absorption spectrometry measurements were carried out on a Philips PU 9200X spectrometer equipped with an Philips PU 9390 X

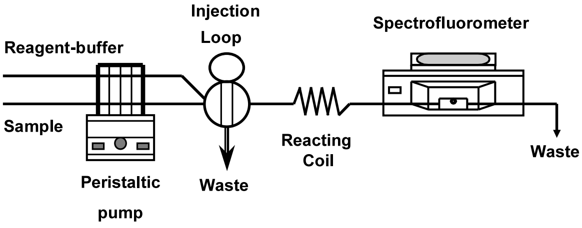

Fig. 1. Manifold for reverse flow injection analysis of aluminum.

graphite furnace. A UNICAM (aluminum) hollow-cathode lamp was operated at 12 mA. Argon flow was 200 ml min^{-1} except during sample atomization. Pyrolytical coated graphite tubes were used.

Furnace settings were: drying at 120 °C; ramp for 5 s, hold for 5 s, ashing at 1400 °C, ramp for 40 s, hold for 20 s; atomizing at 2700 °C, with no ramp and 3 s hold; and cleaning at 2800 °C with no ramp and 3 s hold.

2.4. Analytical procedure

Firstly, a batch procedure was developed. In this way, a systematic variation of the parameters controlling the formation of the fluorescence complex Al–SAPH was carried out. Thus, the effect produced by the acidity, concentration of reagent, percentage of ethanol and concentration of acetate in buffer solutions were investigated. Secondly, the developed analytical procedure was applied to the reverse flow injection analysis of aluminum in drinking water. The influence of several variables on the fluorescence of the Al–SAPH complex (reagent–buffer concentrations, injected volumes, reaction coil length and flow-rate) was studied in order to optimize the method. The obtained data were used to construct calibration plots that were used to quantify the Al^{3+} in commercial drinking water and soft drinking water.

3. Results and discussion

3.1. Batch procedure: optimization of the Al(III)–SAPH system and the spectrofluorimetric determination

The Al–SAPH complex was characterized in a previous study [5]. In ethanol medium, buffered with acetate ions (pH 5.4), the formation of the complex appears to be controlled by the reaction:

$$Al^{3+} + 3SAPH^{+} = Al(SAPH)_3^{3+} + 3H^{+}$$

The fluorescence of the complex ($\lambda_{ex} = 384$ nm and $\lambda_{em} = 468$ nm), in acetate medium and aqueous-ethanol solution (24%, v/v), increased when the SAPH was added to Al^{3+}, but when the SAPH molar ratios were between 40 and 250, no fluorescence change was observed and remained stable for at least 12 h, after a reaction time of 20–25 min. The maximum constant relative fluorescence was obtained within a 10–30 °C temperature range. A value of 2.10×10^{-4} mol l^{-1} SAPH was chosen for the batch procedure.

The effect of ethanol and acetate ions, was also studied; the fluorescence does not vary significantly with EtOH when the percentage is between 20 and 50, and up to 3 M buffer (HAc/Ac^{-}, pH 5.4). Optimum values of 24% (v/v) ethanol and 0.5 M buffer were chosen.

3.1.1. Interferences

The potential interferences caused by several ions present in drinking water were evaluated. The tolerance limit was the concentration of a species which gives a relative error lower than 4% for the 50 μg l^{-1} Al^{3+} concentration. Cations were added as chloride, nitrate or acetates and anions were added as sodium or potassium salts. As can be seen from Table 1, almost all the anionic species are tolerated at maximum tolerable concentration of foreign ions according to the European regulations for drinking water [35,36]. The cationic species copper, iron and zinc interfered at the same concentration as the aluminum. In order to reduce the interference levels, different masking reactions were tested. We found that, Cu^{2+}, Fe^{2+}, Fe^{3+} and Zn^{2+} notably increased their tolerance limits with thioglicolyc acid (TGA), $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ and TGA, respectively, used as masking agents (Table 1).

