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Mixed Micelle-mediated Extraction and Separation of Scandium from Yttrium and Some Lanthanide Ions

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A simple mixed-micelle mediated extraction was elaborated for the preconcentration and determination of scandium(III) by inductively coupled plasma optical emission spectrometry. Scandium(III) was complexed with Alizarin Red S and cetyltrimethylammonium bromide at pH 3 to form hydrophobic chelates, which could be extracted with Triton X-114 at room temperature (25°C) in the presence of KI as a salting-out electrolyte. The main parameters of the extraction procedure were investigated in regard to the extraction efficiency of scandium(III). Under the optimum conditions, a linear range of 0.5 – 150 ng mL^{-1} and a detection limit of 0.2 ng mL^{-1}, along with a preconcentration factor of 100, were achieved. Furthermore, the interference of diverse ions accompanying scandium(III) was extensively studied. The obtained results indicate the high selectivity of the proposed procedure. The accuracy of the procedure was verified through recovery experiments on spiked water samples and synthetic mixtures. The procedure was successfully applied to a scandium(III) determination in clay samples.

Keywords Scandium, mixed micelle-mediated extraction, Alizarin Red S, clay samples

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Introduction

Scandium (Sc) has become an ever more important metal in high-technology fields and other sophisticated applications. The scarcity of scandium makes it a very expensive metal. The growing demand of scandium is due to its important application in laser glass,[1] catalysis,[2] electronic components, nuclear technology, alloys, high-intensity metal halide lamps, solid oxide fuel cells and metallurgical industry.[3]

Scandium is found in nature together with yttrium (Y) and lanthanides because of their similar physicochemical properties, so it cannot be easily recovered.[4] Also, the low level of the scandium concentration in different matrices makes its direct determination by instrumental techniques difficult.

Various chromogenic reagents have been used for the spectrometric determination of Sc(III), including, Alizarin Red S,[5] Arsenazo-III,[6] Nile Blue[7] and Bromopyrogallolo Red.[8] These spectrometric methods show a lack of selectivity and sensitivity.

Consequently, the development of analytical methods for the selective separation of and preconcentration of Sc(III) traces in various matrices is mandatory to improve the detection limit and to achieve accurate determination with several analytical techniques. Many strategies have already been proposed for the separation and determination of scandium, including solid-phase extraction (SPE), solvent extraction (SE) followed by different determination techniques,[9-15] electrophoresis,[16] high-performance liquid chromatography (HPLC),[17] ion exchange, flotation and cloud point extraction (CPE) with spectrometric detection.[18-20]

CPE is an alternative powerful separation technique that has been demonstrated to have the distinct merits of simplicity, speed, higher extraction and excellent preconcentration factors. Also, a simple combination of CPE with different analytical instruments allows for elaborating highly sensitive analytical methods.[21]

Moreover; it complies well with the principles of green chemistry.[22] Thus, the use of CPE for the separation and preconcentration of metal ions from different matrices is of continuing interest.[23-25] CPE occurs in surfactant micellar solutions that become turbid when heated to a certain temperature, known as the cloud point temperature (CPT), or by the addition of a salting-out electrolytes, thus forming a two-phase system.[21] In order to accomplish both ideal hydrophobic and non-ideal electrostatic interactions, a mixed micelle-mediated extraction (mixed-MME) system has been used. The interaction of an ionic surfactant with a charged complex leads to the formation of neutral molecules that could be extracted by a non-ionic surfactant.[26,27] Therefore, a mixed-MME system is becoming important for the separation and preconcentration of many metal ions.[28,30] It is worth mentioning that the use of CPE for the preconcentration of Sc(III) is rarely reported in the literature of specialization. Furthermore, the mentioned procedure is used for the preconcentration of Sc(III) and Y(III) together; also, it suffers from a high CPT and a long time elapsed.[20]

In this study, a simple, low-CPT and rapid CPE procedure has been suggested for the selective separation of scandium from yttrium, some lanthanide ions and other commonly encountered matrix components prior to its determination using inductively

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coupled plasma optical emission spectrometry (ICP-OES). The procedure is based on the complexation of Sc(III) with Alizarin Red S (ARS) at pH 3 using an ionic surfactant, cetyltrimethylammonium bromide (CTAB). The formed complex is extracted with Triton X-114 as non-ionic surfactant at room temperature (25°C) in the presence of KI as a salting-out electrolyte. The effects of various experimental parameters were investigated and optimized. The developed procedure was successfully applied to the separation, preconcentration and determination of Sc(III) in real clay and water samples as well as synthetic mixtures.

