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Aluminium traces determination in biological and water samples using a novel extraction scheme combined with molecular fluorescence

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ABSTRACT

A ternary surfactant system is for the first time proposed as an extraction strategy of aluminium traces using 8-hydroxyquinoline as complexing agent and applied for selective preconcentration of this metal. The analyte was quantified in the enriched solution by molecular fluorescence. After optimization of the complexation and extraction conditions, an enrichment factor superior to 30-fold was obtained with improved sensitivity of 2.5 times compared to the conventional extraction system using only a nonionic surfactant. The calibration curve in the range of 0.853–79.87 μg L^{-1} was linear and the limit of detection was 0.281 μg L^{-1}. The proposed method was successfully applied to the determination of aluminium in biological and water samples.

1. Introduction

Aluminium (Al) is a non-essential, toxic metal to which humans are frequently exposed and compounds containing Al have been used in manufacturing (e.g., clays, glasses, and alum) for centuries. This metal is also used to manufacture kitchen tools and pharmacological agents including antacids and antiperspirants exposing human body to this element. It has also been considered as a possible cause of renal osteodystrophy, Parkinson and Alzheimer's diseases [1–3]. The determination of very low levels of aluminium has become very important in environmental and clinical chemistry since its negative role in the human life.

Normally Al is found at low levels (μg L^{-1}) in most drinking water because it is still used as a flocculating agent in potable water treatment units. The maximum permissible content of Al in drinking water is 0.2 mg L^{-1} [4]. Therefore, it is important monitoring Al in water and other samples. Moreover, the evaluation of Al levels in biological fluids for prevention of associated diseases has attracted considerable attention in the field of clinical chemistry.

Nowadays, there are many analytical techniques for the direct detection of the Al in real samples like spectrophotometry [5–7], spectrofluorometry [8,9], flame atomic absorption spectrometry (FAAS) [10] and the graphite furnace atomic absorption spectrometry (GFAAS) [11–13]. Before analytical determination of low Al concentration levels in complex samples analysis, it is necessary separation and preconcentration steps.

The most used techniques for the separation and preconcentration of this element include solid-phase extraction [5], conventional liquid–liquid extraction [14,15], and cloud point extraction (CPE) [8,10,11], among others. CPE is becoming an important and practical application of surfactants in analytical chemistry because of the versatility in recuperation of both organic and metallic analytes. CPE has been recognized as green procedure owing to the use of inexpensive surfactant extractants, the generation of less laboratory wastes and the fact that surfactants are non-volatiles, non-toxics and non-inflammable in contrast to organic solvents [16].

To date, nonionic surfactants have been the most widely employed for CPE, although zwitterionic surfactants and mixtures of nonionic and ionic surfactants have been also used [16–17]. Clouding is ascribed to the efficient dehydration of hydrophilic portion of micelles at higher temperature condition. Additionally, it has been reported the ability of different substances to induce phase separation in aqueous solutions of bile salts as sodium cholate (NaC) at room temperature [18]. On the other hand, among cationic surfactants, cetyltrimethylammonium bromide (CTAB) constitutes undoubtedly an example of self-assembled ordered medium as micelles, and other structures and phases, having been widely employed in analytical chemistry with different purposes [19–25].

In the present work, a new extraction scheme that uses polyethyleneglycolmono-p-nonylphenylether (PONPE 5.0) as nonionic surfactant and (CTAB) as cationic and (NaC) as anionic surfactants is

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proposed for separation and preconcentration of Al(III) complexed with 8-hydroxyquinoline (8-HQ), before its determination by molecular fluorescence. Experimental variables affecting sensitivity and precision of the proposed method were in detail investigated and optimized in order its application to determinate of metal traces in biological fluids and water samples.

2. Experimental

2.1. Instrumentals

Shimadzu RF-5301PC spectrofluorometer (Shimadzu Corporation Analytical Instrument Division, Kyoto, Japan) equipped with a discharged Xenon lamp was used for recording fluorimetric measurements using semi-micro quartz cells (300 μL).

Measurements of aluminium were performed with a Shimadzu Model AA-6800 Atomic Absorption Spectrometer (Tokyo, Japan) equipped with a deuterium background corrector, EX7-GFA electrothermal atomizer and ASC-6100 autosampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) was used in all experiments. Aluminium hollow-cathode lamps (Hamamatsu, Photonics K., Japan) were employed as radiation sources. Wave length used was 309.4 nm (Slit Width: 0.5 nm) using a pyrolysis times of 10 s at 250 °C and atomization time of 3 s at 2500 °C.

Adjustments of pH were carried out using Orion Expandable Ion Analyzer pH-meter (Orion Research, MA, USA) Model EA 940 with a combined glass electrode.