3.1.2. Analytical features

In the batch procedure, two calibration curves (≤ 50 and ≤ 10 μg l^{-1} of Al^{3+}) for aqueous-ethanolic medium (24% v/v, EtOH) were prepared. In a first and second time, respectively, the analytical features were: regression, $1.15x - 0.06$ and $5.77x - 0.15$; correlation coefficient, 0.9962 and 0.9998; relative standard deviation for 11 samples: 1.98% for sample concentration of 20 μg l^{-1} Al^{3+} and 0.78% for sample concentration of 6 μg l^{-1} Al^{3+}; detection limit: 0.56 μg l^{-1} and 0.20 μg l^{-1} [calculated from $\mu_B + 3\sigma_B$ (μ_B: average

Table 1
Tolerated concentrations in the determination of 50 μg l^{-1} Al^{3+} concentration

Tolerated[a] concentrations	Species tested	Masking agents[c]
14528 mg l^{-1}	Cl^{-} (added as NaCl)	–
356.7 mg l^{-1}[b]	HCO_3^- (added as $NaHCO_3$)	–
3222 mg l^{-1}	SO_4^{2-} (added as Na_2SO_4)	–
500 μg l^{-1}	F^{-} (added as NaF)	–
2500 μg l^{-1}	F^{-} (added as NaF)	Be^{2+} (2 mg l^{-1})
3000 μg l^{-1}	F^{-} (added as NaF)	Be^{2+} (3 mg l^{-1})
439 mg l^{-1}[b]	Mg^{2+} (added as $MgCl_2 \cdot 6H_2O$)	–
407 mg l^{-1}	Ca^{2+} (added as $CaCl_2 \cdot 2H_2O$)	–
354 mg l^{-1}	K^{+} (added as KCl)	–
9412 mg l^{-1}	Na^{+} (added as NaCl)	–
750 μg l^{-1}	Mn^{2+}	–
1000 μg l^{-1}[b]	Fe^{2+}	$Fe(CN)_6^{3-}$ (5 mg l^{-1})
1000 μg l^{-1}[b]	Fe^{3+}	$Fe(CN)_6^{4-}$ (20 mg l^{-1})
1000 μg l^{-1}[b]	Cu^{2+}	TGA (10 μg l^{-1})
500 μg l^{-1}[b]	Zn^{2+}	TGA (10 μg l^{-1})

[a] Maximum concentration of foreign ion investigated.
[b] Tolerance limits (4% error).
[c] TGA, thioglycolic acid.

of the blank for $n = 10$; σ_B: standard deviation of the blank)]. In both cases, slits widths were 5 and 10 nm, respectively, for excitation and emission.

3.2. Optimization of the rFIA procedure

To optimize the perfomance of the method, the influence of several variables on the fluorescence of the Al–SAPH complex was studied.

3.2.1. SAPH concentrations

The influence of SAPH concentration, used in buffered solutions (HAc/Ac^{-}, pH 5.4), on complex formation was also studied within the range 2×10^{-4} to 8×10^{-4} M. The experiments were performed with 50 μg l^{-1} Al^{3+}. As shown in Fig. 2, the fluorescence increased rapidly up to 7×10^{-4} M, and then, an increase in SAPH concentration showed no significant variation in the fluorescence measured. A solution containing 24% EtOH and 7×10^{-4} M SAPH was chosen for further experimental work.

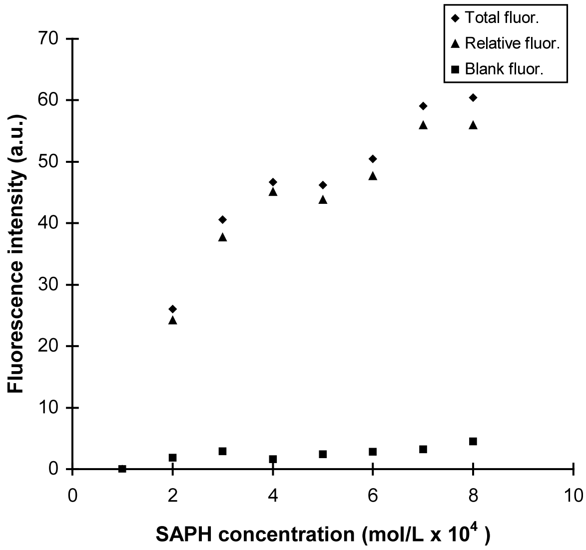

Fig. 2. Influence of SAPH concentration on the complexation reaction.

3.2.2. Buffer solutions

Buffer concentration (HAc/Ac^{-}, pH 5.4) was studied within the range 0–4 M for the analysis of non-acidified samples (pH 5.5–7.5) and acidified samples (pH $\cong$ 1 with HNO_3). Other conditions were those previously optimized.

