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Analytica Chimica Acta 355 (1997) 157–161

ANALYTICA
CHIMICA
ACTA

Direct fluorimetric determination of dissolved aluminum in seawater at nanomolar levels

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Received 23 February 1997; received in revised form 15 July 1997; accepted 9 August 1997

Abstract

A highly sensitive method for the direct determination of dissolved aluminum in seawater at nM levels has been developed. This method is based on the formation of an aluminum complex with salicylaldehyde picolinoylhydrazone (SAPH), which shows a maximum blue–green fluorescence (λ_{ex}=384 nm, λ_{em}=468 nm) at pH 5.4. The studied method has an average limit of detection of 9.8 nM (calculated in the concentration range of 3.7×10^{-8}–9.3×10^{-7} and a precision of 1.85% at 1.66×10^{-7} M, and it has been successfully applied to the determination of dissolved aluminum in seawater in both synthetic and real samples by using an external calibration and/or the standard addition method. The tolerance limits of foreign ions have been also evaluated, before and after the addition of masking agents. Finally, the proposed method has been compared with a spectrophotometric method. © 1997 Elsevier Science B.V.

Keywords: Aluminum; Salicylaldehyde picolinoylhydrazone; Seawater; Spectrofluorimetric determination

1. Introduction

The success of studies on oceanic chemistry, as in many fields, usually depends on the availability of adequate analytical methodology. Trace elements with short residence times in the ocean are typically used as tracers of oceanic input processes. Aluminum is one of these elements. Therefore, studies on the distribution of Al in seawater are important, making analytical methods suitable for directly determining the aluminum contents in seawater highly desirable.

Aluminum occurs in seawater as both dissolved and particulate species [1]. The former include aluminum in true solution and in the colloidal size range, being mainly hydroxy complexes of the metal. The particulate species consist of alumino-silicate mineral of detrital and terrigenous origin. Depending on the studied area, the concentration of dissolved aluminum in non-polluted seawater lies between 0.1 and 20 µg l^{-1} [2–4].

In recent years, the determination of Al in seawater has been studied by using different techniques. Among them, fluorimetry has been applied by several authors. For instance, Hydes and Liss [5] developed a method based on using Lumogallion as selective reagent. This method has a detection limit of 1.9 nM and a precision of 5% at 37 nM, and was later improved by Howard et al. [6], who by adding a surfactant, Triton X-100, reported a detection limit of 0.02 µg l^{-1} and a relative standard deviation of 5%

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PII S0003-2670(97)00487-X

at 0.1 µg l^{-1}, and by Hydes and Kremling [7], who improved the batch lumogallion method to reach a detection limit of 0.4 nM and a precision of 3% at 10 nM. Fluorimetry has also been applied by using other reagents as oxine-XAD-2 [8] or 8-hydroxyquinoline [9]. Resing and Measures [10] applied the lumogallion method in flow injection analysis (FIA) with in-line pre-concentration onto a column of immobilized 8-hydroxyquinoline, and reported a detection limit of about 0.15 nM and a precision of 1.7% at 2.4 nM.

Besides fluorimetry, the determination of Al in seawater has been performed by spectrophotometry with pyrocatechol violet [11]. To improve the sensitivity, this reagent has also been applied with a preconcentration step by solvent extraction with zephiramine (tetradecyldimethylbenzylammonium chloride) [12]. Atomic absorption spectroscopy [13] and electron capture detection gas chromatography [14] have been also used to determine the dissolved Al in seawater with a preceding step by solvent extraction with 8-hydroxyquinoline and 1,1,1-trifluoro-2,4-pentanedione, respectively. Other techniques as graphite furnace atomic absorption spectroscopy [15], cathodic stripping voltammetry [16,17] or co-precipitation with $Fe(OH)_3$ [18] have also been applied.

This paper reports the application of salicylaldehyde picolinoylhydrazone (SAPH) as a selective reagent for the direct fluorimetric determination of dissolved aluminum in seawater. SAPH forms a fluorescent chelate with aluminum with a stoichiometric ratio of 1 : 3, Al : reagent, $[Al(SAPH)_3^{3+}]$. The synthesis, characterization and application of SAPH to the determination of aluminum in agricultural soils was previously reported [19].