Termostatized bath Arcano 78 HW-1with magnetic stirrer (Arcano, Buenos Aires, Argentine) was used for extraction in this experiment.

A centrifuge equipment (ROLCO SRL, Buenos Aires, Argentine) with an angle rotor (6-place, 3500 rpm) was used to accelerate the phase's separation process.

2.2. Reagents

Working standard Al(III) solutions were obtained by appropriate dilution of standard solution of $Al(NO_3)_3.9\ H_2O$ (E-Merck, Darmstadt, Germany) of 1000 mg L^{-1}, using ultrapure water.

A 1×10^{-3} mol L^{-1} solution of 8-HQ (E-Merck) was prepared by dissolving appropriate amount of this reagent in ethanol (Sigma Chemical Co., St. Louis, MO, United States) and was kept in refrigerator (4 °C) for one week.

Surfactant PONPE 5.0, (Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) 50% (v/v) in ethanol (Sigma Chemical Co.), was employed without further purification.

NaC ($C_{24}H_{39}NaO_5$, Sigma Chemical Co.) 1×10^{-2} mol L^{-1}, CTAB ($C_{16}H_{33}N(CH_3)_3Br$, Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) 1×10^{-2} mol L^{-1} and sodium dodecylsulphate (SDS, Tokyo Kasei Industries) 1×10^{-2} mol L^{-1} solutions were prepared using an adequate weight of reagents, respectively, and dissolving in ultrapure water.

A stock solution, acetic acid (1.0 mol L^{-1}) (Riedel-de Haen) was prepared by diluting appropriate amounts of this compound in ultrapure water and adjusting to pH 5.8 by adding diluted NaOH (Mallinckrodt Chemical Works, St. Louis, Mo.) solution. A 25% (*w*/*v*) NaCl (*E*-Merck, Darmstadt, Germany) solution was used, in order to adjust ionic strength.

Methanol (Sigma Chemical Co.) was used as diluents of surfactant rich phase.

All used chemicals were of analytical grade and ultrapure water was throughout used.

2.3. Samples treatment

2.3.1. Tap and beverage waters

Bottled mineral water samples were obtained from local sources. Tap water samples were freshly collected after allowing the water flow for 5 min. All samples were filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter and were stored at 4 °C in the dark. 1 mL was taken of each water sample and was subjected to the General Procedure as described in the previous section.

2.3.2. Collection and treatment of biological samples

According to regulations, all participants of present research signed the written informed consent.

The first morning urine sample was collected from occupationally unexposed subject in polystyrene test tubes, between 8 and 10 h to reduce possible circadian contributions. Sample was centrifuged for 10 min at 1000 × *g* and processed immediately after arriving to the laboratory. It is not recommended to add a none stabilizer because of the risk of incorporating analyte as impurity.

Blood sample, from the same subject (each 10 mL), was obtained by vein puncture of forearm. It was placed in two tubes, one with Li-heparin (anticoagulant) and the other without it. The tubes with anticoagulant were homogenized and centrifuged (1500 g) during 15 min. Then the clear and transparent supernatant corresponding to plasma was extracted and reserved at 4 °C until Al(III) assays. In order to accelerate the coagulation process to make the serum separation, tubes containing blood without heparin were maintained thermostated at 37 °C during 30 min. Then, systems were centrifuged (1500 g) during 15 min and the supernatant was put in polypropylene tubes with hermetic closing.

They were taken 100 μL of each sample, then were diluted to 10 mL with ultrapure water. General Procedure was applied to 100 μL of each diluted sample.

2.4. General Procedure

A volume of 0.5 mL chelating solution 8-HQ 1×10^{-3} mol L^{-1}, sample/standard containing from 0.853 to 79.87 μg L^{-1} of Al(III), 0.25 mL of buffer solution 1 mol L^{-1} (pH 5.8), 0.5 mL CTAB 1×10^{-2} mol L^{-1}, 0.5 mL NaC 1×10^{-2} mol L^{-1}, 0.10 mL PONPE 5.0 50% (v/v) and 0.5 mL NaCl 25% (*w*/*v*) were placed in a centrifuge tube. The mixture was diluted to 10 mL with ultrapure water then it was homogenized. The resultant solution was equilibrated at 70 °C for 15 min. In order to separate the phases, the turbid solution was centrifuged 10 min at 3500 rpm (1852.2 × *g*). The supernatant aqueous phase was separated with an automatic pipette. This phase was later discard. A volume of 100 μL of MeOH was added to the surfactant rich phase (200 μL). The diluted surfactant rich phase was transferred to a 300 μL quartz cell and fluorescent emission was determined at 515 nm using $\lambda_{exc} = 373$ nm (Fig.1).