After an initial variation of fluorescence with acetate concentration, both non-acidified and acidified samples were correctly buffered with acetate concentrations higher than 0.5 and 1.5 M, respectively. Then fluorescence become independent on buffer concentration up to, at least, 4 M HAc/Ac^{-}.

3.2.3. Injection volumes

In this experiment, the effect of reagent–buffer volumes was investigated, for optimum fluorescence of the Al–SAPH system. As shown in Fig. 3, the volume was varied from 50 to 1200 μl. Variations of volumes from 125 to 550 μl did not affect the relative fluorescence of system, but an increase in the volume decreased the signal, probably due to the worse mixing of sample and reagent. Under these experimental conditions, the

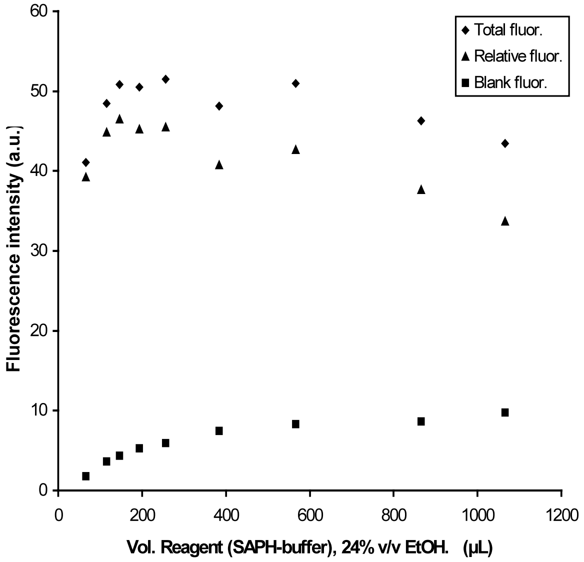

Fig. 3. Influence of reagent (SAPH-buffer) volumes on the relative fluorescence of complex.

optimum fluorescence intensity was obtained for an injection volume of 194 µl.

3.2.4. Reacting coil

The influence of reacting coil volume on the complexation of aluminum was investigated in terms of coil length within range of 100–400 cm (Fig. 4). After an initial increase in the fluorescence caused by a better mixing of sample and reagent–buffer, a maximum was reached and then, a decrease of fluorescence was observed, probably due to the dispersion of the sample into the reaction coil. A coil length of 300 cm was selected as optimum.

3.2.5. Flow-rate

Finally, in order to investigate the effect of flow-rate on the fluorescence of the Al–SAPH system a range of 0.2–1.4 ml min^{-1} was evaluated. Although maximum fluorescence was obtained at a flow-rate of 0.4 ml min^{-1} (Fig. 5), at this flow-rate we observed a higher dispersion of the signal (double-peaks). A value of 0.92 ml min^{-1} flow-rate has been chosen for further experiments.

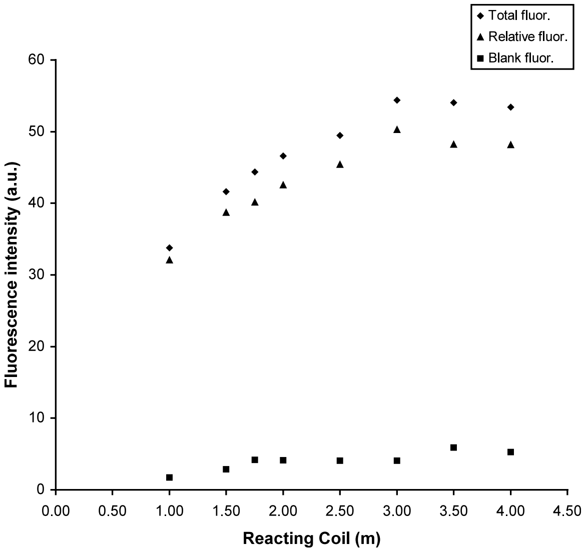

Fig. 4. Effect of reacting coil length on the complexation reaction.