Experimental

Instrumentation

All ICP-OES measurements were performed with a Perkin Elmer ICP-OES (Optima 8300, USA). The instrumental operating parameters are summarized in Table 1. A PANalytical Axios Advanced XRF was used for clay samples (clay 1, clay 2 and clay 3) analysis (Table 2). The pH of the solutions was adjusted by a Hanna pH meter, Model 8519 (Hanna Instruments, Germany). A thermostatic water bath maintained at a desired temperature was employed for cloud-point experiments. A CH90-2 centrifuge (Hinotek Technology Co. Ltd., China) was utilized to accelerate the phase separation.

Reagents and solutions

Unless otherwise specified, all reagents used were of analytical reagent grade. Double-distilled water was used throughout the experimental work. Stock solutions of 1000 μg mL^{-1} scandium, yttrium and lanthanide ions were prepared by dissolving an appropriate amount of their pure oxides (BDH, England) in a few milliliters of perchloric acid and evaporating to dryness. The resulting residues were dissolved in double-distilled water and standardized by EDTA titration. Working standard solutions were freshly prepared by suitable dilutions. A solution of 5×10^{-3} mol L^{-1} of ARS (Merck, Germany) was prepared by dissolving 1.8 g of $C_{14}H_7NaO_7S \cdot H_2O$ in double-distilled water and diluting to 1000 mL. The surfactants, Triton X-114 and CTAB, were purchased from (Sigma-Aldrich, USA and Acros Chemicals, Ottawa, ON, Canada, respectively) and were used without further purification. Solutions of different pH ranging from 1 to 2.5 were prepared with hydrochloric acid–sodium acetate (1 mol L^{-1}) and from pH 3 to 7 with acetic acid–sodium acetate 0.2 mol L^{-1} using double-distilled water. Appropriate concentrations of interfering ions were prepared by dissolving their nitrate salts in double-distilled water. A masking mixture to be used during the analysis of real samples and synthetic mixtures was prepared by mixing equal volumes of (0.05 mol L^{-1} ascorbic acid and 5×10^{-3} mol L^{-1} NaH_2PO_4).

Table 1 Optimized conditions for ICP-OES measurements

RF generator power/W	1350
Plasma gas flow rate/L min^{-1}	15
Auxiliary gas flow rate/L min^{-1}	0.2
Nebulizer gas flow rate/L min^{-1}	0.45
Pump rate/mL min^{-1}	2.5
Sample uptake rate/mL min^{-1}	2.5
Delay time/s	7
Integration time/s	3
The number of measurements	3
Wavelength/nm	Sc 361.384,Y 324.228, Gd 335.047, Sm 330.639, Nd 401.225, La 408.672

General procedure

For CPE, an aliquot of a standard solution containing Sc(III) in the range of 0.5 – 150 ng mL^{-1} was transferred to a 50-mL centrifuge tube. After a pH adjustment with 5 mL of acetate buffer (pH 3), 1 mL of 5×10^{-3} mol L^{-1} ARS, 1 mL of 5×10^{-3} mol L^{-1} CTAB and 5 ml of 1 mol L^{-1} KI were added. Then, 2 mL of (2.5% w/v) Triton X-114 was introduced, and the final volume of the solution was adjusted to 50 mL using double-distilled water. The solution was shaken well until it became turbid at room temperature (25°C). It was found that shaking for 3 min is sufficient to turn the solution turbid. Afterwards, separation into two phases was accomplished by centrifugation at 3500 rpm for 10 min, followed by keeping the tubes in an ice bath for 5 min to increase the viscosity of the surfactant-rich phase, so that the aqueous phase could be easily separated from the surfactant-rich phase by decantation. Finally, the surfactant-rich phase was dissolved and diluted to 0.5 ml with HNO_3 (65%, w/w) to reduce its viscosity and to increase the sample volume for the ICP-OES measurement. The blank solution was submitted to the same procedure and measured parallel to the samples.