2.5. Interferences study

Different amounts of ions, which may be present in samples, (1/1, 1/10, 1/50 and 1/100 Al(III)/interferent ratio) were added to the test solution containing 24.95 μg L^{-1} Al(III) and the General Procedure was applied. Interferences studies were realized in samples without addition of masking or anticoagulant agents.

2.6. Accuracy study

Adequate volume of each sample was spiked with increasing amounts of Al(III) (9.98 and 24.95 μg L^{-1}). Analyte concentrations were determined by proposed methodology.

2.7. Validation

Al(III) contents in water samples were determined by ETAAS, using operational conditions previously consigned in apparatus item.

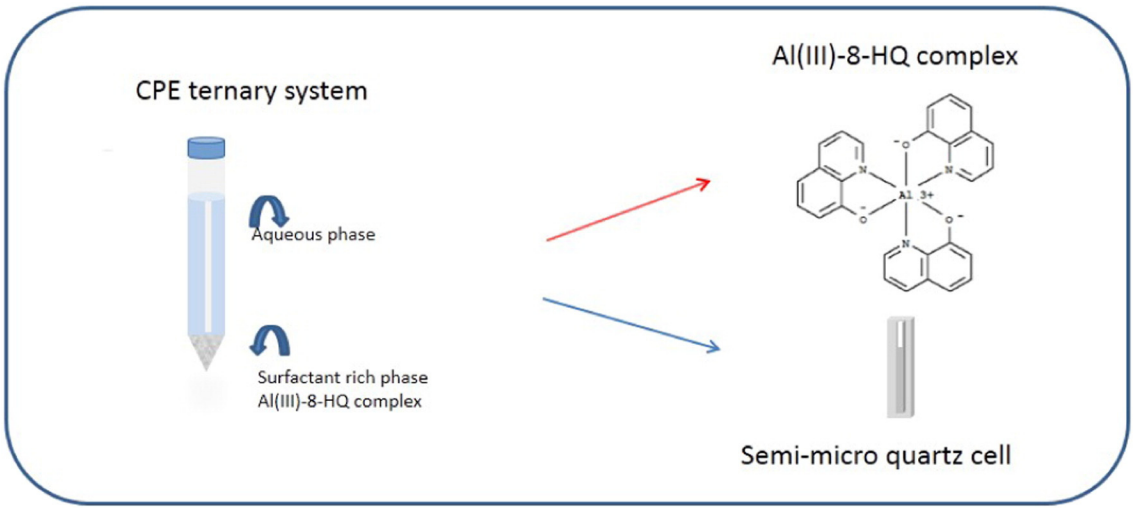

Fig. 1. Schematic representation of General Procedure of developed methodology.

3. Results and discussion

It is well known that 8-HQ and its derivatives have been successfully used for Al(III) determination, but the poor selectivity over other metals hinders its practical applications [8,14,26]. In addition, the 8-HQ metallic chelates have low solubility in water, which leads to the need for extraction steps using toxic organic solvents.

In this opportunity, the capacity of 8-HQ to form chelates will be associated to a new CPE procedure in order to isolate the analyte of matrix components as potential interferences, and preconcentrate the low levels of Al(III) present in selected samples (Fig. 2).

For achieving the preconcentration of metal traces and their isolation from the sample matrix, a new scheme of CPE was assayed. The aim was directed to improve the CPE analytical performance obtained when it is only employed nonionic surfactant. The efficiency of the CPE process depends on the hydrophobicity of the ligand and the produced complex, the apparent equilibrium constants, kinetics of complex formation and transference of phases, among other experimental factors.

Experimental trials included surfactants of different nature and electrostatic charge. Among the available surfactants (nonionic, anionic and cationic), PONPE 5.0, CTAB, SDS, NaC were separately studied for CPE of Al(III)-8-HQ complex, as well as in binary and ternary surfactant mixes.

The best results that attend to operational convenience (lower temperature and equilibration time) and quality analytical parameters related to sensitivity associated to a better preconcentration and quantitative Al(III) extraction were obtained for ternary surfactant systems. PONPE 5.0, CTAB and NaC (0.5%, 5×10^{-4} mol L^{-1} and 5×10^{-4} mol L^{-1} concentrations, respectively) improved sensitivity of 2.5 times compared to the extraction system using only the nonionic surfactant (Fig. 3).