2. Experimental

2.1. Reagents and solutions

Salicylaldehyde picolinoylhydrazone (SAPH) was synthesized as described elsewhere [19]. Once synthesized, a stock solution of 0.045% w/v in ethanol was prepared. A commercial stock solution of 1000 µg ml^{-1} of Al(III) was purchased from Merck (Daarmstadt, Germany). Further dilutions were made daily as required. As aluminum is very rapidly released from glassware, all reagent and sample bottles and reaction flasks were made from poly-ethylene or PVC material. Synthetic seawater was prepared by dissolving the needed amounts of different salts of analytical grade, Merck (Daarmstadt, Germany), to a final composition, in g l^{-1}, of: 23.926 (NaCl); 4.008 (Na_2SO_4); 0.677 (KCl); 0.196 ($NaHCO_3$); 0.098 (KBr); 0.026 (H_3BO_3); 0.003 (NaF); 10.826 ($MgCl_2{\cdot}6H_2O$); 1.518 ($CaCl_2{\cdot}2H_2O$); 0.024 ($SrCl_2{\cdot}6H_2O$).

A 0.5 g l^{-1} Be(II) stock solution was prepared by dissolving $Be(NO_3)_2{\cdot}4H_2O$ in water. The acetate buffer solutions were prepared by using CH_3COOH and CH_3COONa of Suprapur quality reagent, Merck (Daarmstadt, Germany). Water, analytical grade, Merck (Daarmstadt, Germany) was used.

All other reagents were also of analytical grade, Merck (Daarmstadt, Germany).

2.2. Apparatus

A Perkin–Elmer LS-5B spectrofluorimeter with 1 cm quartz cells and a Xenon-arc source was used to measure the fluorescence of developed complexes. Spectrophotometric experiments were performed with a Lambda 11 UV–VIS spectrophotometer (Perkin–Elmer, Germany).

Acidity was measured with a model 2001 pH meter (Crison, Spain) equipped with a model 52-02 combined glass-Ag/AgCl electrode (Crison, Spain).

2.3. Procedures

2.3.1. Optimization of the system Al(III)–SAPH

A systematic variation of the parameters controlling the formation of the fluorescent complex Al–SAPH was carried out. Thus, the effect produced by the acidity, concentration of SAPH, percentage of ethanol and concentration of acetate in buffer solutions were investigated. On the other hand, the influence of the salts present in seawater and of the most common cationic metals was also studied.

2.3.2. Spectrofluorimetric determination of aluminum in seawater

To 25 ml volumetric flasks, containing the appropriate volumes of Al(III) solutions (to give a final concentration of aluminum between 1 and 50 µg l^{-1}), 5 ml of acetate buffer solution (pH 5.4), 0.1 ml of Be(II) stock solution and 6 ml of SAPH stock solution were added, and the mixture was diluted to the mark with synthetic seawater. After 30 min, the fluorescence intensity (λ_{ex}=384 nm and λ_{em}=468 nm) of the solution was measured against a blank prepared in a similar way without aluminum, using the appropriate widths for both excitation and emission slits. The obtained data were used to construct the calibration plots that were used to quantify the dissolved aluminum in both synthetic and real samples. These samples were treated by following the experimental procedure described earlier for calibration solutions. While using real samples, they were filtrated, using a cellulose nitrate filter with 0.45 μm pore size, and preserved by adding 1 ml l^{-1} HNO_3.

Besides the direct calibration, and for the sake of comparison, some samples were analyzed by the standard additions method.

Finally, the optimized spectrofluorimetric method was tested against a spectrophotometric method based on the formation of a coloured complex with pyrocathecol violet, described by Dougan and Wilson, and later modified by Koroleff [11].

3. Results and discussion

3.1. Optimization of the system Al(III)–SAPH

As mentioned before, the Al–SAPH complex was characterized in a previous work [19]. The formation of the complex is probably controlled by the reaction:

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

This reaction is strongly influenced by the acidity of the solution, as can be observed in Fig. 1. Thus, the complex is mainly formed between pH 5 and 6, the optimum being at pH 5.4.