Procedure for real samples and synthetic mixtures

Clay samples. Three clay samples (different locations in El-Minya Governorate, Egypt) were delivered from the Geology Department, Faculty of Science, Mansoura University.

Powdered clay samples were dried at 100°C for 2 h and homogenized. For decomposition, 5 ml of aqua regia was added to 0.20 g of each sample in a Teflon cup, and the mixture was slowly heated to dryness. This step was repeated twice using another 5 mL of aqua regia every time. To dissolve the residue, 5 mL of concentrated HF was added, followed again by heating to almost dryness. Then, 1 mL of concentrated H_2SO_4 was added dropwise and heated to volatilize any excess HF. The dissolved samples were transferred into 100 mL volumetric flasks and diluted to the mark with double-distilled water. The work solutions used were prepared by appropriate dilution. Five milliliters of each sample solution were transferred to 50 mL centrifuge tubes, and 2 mL of the masking mixture was added.

Table 2 Composition of clay samples with XRF analysis

	Component, %										Component/μg g^{-1}						
	Fe_2O_3	MgO	Na_2O	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Cr_2O_3	MnO	Ba	Ni	Zr	Sr	Nb	Y	Sc
Clay 1	10.66	3.29	0.7	10.55	52.34	0.45	1.27	3.48	0.013	0.09	270	33	810	234	30	40	10
Clay 2	6.04	1.62	1.81	21.4	47.77	0.1	0.79	0.06	0.017	—	159	22	253	114	44	26	17
Clay 3	6.02	1.48	1.31	18.86	51	0.07	1.36	0.65	0.016	0.01	212	—	344	275	36	17	15

LOI%: clay 1, 16; clay 2, 19.1; clay 3, 18.

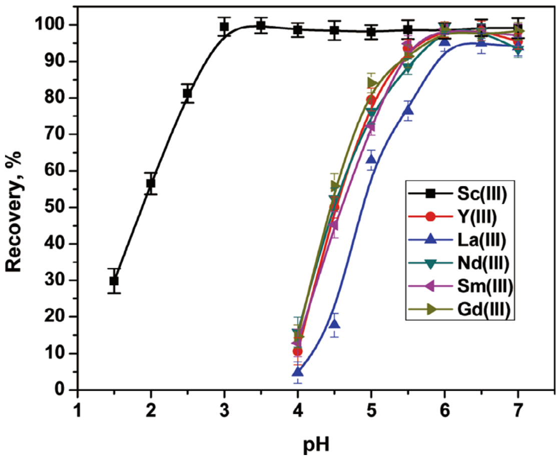

Fig. 1 Effect of the pH on the extraction recovery of Sc(III), Y(III), La(III), Nd(III), Sm(III) and Gd(III). Conditions: 50 ng mL^{-1} metal ion; 1.0×10^{-4} mol L^{-1} ARS; 0.1 mol L^{-1} KI; 0.1% w/v Triton X-114; 1.0×10^{-4} mol L^{-1} CTAB; centrifuge time, 10 min.

Finally, the general procedure described above was applied.

Water samples. Tap, river and mineral-water samples from different locations in Egypt were filtered through a 0.45-µm pore size membrane filter to remove any suspended solids. Then, 25 mL water samples were taken into 50 mL centrifuge tubes and the general procedure given above was applied without any further treatment.