The first experimental parameter evaluated was pH, due to its effect on the complexation equilibrium of Al(III) with 8-HQ. Furthermore, pH plays an important role on the subsequent metal extraction. The influence of pH of the sample solution on recoveries of Al(III) were investigated in the pH range 2.0–11.0 by adjusting pH to the model systems with acetic acid-acetate buffer. The results of this study were depicted in Fig. 4. It can be seen that the highest emission of Al(III)-8HQ was obtained at

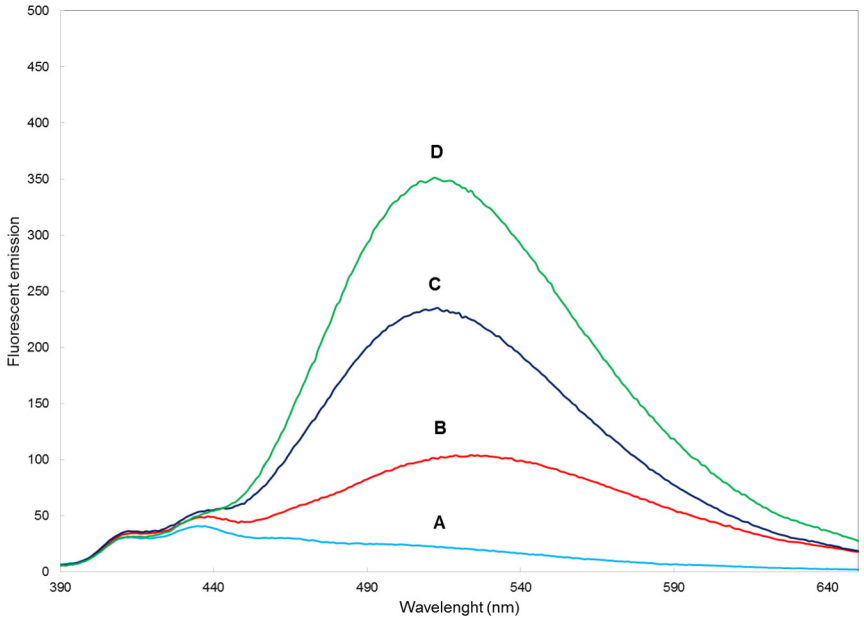

Fig. 2. Emission spectra for CPE/Al(III) quantification. A: Blank solution 8-HQ ($C_{8\text{-HQ}} = 5 \times 10^{-5}$ mol L^{-1}). B: Idem A ... with Al(III) 4.94 μg L^{-1}. C: Idem A with Al(III) 10.60 μg L^{-1}. D: Idem A with Al(III) 16.49 μg L^{-1}. Conditions: $\lambda_{em} = 515$ nm; $\lambda_{exc} = 373$ nm; $C_{CTAB} = 5 \times 10^{-4}$ mol L^{-1}; $C_{NaC} = 5 \times 10^{-4}$ mol L^{-1}; volume extracting solution = 0.1 mL; pH 5.80; $C_{buffer\ acetic/acetate} = 2.5 \times 10^{-2}$ mol L^{-1}. Other experimental conditions are described under procedure.

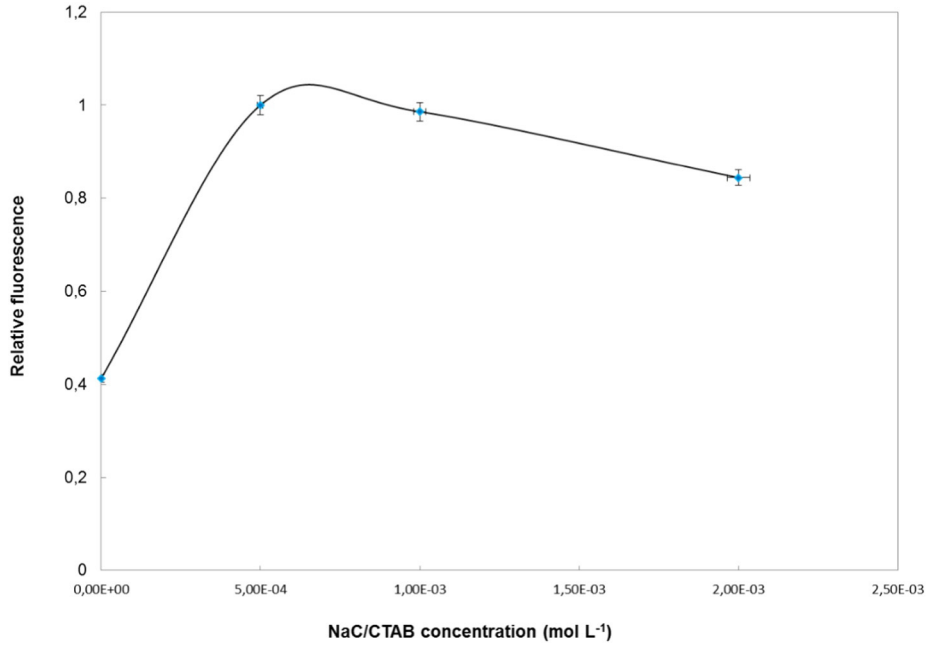

Fig. 3. Influence of ionic surfactant concentrations (CTAB and NaC) on the CPE of aluminium. Conditions: $\lambda_{em} = 515$ nm; $\lambda_{exc} = 373$ nm; $C_{8\text{-HQ}} = 5 \times 10^{-5}$ mol L^{-1}; volume extracting solution = 0.1 mL; $C_{\text{buffer acetic/acetate}} = 2.5 \times 10^{-2}$ mol L^{-1}, pH 5.80; $C_{Al(III)} = 24.95$ μg L^{-1}. Other experimental conditions are described under procedure.