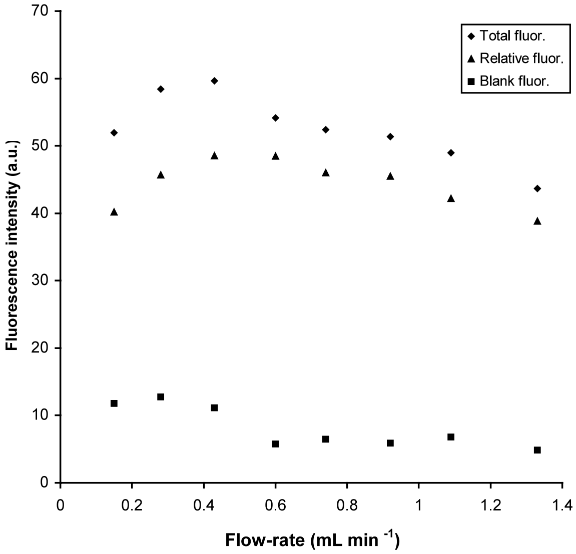

Fig. 5. Influence of flow-rate on the fluorescence of system.

3.2.6. Analytical features

In the rFIA procedure, two calibration curves (5–30 µg l^{-1} of Al^{3+}, $n = 6$ and 5–100 µg l^{-1} of Al^{3+}, $n = 7$) were prepared. In a first and second time, respectively, the analytical features were: regression, $0.92x + 1.30$ and $0.99x + 3.37$; correlation coefficient, 0.9968 and 0.9960; detection limit, 1.9 µg l^{-1}and 8.0 µg l^{-1} of Al^{3+}. The detection limit (calculated from $\mu_B + 3\sigma_B$; μ_B: average of the blank for $n = 10$; σ_B: standard deviation of the blank) found for the rFIA procedure was, as in the batch procedure, in the low-ppb range. In both cases, slits widths were 5 and 10 nm, respectively for excitation and emission.

The analytical parameters for the determination of aluminum (5–30 µg l^{-1}) are shown in Table 2, and compared to the analytical features established for the batch procedure.

4. Applications

The proposed rFIA method was applied successfully to the determination of Al^{3+} in commercial drinking water, soft drinking water and tap water samples. As shown in Table 3, the results obtained by the standard addition method (in commercial drinking water) were satisfactory with $< 7\%$ error. Five and seven standard additions were made on samples A and B, respectively, with three replicates for each concentration. The rFIA method was tested against a reputable GF-AAS method with five samples (1, soft drinking water—C.R.M; 2, tap water and 3–5 mineral waters). As shown in Table 4, the methods gave results in good agreement with each other.

Acknowledgements

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Table 2
Analytical features of the reverse flow injection analysis proposed compared to the batch procedure

	rFIA procedure	Batch procedure
Concentration range (µg l^{-1})	5–30	2–50
Limit of detection (µg l^{-1})	1.90	0.56
RSD ([Al^{3+}] = 20 (µg l^{-1})^{a}	1.62	1.98

[a] RSD: relative standard deviation (%).

Table 3
Standard addition of Al^{3+} in commercial drinking water

Sample	[Al^{3+}] (µg l^{-1}) ($n = 3$)		
	Added	Found	Error (%)
A	10	9.6 ± 0.2	−4.0
	20	20.3 ± 0.6	+1.5
	25	26.3 ± 1.3	+5.2
	30	29.9 ± 0.3	−0.3
	100	102.5 ± 0.5	+2.5
B	5	5.1 ± 0.1	+2.0
	10	9.9 ± 0.4	−1.0
	15	14.3 ± 0.1	−4.6
	20	19.6 ± 0.3	−2.0
	25	23.3 ± 0.9	−6.8
	30	30.3 ± 0.4	+1.0
	35	34.9 ± 0.4	−0.3

Samples: A, Lanjaron water (Granada, Andalucía, Spain); B, Viladrau water (Girona, Cataluña, Spain).

Table 4
Determination of Al^{3+} in soft drinking water, tap water and commercial drinking waters

Sample	[Al^{3+}] (µg l^{-1}) ($n = 3$)^{a}	
	Proposed method	GF-AAS
1	10.4 ± 0.2	10.0 ± 0.4
2	20.9 ± 0.4	20.0 ± 1.2
3	9.5 ± 0.3	10.2 ± 0.1
4	19.9 ± 0.7	19.7 ± 0.5
5	30.3 ± 0.4	28.3 ± 0.4

Samples: 1, soft drinking water—certified reference material: LGC6011 (UK); 2, tap water; 3–5, mineral water spiked with 10, 20 and 30 µg l^{-1} Al^{3+}, respectively.

[a] Precision expressed as standard deviations.

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