Synthetic mixtures. Solutions of different synthetic mixtures were prepared by choosing the concomitant metal ions, which are usually accompanied Sc(III) in its ores. Adequate volumes of these interfering ions and Sc(III) were transferred to 50 mL centrifuge tubes, and 2 mL of the masking mixture was added. The general procedure was then applied as previously described.

Results and Discussion

Effect of pH

Since the pH is one of the most important parameters concerning chelate formation and subsequent extraction, it was the first variable optimized in the extraction procedure. The influence of the pH on the extraction of Sc(III), Y(III) and some lanthanide ions was investigated over the pH range 1.5 – 7 (Fig. 1). It is obvious that the extraction of Y(III), La(III), Nd(III), Sm(III) and Gd(III) started above pH 4, and reached its maximum at around pH 6, while the optimum pH for extraction of Sc(III) occurred at pH ≥3. These results indicate that the selective separation and determination of Sc(III) can be achieved by performing the extraction at pH 3. Hence, a pH 3 buffer solution was used for all subsequent studies.

Effect of the ARS concentration

The efficiency of CPE depends on the hydrophobicity and the concentration of the ligand. Since the presence of a sulfonate group in the ARS moiety increases the hydrophilic character of the formed chelates, the effective CPE of Sc(III) was performed in the presence of cationic and non-ionic surfactants.

The effect of the ARS concentration on the extraction efficiency of 50 ng mL^{-1} Sc(III) was examined in the range of 2.0×10^{-5} – 2.0×10^{-4} mol L^{-1} ARS, while keeping all other experimental parameters constant. The data presented in Fig. 2 show that the extraction efficiency increased by increasing the ARS concentration up to 1.0×10^{-4} mol L^{-1}, and remained nearly constant at higher concentrations. A concentration of 1.0×10^{-4} mol L^{-1} ARS was selected as being the optimum.

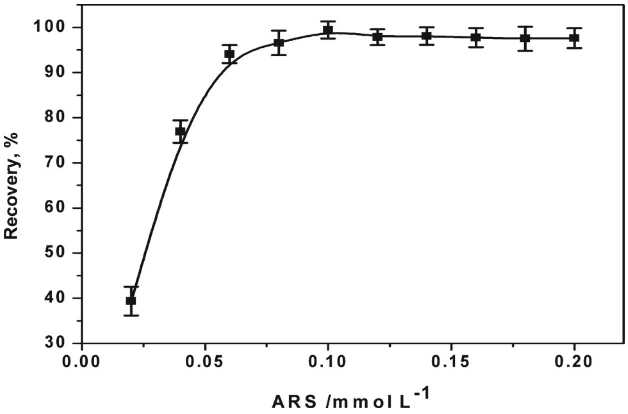

Fig. 2 Effect of the ARS concentration on the extraction recovery of Sc(III). Conditions: 50 ng mL^{-1} Sc(III); pH 3; 0.1 mol L^{-1} KI; 0.1% w/v Triton X-114; 1.0×10^{-4} mol L^{-1} CTAB; centrifuge time, 10 min.

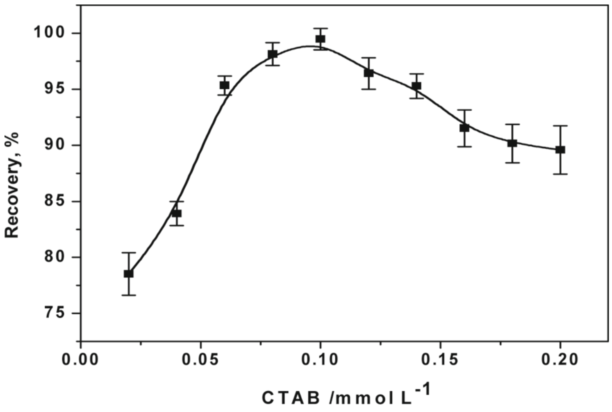

Fig. 3 Effect of the CTAB concentration on the extraction recovery of Sc(III). Conditions: 50 ng mL^{-1} Sc(III); pH 3; 0.1 mol L^{-1} KI; 0.1% w/v Triton X-114; 1.0×10^{-4} mol L^{-1} ARS; centrifuge time, 10 min.