pH 5.8. After the optimum pH was found (pH 5.8, with acetic acid-acetate buffer), the incidence of buffer concentration was studied. The maximum emission signal was achieved using 2.5×10^{-2} mol L^{-1} of the mentioned buffer. These experimental conditions were used for the following studies.

The chelating reagent concentration was also studied to obtain an optimum generation between the metal association and the chelating reagent. The effect of 8-HQ concentration on the fluorescent signal was evaluated by preparing solutions with the metal and different concentrations of chelating reagent. The best results were obtained using 8-HQ at 5×10^{-5} mol L^{-1} concentration, taking into account sensitivity and reproducibility (Fig. 5).

The presence of neutral electrolytes often produces decreased cloud point temperature, accompanied by the consolidation of the surfactant-rich phase [27]. In order to obtain a properly consolidated surfactant-rich phase, NaCl solution was added in variable concentrations to the systems. The best results were showed by the systems with an electrolyte concentration of 0.125%.

It is well known that the recuperation and enrichment factor (defined as the ratio between Al(III) concentration in the surfactant-rich phase and in the original solution) is affected by equilibration time and temperature. Therefore, these parameters were studied within the ranges: 25–80 °C and 2–30 min, respectively. A temperature of 70 °C was selected in order to achieve the minimum equilibration time (5 min), to avoid complex decomposition and to reach the optimal enrichment factor. Centrifugation speed is an important operational variable for the high performance of CPE process and to minimize the time required to the demixing to two transparent liquid phases. Thus,

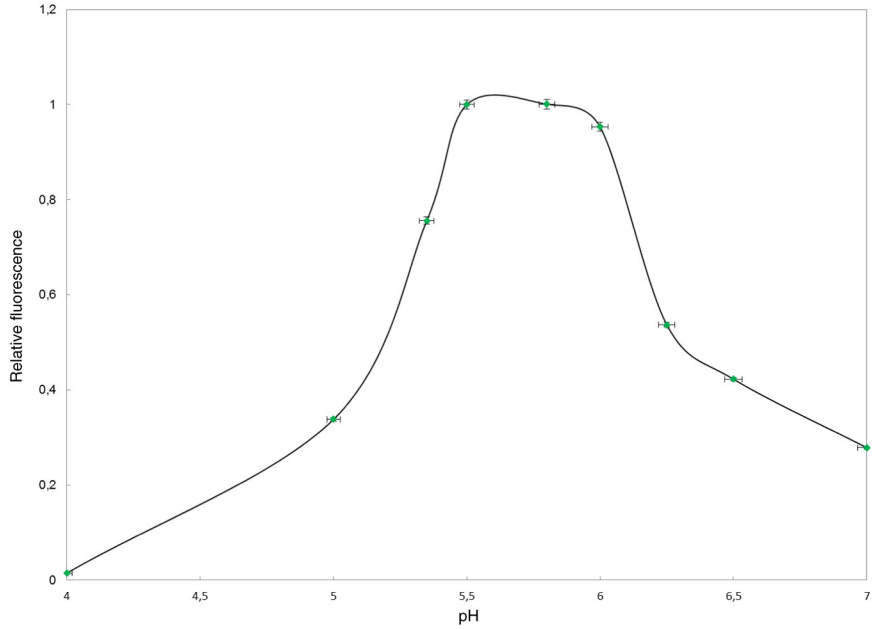

Fig. 4. Influence of pH on CPE/Al(III) determination. Conditions: $\lambda_{em} = 515$ nm; $\lambda_{exc} = 373$ nm; $C_{8\text{-HQ}} = 5 \times 10^{-5}$ mol L^{-1}; $C_{CTAB} = 5 \times 10^{-4}$ mol L^{-1}; $C_{NaC} = 5 \times 10^{-4}$ mol L^{-1}; volume extracting solution = 0.1 mL; $C_{\text{buffer acetic/acetate}} = 2.5 \times 10^{-2}$ mol L^{-1}; $C_{Al(III)} = 24.95$ μg L^{-1}. Other experimental conditions are described under procedure.