The influence of SAPH in the fluorescence of the complex was investigated in terms of [SAPH]/[Al^{3+}] ratio in the range of 20–1200. Fluorescence increased rapidly up to 80–100, then, an increase in reagent concentration showed no significant variation in the fluorescence measured. A value of 4.48 × 10^{-4} M was chosen for further experimental work, the [SAPH]/[Al^{3+}] ratio being included in the plateau.

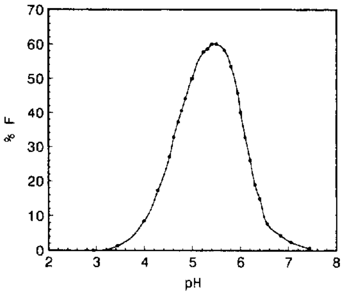

Fig. 1. Dependence of relative fluorescence of Al–SAPH complex on pH. Reaction conditions: 40 μg l^{-1} Al(III); 24% v/v EtOH; 4.48 × 10^{-4} mol l^{-1} SAPH; 1 mol l^{-1} acetate.

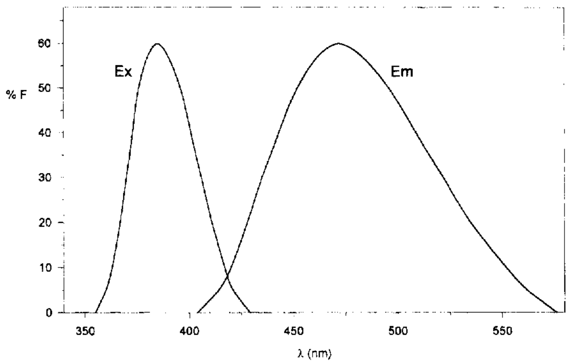

Fig. 2. Excitation and emission spectra of Al–SAPH complex. Reaction conditions: 40 μg l^{-1} Al(III); 24% v/v EtOH; 4.48 × 10^{-4} mol l^{-1} SAPH; pH 5.4; 1 mol l^{-1} acetate.

The effect of ethanol and acetate ions, used in buffer solutions, was also studied. The fluorescence of the system was found not to vary in the range of 20–35% of ethanol, and up to 1 mol l^{-1} acetate concentration. At optimum values, 24% ethanol and 1 mol l^{-1} acetate were chosen. Under optimum conditions, the excitation and emission spectra of Al–SAPH system were obtained and presented in Fig. 2.

The effect of principal salts present in seawater were evaluated. The tolerance limit was the concentration of a salt which gives a relative error lower than 4% in the fluorescence of a solution containing 50 μg l^{-1} Al(III). The concentration ranges (g l^{-1}) 0–24 NaCl, 0–10 $NaSO_4$, 0–24 KCl, 0–10 $NaHCO_3$, 0–12 $MgCl_2{\cdot}6H_2O$, 0–3 $CaCl_2{\cdot}2H_2O$, 0–1 $SrCl_2{\cdot}6H_2O$, 0–0.003 NaF, 0–0.01 KBr and 0–0.03 H_3BO_3 were investigated. Among the studied salts, only the last three caused some interferences. The presence of KBr and H_3BO_3 caused only slight interferences, while the main interference was produced by fluoride ions. To minimize this interference, Be(II) and Mg(II) were tested as masking reagents. The observed interference was notably reduced for both reagents. The best results were obtained with Be(II). In this sense, when 2 $mg\,l^{-1}$ Be(II) were present, up to 3000 $\mu g\,l^{-1}$ of fluoride ions were found not to interfere.

The cationic species copper, iron, zinc, and cobalt, showed a negative interference at the same concentration as that of aluminum. In order to reduce the interference levels, different masking reactions were tested. In this way, Cu(II), Fe(II), Fe(III), Zn(II), and Co(II), notably increased their tolerance limits with thioglicolyc acid (TGA), $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, TGA, and CN^-, respectively, used as masking agents.