Effect of the ionic surfactant concentration

Mixed micelle formation depends on the cationic and nonionic surfactant concentrations and on the balance between these factors. It was observed that the extraction efficiency of Sc(III) is greatly enhanced by the presence of a cationic surfactant (CTAB). This is may return to the sufficient hydrophobicity of the (Sc(III)-ARS-CTAB) complex, which can be easily extracted by non-ionic surfactants (Triton X-114).

Therefore, the effect of the CTAB concentration on the extraction efficiency was evaluated throughout a wide range of concentrations (2.0×10^{-5} – 2.0×10^{-4} mol L^{-1}). As shown in Fig. 3, the extraction efficiency increased by increasing CTAB concentration up to 1.0×10^{-4} mol L^{-1}. By increasing the CTAB concentration, it can induce a charge in the micelles, while creating repulsion among the micelles, which makes them more hydrophilic, leading to a decrease in the extraction efficiency.[31] Therefore, a concentration of 1.0×10^{-4} mol L^{-1} of CTAB, was chosen for further studies.

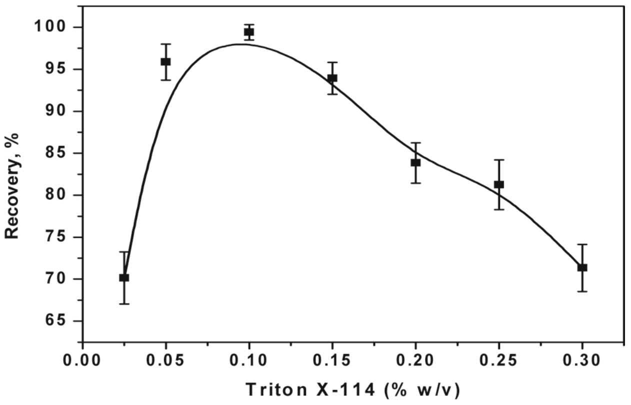

Fig. 4 Effect of the Triton X-114 concentration (% w/v) on the extraction recovery of Sc(III). Conditions: 50 ng mL^{-1} Sc(III); pH 3; 0.1 mol L^{-1} KI; 1.0×10^{-4} mol L^{-1} CTAB; 1.0×10^{-4} mol L^{-1} ARS; centrifuge time, 10 min.

Effect of the non-ionic surfactant concentration

For a low cloud-point temperature and high density of the surfactant-rich phase, Triton X-114 was chosen as a surfactant for the extraction.[32] Moreover, to develop a successful CPE procedure with the maximum extraction efficiency and the minimum volume of the surfactant-rich phase, optimization of Triton X-114 concentration is required. Hence, the effect of the Triton X-114 concentration on the extraction efficiency was investigated in the range of 0.02 – 0.30% (w/v). As shown in Fig. 4, the extraction efficiency increased by increasing the Triton X-114 concentration up to 0.1% (w/v). With a further increase of the Triton X-114 concentration, the signals decreased due to the increment in the overall volume and the viscosity of the surfactant phase.[33] Therefore, a concentration of 0.1% (w/v) Triton X-114 was chosen.

Effect of electrolytes on the cloud-point temperature and the extraction efficiency

It was reported that the cloud-point temperatures of mixed surfactant systems decrease with the addition of small amounts of electrolytes (salting-out effect).[26,34] Accordingly, to achieve separation as efficiently as possible at lower cloud-point temperatures, several additives including (KI, KNO_3, KCl and Na_2SO_4) in the concentration range of (0.1 – 1 mol L^{-1}) were investigated. It was found that the addition of KI up to 0.1 mol L^{-1} resulted in clouding phenomena at room temperature (25°C), and better separation of Sc(III) than other electrolytes. Consequently, a 0.1 mol L^{-1} of KI was used in the further experiments.