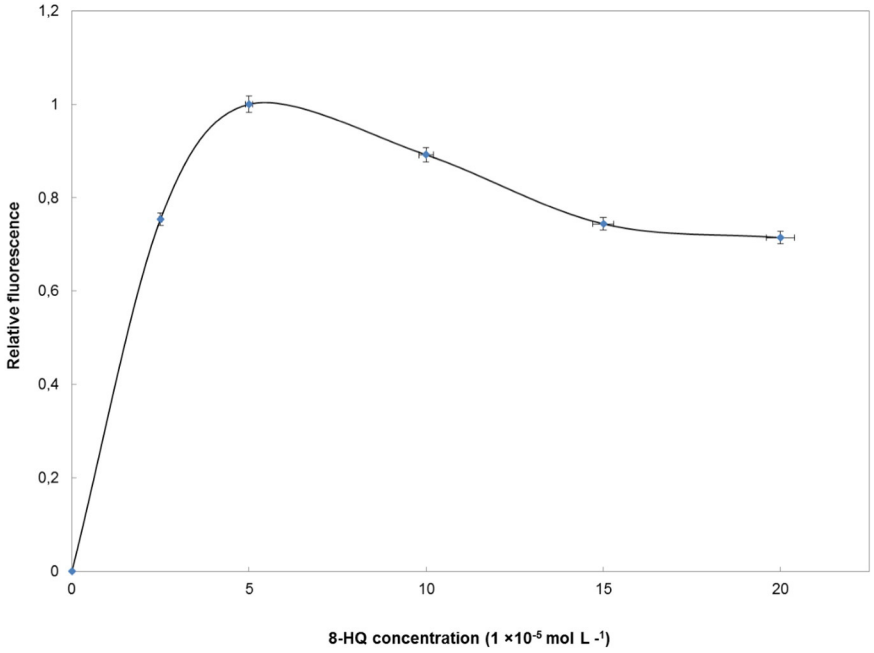

Fig. 5. Effect of 8-HQ concentration on the CPE/Al(III). Conditions: $\lambda_{em} = 515$ nm; $\lambda_{exc} = 373$ nm; $C_{CTAB} = 5 \times 10^{-4}$ mol L^{-1}; $C_{NaC} = 5 \times 10^{-4}$ mol L^{-1}; volume extracting solution = 0.1 mL; $C_{buffer\ acetic/acetate} = 2.5 \times 10^{-2}$ mol L^{-1}, pH 5.80; $C_{Al(III)} = 24.95$ μg L^{-1}. Other experimental conditions are described under procedure.

the influence of this parameter and the centrifugation time on the Al(III) extraction were investigated and optimized, maintaining constant the other variables.

High-speed centrifugation was used showing a relative high efficiency to minimize the water amount remaining in the surfactant-rich phase. A centrifugation time of 10 min at 3500 rpm was selected as optimum, since the complete separation occurred at this time and speed. It was not appreciated improvements with longer centrifugation times.

Under the optimal experimental conditions, an extraction percentage higher than 99.9% was achieved (Table 1) and consequently, the enrichment factor achieved for this system was 50-fold (surfactant rich phase volume = 200 μL).

Prior to determination step, surfactant-rich phase containing Al(III)-8-HQ complex was separated to aqueous phase, resulting very dense and viscous (20 cP, approximately). In order to transfer this phase to measurement cell, a convenient dilution must be realized. With this aim, different solvents were assayed to select the one that produce the optimal results, regarding sensitivity and decreasing the viscosity. Among the soluble solvents, the addition of methanol, ethanol, 1-propanol and acetonitrile were assayed as diluents of surfactant-rich phase containing Al(III)-8-HQ complex. Mixes of organics solvent/mineral acids have showed to be effective in reducing the viscosity of the surfactant-rich phase (reference 10), but in this case, they were disesteemed due to the risk of complex decomposition by pH change. The best results were achieved diluting the surfactant-rich phase with 100 μL of methanol, attaining so an appropriate viscosity for the manipulation of extract and the best signal of fluorescence in the semi-micro quartz cells.

The necessary dilution constitutes a disadvantage associated to CPE because of the decrease of the sensitivity; for this, a semi-micro cell of 300 μL was used, minimizing the addition of solvent and the loss of sensitivity.

Table 1
Experimental conditions and analytical parameters for aluminium determination.

Parameters	Studied Range	Optimal conditions
pH	4.0–8.0	5.80
Buffer concentration	1×10^{-2}–0.25 mol L^{-1}	2.5×10^{-2} mol L^{-1}
NaC concentration	0–4×10^{-3} mol L^{-1}	5×10^{-4} mol L^{-1}
CTAB concentration	0–2×10^{-3} mol L^{-1}	5×10^{-4} mol L^{-1}
Extracting solution volume	0–0.500 mL	0.1 mL
8-HQ concentration	2.5×10^{-5}–0.2 mol L^{-1}	5×10^{-5} mol L^{-1}
LOD	–	0.281 μg L^{-1}
LOQ	–	0.853 μg L^{-1}
LOL	–	0.853–79.87 μg L^{-1}
r^2	–	0.986
CI (water samples)	–	0.02 mL

Table 2
Comparison of the published methods employing CPE with the proposed method in this work.