3.2. Spectrofluorimetric determination of aluminum in seawater

Two calibration methods, direct and standard additions (SAM), were performed. By using the direct calibration method, three calibration lines were made. Table 1 shows the results obtained. Appropriate width of both excitation and emission slits, and integration time were selected to construct each calibration plot. The best precision obtained for a synthetic seawater sample of 3 $\mu g\,l^{-1}$ Al(III) was 1.02%.

The SAM was successfully compared with the direct calibration method, using seawater (both synthetic and natural) samples. To this aim, the total aluminum content was determined in six samples of seawater from the Bay of Gibraltar. The results obtained ($\mu g\,l^{-1}$ Al(III)) were: 60.38±1.74; 60.21±1.73; 59.49±1.71; 66.33±1.91; 64.68±1.86; 65.25±1.88 and 58.18±1.09; 56.82±1.07; 58.75±1.10; 64.19±1.21; 66.47±1.25; 62.94±1.18, by the direct and SAM method, respectively. At a significance level (α=0.05), the comparison of the null hypothesis (H_0: $\mu_1=\mu_2$) that both means are equal against the alternative hypothesis (H_A: $\mu_1 \neq \mu_2$) shows that the experimental value of $/t/$, denoted as T, is smaller than the corresponding $/t/$ value for normal distribution, so $T=0.7506 < t= 2.228$. Therefore, the alternative hypothesis is rejected [20].

As mentioned before, several methods have been previously used for the determination of aluminum in seawater. Only a few of them reach limits of detection at nanomolar levels without a pre-concentration step. The fluorescence-based methods (like lumogallion or the present method) are included among them.

3.3. Comparison between spectrophotometric and spectrofluorimetric methods

The direct fluorimetric method was tested against a reputable spectrophotometric method based on the reaction of Al(III) with pyrocathecol violet. Four synthetic samples containing 10, 20, 40 and 50 $\mu g\,l^{-1}$ were analyzed by using both methods. The results obtained were: 9.73±0.47; 21.32±1.03; 41.34±1.99; 53.34±2.58 and 10.31±0.30; 21.06±0.61; 39.87±1.15; 51.39±1.48, for the spectrophotometric and fluorimetric methods, respectively. To validate the new method, we used the accepted procedure of using a regression line for comparing two analytical methods [20]. This method consists of constructing a

Table 1
Results obtained for the determination of Al(III) in seawater by the direct calibration method.

Linear Range ($\mu g\,l^{-1}$ Al(III))	Regression ($ax+b$)	Correlation coefficient	Slits ex/em	Detection limit[a] ($\mu g\,l^{-1}$ Al(III))	Precision[b] %, ($\mu g\,l^{-1}$ Al(III))
1–5	$44.6x-7.92$	0.9989	5/10	0.270	1.39 (3)
1–5	$38.97x-9.63$	0.9994	10/10	0.189	1.60 (3)
1–10	$40.50x+1.73$	0.9999	10/10	0.125	1.66 (5)
5–25	$8.36x-3.06$	0.9999	2.5/5	0.308	1.70 (10)
5–25	$6.63x-3.19$	0.9999	5/5	0.437	1.78 (10)
10–50	$2.23x-0.69$	0.9995	2.5/2.5	1.78	5.05 (30)
10–50	$8.76x-2.84$	0.9995	2.5/5	1.71	5.06 (30)
10–50	$7.74x-6.45$	0.9997	5/5	1.31	5.00 (30)

[a] Calculated as $3s_0$/slope, where s_0 represents the standard deviation of the intercept on the ordinate

[b] % of relative standard deviation for 11 samples, with α=0.05, calculated at the Al(III) concentration in brackets

regression line by using the results obtained by the new method in one axis and those obtained by applying the reference method in the other one. By following this procedure, the regression line obtained was y=1.0607x +0.9416, with r=0.99998. The use of the appropriate t-value (t=4.30) gives the 95% confidence limits for the intercept and slope as a=1.061±0.622 and b=0.942±0.017. From these figures, it can be concluded that there is no significant difference between both analytical methods.

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