Effect of the centrifugation time

To achieve easy separation of the surfactant-rich phase, the centrifugation time was optimized. The effect of the centrifugation time upon the extraction efficiency was examined in the range of 5 – 20 min at 3500 rpm. Complete phase separation was achieved after 10 min. Hence, this time was selected during this work.

Selectivity of the proposed procedure

To assess the selectivity of the developed procedure, the effect of different concentrations of diverse ions on the separation and determination of 100 ng mL^{-1} Sc(III) was tested under the optimized conditions. The tolerance limit was set as the amount of foreign ions causing a deviation greater than ±5% in the recovery percentage of Sc(III). This study is directed to obtain real advantages in terms of the selectivity by studying the effect of the pH and the use of masking agents on the interference caused by different ions.

The presence of large amounts of commonly occurring cations and anions as well as some masking agents has no obvious influence on the separation and determination of Sc(III) under the optimum work conditions. Therefore, 2500-fold Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, I^-, NO_3^-, SO_4^{2-}, thiocyanate, thiourea, thiosulfate, acetate, L-ascorbic acid and 400 fold PO_4^{3-} do not affect the extraction.

ARS forms stable complexes with various metal ions, including many lanthanides and transition-metal ions. At pH 3, it was noticed that the separation of Sc(III) was proved to be highly selective, since the separation of many lanthanide and transition metal alizarinate complexes occurs at different pH ranges. Thus, 1000 fold Mn^{2+}, Hg^{2+}, Cd^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+} and 250 fold La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Y^{3+} ions do not interfere with the extraction.

Furthermore, metal ions that react with ARS-CTAB at pH 3 and cause interference are masked by the addition of suitable masking reagents. A 1000-fold of Fe(III) could be tolerated by reducing it to Fe(II) using L-ascorbic acid. Also, the interference of a 400-fold Al^{3+} and a 250-fold UO_2^{2+}, Zr^{4+}, Hf^{4+} were eliminated using NaH_2PO_4 as a masking agent.

Fluoride, oxalate and citrate decrease the reactivity of scandium with ARS-CTAB when present in a 50-fold excess. The effect of these ions could be minimized by a prior digestion of samples in the presence of potassium persulfate and sulfuric acid.

It can be deduced that the developed procedure has the potential to be applied to analyze real samples with high accuracy and precision.

Analytical features

Under the optimized conditions, the calibration curve for Sc(III) is found to be linear in the range of 0.5 – 150 ng mL^{-1} with a correlation coefficient (R^2) of 0.9976, which indicates good linearity in the studied range. The limit of detection (LOD) and the limit of quantification (LOQ) were estimated to be $C_{\text{LOD}} = 3S_{\text{B}}/m$ and $C_{\text{LOQ}} = 10S_{\text{B}}/m$, respectively (where S_{B} was obtained from the standard deviation for 10 replicate measurements of a blank solution, and m is the slope of the calibration graph). By using the foregoing formula 0.2 and 0.66 μg mL^{-1} are obtained for LOD and LOQ, respectively. Since the amount of the Sc(III) in 50 mL of sample solution is measured after CPE in a final volume of 0.5 mL, the solution is preconcentrated by a factor of 100. The precision of the method, calculated as the relative standard deviation (RSD) of 10 replicate measurements of 50 ng mL^{-1} of Sc(III), was 2.94%.

A comparison between the analytical features of the proposed procedure and other procedures previously reported in the literature are presented in Table 3.

Analytical application of the proposed procedure

The accuracy of the proposed method was assessed by recovery experiments in spiked water samples and several synthetic mixtures. The results are given in Tables 4 and 5. A good agreement was obtained between the added and measured analyte amounts. The recovery of the analyte is in the range of 98 – 103%, thus confirming the high accuracy of the procedure and its capability in the preconcentration and determination of Sc(III) in real samples.