Surfactants	Detection	Comments	Reference
PONPE 7.5	ICP-OES	LOD = 0.25 μg L^{-1} r^2 = 0.9997 Samples: parenteral solutions	[6]
CTAB and Triton X-114	Spectrophotometry	LOD = 0.52 μg L^{-1} Linearity = 3–100 μg L^{-1} Samples: water	[7]
Triton X-114	Spectrofluorimetry	LOD = 0.79 μg L^{-1} r^2 = 0.998 Samples: tap water, mineral water and food	[8]
Tween-20	Spectrofluorimetry	LOD = 3 μg L^{-1} RSD = 2.9% r^2 = 0.986 Samples: natural water	[9]
Triton X-114	GFAAS	LOD = 0.09 μg L^{-1} RSD = 4.7% r^2 = 0.9981 Samples: biological fluids and water	[11]
Triton X-114	GFAAS	LOD = 0.06 μg L^{-1} RSD = 3.6% Samples: human albumin	[13]
CTAB, NaC and PONPE 5.0	Spectrofluorimetry	LOD = 0.281 μg L^{-1} LOQ = 0.853 μg L^{-1} Samples: tap and beverage water, serum, plasma and urine	This work

Table 3
Tolerance limits of interfering species in Al(III) determination.

Interferent/Al(III) mole ratio	Interferent specie
100:1	Na^+, K^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} Cl^-, F^-, I^-, NO_3^-

Conditions: $\lambda_{em} = 515$ nm; $\lambda_{exc} = 373$ nm; $C_{8\text{-HQ}} = 5 \times 10^{-5}$ mol L^{-1}; $C_{CTAB} = 5 \times 10^{-4}$ mol L^{-1}; $C_{NaC} = 5 \times 10^{-4}$ mol L^{-1}; $V_{Extracting\ solution} = 0.1$ mL; $C_{buffer} = 2.5 \times 10^{-2}$ mol L^{-1}, pH 5.80; $C_{Al(III)} = 24.95$ μg L^{-1}. Other experimental conditions are described under procedure.

4. Analytical figures of merit

The limit of detection (LOD) of the proposed method was studied under optimal experimental conditions by applying the General Procedure for blank solutions. The detection limits based on three times the standard deviations of the blank (N = 15), was 0.281 μg L^{-1}. The calibration graph is linear in the range 0.853–79.87 μg L^{-1} for Al(III). Table 1 summarizes the main characteristics of calibration plot and the optimized experimental conditions, which sustain the proposed procedure for metal traces quantification.

The proposed method characteristics have been compared with those of other methods. Table 2 compares analytical quality parameters of the proposed method with those reported previously for Al(III) determination.

It was shown that the proposed method is comparable in detection limit to the previous studies for single element determination. Therefore, CPE combined with fluorescence detection is a very simple and sensitive method for the preconcentration and determination of Al(III).

Other parameter related to analytical performance, the consumptive index (CI = sample volume/EF) defined as the sample volume, in milliliters, consumed to reach an unit of enrichment factor, was calculated for optimized methodology given a value of 0.02 mL (water samples) and 2×10^{-4} mL for studied biological samples.

Taking into account that all samples were simultaneously processed, the frequency of analysis was 20 samples h^1 approximately, being the total sampling time controlled by the step heating [28].

4.1. Interferences study

Cations that may react with 8-HQ or reagents that can react with the analyte could decrease the extraction efficiency. Thereby, the effect of foreign ions on the recovery of Al(III) was tested. Different amounts of ions that are commonly present in samples were added to the test solution containing 24.95 μg L^{-1} of Al(III), and the General Procedure was applied. An ion was considered as interferent, when it caused a variation in the fluorescent signal of the test system greater than ±5%. The tolerance limits of various foreign ions are given in Table 3. These results demonstrate that excess amounts of some common cations and anions do not interfere on the determinations of the analyte, putting in evidence the adequate selectivity of the developed methodology. However, Fe(III) and Cu(II) can interfere with the determination of Al(III) even in a ratio 1/1. The foreign ions can be removed adding masking agents as ascorbic acid and 1,10-phenanthroline, that form strong hydrophilic complexes.

5. Applications. Aluminium determination in biological fluids and water samples

The usefulness of the proposed method was evaluated for the determination of the analyte in biological samples (blood plasma, serum and urine), tap water samples and beverages. Attending to the absence of matrix interference and analite concentration level, tap water samples were used without previous dilution. Thereby, 1 mL of each water sample was treated as it was indicated in General Procedure. The other samples were adequately diluted considering two aspects, the instrumental sensitivity and the reduction of matrix effect. The accuracy of the methodology was carried out using the standard addition method and was

Table 4
Recuperation and validation studies by aluminium determination in water samples.

Sample[a]	Al(III) added (μg L^{-1})	Proposed methodology			ETAAS	%RE[c]
		Al(III) found ± CV (μg L^{-1})	Recovery (%, n = 3)	Real Al(III) contents (μg L^{-1})[b]	Al(III) found ± SD (μg L^{-1})	
1	–	3.16 ± 0.01	–	0.948	0.926 ± 0.01	2.37
	9.98	12.93 ± 0.10	93.35			
	24.95	28.41 ± 0.18	109.49			
2	–	4.06 ± 0.16	–	1.22	1.29 ± 0.02	5.42
	9.98	14.62 ± 0.19	114.29			
	24.95	28.90 ± 0.17	97.29			
3	–	8.31 ± 0.25	–	2.493	2.19 ± 0.02	13.8
	9.98	18.70 ± 0.19	104.94			
	24.95	33.02 ± 0.22	97.11			
4	–	4.00 ± 0.01	–	1.20	1.33 ± 0.01	9.77
	9.98	14.52 ± 0.02	113.50			
	24.95	28.73 ± 0.01	94.50			
5	–	4.81 ± 0.09	–	1.443	1.48 ± 0.01	2.5
	9.98	14.88 ± 0.12	101.87			
	24.95	29.82 ± 0.17	101.25			
6	–	4.23 ± 0.14	–	1.269	1.36 ± 0.01	6.7
	9.98	14.16 ± 0.21	98.82			
	24.95	29.21 ± 0.15	100.71			

1 - Tap water (Campus Universidad Nacional de San Luis, San Luis, Argentina).
2 - Tap water (San Luis city zone south, Argentina).
3 - Local mineral water A.
4 - Local mineral water B.
5 - Local mineral water C.
6 - Local mineral water D.
[a] Volumen = 1 mL.
[b] Real Al(III) contents (μg L-1) = Al(III) found (μg L^{-1}) × fd.
[c] %RE = 100 × (|measured value − actual value|)/actual value.

Table 5
Recuperation and validation studies by aluminium determination in biological samples.

Sample[a]	Al(III) added ($\mu g\ L^{-1}$)	Proposed methodology		
		Al(III) found ± CV ($\mu g\ L^{-1}$)	Recovery (%, n = 3)	Real Al(III) contents ($\mu g\ L^{-1}$)[b]
Plasma	–	14.76 ± 0.37	–	
	9.98	25.87 ± 0.15	107.65	0.449
	24.95	39.27 ± 0.22	97.02	
Serum	–	14.81 ± 0.38	–	
	9.98	24.38 ± 0.49	97.23	0.444
	24.95	39.93 ± 0.19	101.15	
Urine	–	9.60 ± 0.33	–	
	9.98	18.72 ± 0.62	91.04	0.288
	24.95	34.90 ± 0.35	103.65	

[a] Volume = 100 μL diluted to 10 mL with ultrapure water. General Procedure was applied to 100 μL of each diluted sample.
[b] Real Al(III) contents ($\mu g\ L^{-1}$) = Al(III) found ($\mu g\ L^{-1}$) × fd.

validated by ETAAS. The sample aliquots were spiked with increasing amounts of Al(III). A comparison using *t*-test at 95% confidence interval demonstrates that there is no significant difference among the achieved results using the proposed method and the ET-AAS method. The reproducibility of the method was evaluated repeating the proposed methodology, 4 times for each sample. Table 4 y Table 5 show the recovery results Al(III) achieved for each sample. The obtained results indicate that the proposed method is suitable for determination of this analyte in the studied samples.

6. Conclusions

A new ternary surfactant system as a separation and preconcentration strategy has been developed and proposed for determination of Al(III) traces. Bile salt like NaC, cationic surfactant, CTAB and nonionic surfactant, PONPE 5.0 in CPE scheme shows advantages respect to the nonionic surfactant extraction. The use of 8-HQ as fluorescent chelant reagent for Al(III) permitted the determination of analyte in tap and beverage waters and biological fluids (plasma, serum and urine), and potentially applicable to other complex samples. Results were validated by ETAAS with an adequate concordance. The method is selective showing low limit of detection and satisfactory a SD. It constitutes a green alternative of conventional preconcentration methods with additional advantages including low cost, safety and an efficient extraction. The analyzed samples exhibited Al(III) levels lower than 0.2 mg L^{-1} according to the with Argentinian food legislation. The proposed methodology represents a contribution for routine analysis in clinical and chemical laboratories for accurate determination of aluminium in studied samples.

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