To demonstrate the potential applicability of the developed procedure, separation and determination of Sc(III) in different

Table 3 Comparison of the proposed CPE procedure with other published methods in the literature for the separation and determination of Sc(III)

Method	Detection technique	LOD	pH	Linearity	Sample	Reference
Sorption on a minicolumn packed with oxidized multiwalled carbon nanotubes	ICP-OES	4 ng L^{-1}	1.5	Up to 10 mg L^{-1}	Acid drainage	11
Preconcentration in a minicolumn packed with Amberlite XAD-4 resin impregnated with nalidixic acid	Spectrometry	0.32 ng mL^{-1}	4.5	5 - 25 ng mL^{-1}	Lake sediment and water samples	12
Flotation using 2-hydroxybenzylidenethiosemicarbazone (HBT) as complexing agent and oleic acid as surfactant	Spectrometry	—	5	—	Synthetic mixtures, stream sediment and water samples	19
Sorption on a minicolumn packed with activated carbon	ICP-OES	4.0 ng mL^{-1}	7	—	River water samples	10
Solid phase extraction using silica gel modified with 4-(2-morinyldiazenyl)-*N*-(3-(trimethylsilyl)propyl)-benzamide	ICP-AES	0.085 μg g^{-1}	3	—	Shrubbery leaves, Tibet soil and kaolin ore samples	9
CPE using ARS as complexing agent and mixed surfactant (CTAB and Triton X-114) in the presence of KI at room temperature	ICP-OES	0.2 ng mL^{-1}	3	0.5 - 150 ng mL^{-1}	Water, clays samples and synthetic mixtures	Present work

LOI%: clay 1, 16; clay 2, 19.1; clay 3, 18.

Table 4 Determination of Sc(III) in spiked water samples by the proposed procedure

Sample	Sc(III)/ng mL^{-1}		Recovery, %
	Added	Found^a	
Tap water	5	4.91 ± 0.11	98.2
	10	10.12 ± 0.06	101.2
River water	5	5.10 ± 0.08	102.0
	10	10.16 ± 0.13	101.6
Mineral water	5	5.14 ± 0.12	102.8
	10	9.92 ± 0.13	99.2

a. The results are the mean of five measurements ± standard deviation.

Table 5 Recovery of 20 ng mL^{-1} Sc(III) in synthesized mixtures in the presence of 100 ng mL^{-1} of each interfering ion

Synthetic mixture	Found/ng mL^{-1} ^{a}	Recovery, %
Fe(III), Al(III), Sr(II), Ba(II)	20.55 ± 0.76	102.75
UO$_2$(II), Zr(IV), Y(III), Co(II)	20.41 ± .78	102.05
Fe(III), Gd(III), Nd(III), La(III)	19.90 ± 1.28	99.50
Mg(II), Sm(III), La(III), Y(III)	20.60 ± 0.91	103.00

a. The results are the mean of five measurements ± standard deviation.

Table 6 Analytical results of Sc(III) analysis in clay samples measured by XRF and ICP-OES

Sample	XRF/ μg g^{-1}	ICP-OES^a/ μg g^{-1}	*t*-test, critical = 2.57
Clay 1	10	9.98 ± 0.24(2.41)	0.19
Clay 2	17	17.13 ± 0.46(2.68)	0.63
Clay 3	15	15.12 ± 0.37(2.45)	0.72

a. The results are the mean of five measurements ± standard deviation (RSD %).

clay samples were attempted. The results of the proposed procedure obtained by ICP-OES were compared with those obtained by solid XRF (Table 6). A statistical treatment of these data, applying the t-test approach of the 95% confidence level and $n = 5$ showed that the calculated values did not exceed the tabulated values.

Conclusions

The proposed CPE procedure based on mixed micelle mediated is well suited for the selective separation of scandium a prior step to its determination by ICP-OES. The use of the proposed procedure provides a low detection limit, very good sensitivity, capability to cause clouding at room temperature with a high extraction efficiency, precision and accuracy. Furthermore, under the optimum working conditions the interference of the encountered matrix components was highly tolerated which makes the procedure highly selective for Sc(III). Additionally, the proposed procedure was verified with real samples, and the obtained results showed that the procedure represents a promising approach for the simultaneous determination of Sc(III) in very complex matrices.

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