

Spectrophotometric determination of samarium(III) with chrome azurol S in the presence of cetylpyridinium chloride[☆]

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Received 28 September 1999; received in revised form 25 February 2000; accepted 3 March 2000

Abstract

A sensitive, simple method for the determination of trace amounts of samarium by spectrophotometry is described based on the formation of the samarium–chrome azurol S (CAS) complex in micellar medium. The molar absorptivities of the complexes at pH 7.5 at 505 nm were 3.6×10^4 and 1.4×10^5 l mol⁻¹ cm⁻¹ for water media and cetylpyridinium chloride (CPC), respectively. Beer's law is obeyed from 0.05–2 mg l⁻¹ of samarium at 505 nm as Sm–CAS–CPC complex. Optimal conditions such as reagent amounts, and pH for the samarium determination were reported. The effects of foreign ions were also investigated. The proposed method was successfully applied to the determination of samarium contents in synthetic samples. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Spectrophotometry; Samarium(III); Chrome azurol S; Cetylpyridinium chloride

1. Introduction

Samarium is used in the electronic, glass, laser, electrical, nuclear and ceramics industries. For example, samarium is used in the nuclear industry as an absorber, used to dope CaF₂ crystals for use in optical masers or lasers. Samarium oxide is catalytic for the dehydration and dehydrogenation of ethanol. Its compounds act as sensitizers for phosphors excited in the infrared [1–3]. Sa-

marium is easily magnetised and is very difficult to demagnetise. This suggests important future solid state and superconductor applications [4,5]. There are many spectrophotometric methods described for the determination of samarium(III) with various organic reagents [6–10].

Chrome azurol S (CAS) is an organic colorimetric reagent which has some desirable characteristics such as high complex formation constants with metal ions, and high molar absorptivities and selectivity of the complex formations with metal ions. CAS provides the basis for sensitive methods for the determination of various elements [11–13]

Surfactants have been used in the development of new methods for colorimetric analysis of metal

[☆] This paper was presented at Colloquium Spectroscopium Internationale XXXI Ankara, Turkey.

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ions. Various methods have been described for the spectrometric determination of metal ions in a micellar medium. The addition of cationic, anionic and nonionic surfactants significantly enhances the sensitivity of the analysis. Cetylpyridinium chloride has been used for the spectrophotometric determination of many metal ions as surfactant [12,13].

In the present work, a sensitive and simple method for the determination of trace amounts of samarium(III) by spectrophotometry is described based on the formation of the samarium(III)–chrome azurol S complex in micellar medium. The method was applied to the determination of samarium in synthetic samples.

2. Experimental

2.1. Apparatus

A Hitachi Model 150-20 UV-VIS double beam spectrophotometer with a 10-mm optical path cell was used for spectrophotometric measurements. The measurements for samarium(III)–chrome azurol S–cetylpyridinium chloride (Sm–CAS–CPC) were performed at 505 nm. A pH meter with a glass and calomel electrode pair (Delta 320 Mettler) was used.

2.2. Reagents and solutions

All chemicals obtained from commercial sources were of super pure grade unless otherwise stated. All aqueous solutions were prepared using doubly distilled water. The samarium stock solution, 1000 mg l^{-1} was prepared from Sm_2O_3 (Sigma, St Louis, MO) in 10^{-3} M HCl . Portions were diluted daily for reference and working solutions.

Borax buffer solution (pH 7.5): 0.1 M sodium hydroxide solution was added dropwise to 0.05 M sodium tetraborate solution (Merck-Darmstadt) to the required pH. Chrome azurol S (CAS) (Sigma, St Louis, MO) solution (0.2% (w/v)) was prepared daily by dissolving in water and adjusting final acid concentration to 10^{-3} M with HCl.

Surfactant solutions: cetylpyridinium chloride (CPC) (Sigma) solution (0.2% (w/v)) and sodium dodecyl sulphate (Sigma) solution (0.2% (w/v)) were prepared in water. Triton X-100 (Sigma) solution (10% (v/v)) was prepared in water.

2.3. General procedure

Ten micrograms of samarium was transferred into a 25-ml calibrated flask and 1.0 ml of 0.2% CAS solution was added. The pH of the solution was adjusted with borate buffer to pH 7.5 and 1.0 ml of 0.2% CPC solution was added. Then the whole solution was mixed and diluted with distilled water to the mark. After 10 min, the absorbance of this solution was measured at 505 nm by spectrophotometer against a reagent blank.

3. Results and discussion

3.1. Absorption spectra

The absorption maxima was obtained for samarium–CAS complex in water at 495 nm. Investigations on the effect of various surfactants on the absorbance of samarium–CAS complex were carried out. The surfactants used were cetylpyridinium chloride as cationic surfactant, sodium dodecyl sulphate as anionic surfactant and Triton X-100 as nonionic surfactant. The study was performed using $10 \text{ }\mu\text{g}$ samarium, $1000 \text{ }\mu\text{l}$ of 0.2% CAS solution and $1000 \text{ }\mu\text{l}$ of surfactant at pH 7.5. The absorbance values and corresponding molar absorptivities at absorption maxima of samarium complexes in these media are given in Table 1.

Table 1
Influences of some surfactants on the absorbance of samarium–CAS complex^a

Surfactant	Type	λ (nm)	ϵ ($\text{l mol}^{-1} \text{ cm}^{-1}$)
Water	–	495	3.6×10^4
Cetylpyridinium chloride (CPC)	Cationic	505	1.4×10^5
Sodium dodecyl sulphate (SDS)	Anionic	500	4.0×10^4
Triton X-100	Nonionic	490	4.8×10^4

^a Sm: $0.4 \text{ }\mu\text{g ml}^{-1}$, $1000 \text{ }\mu\text{l}$ of 0.2% CAS, $1000 \text{ }\mu\text{l}$ of surfactant, pH 7.5.

Enhancement of the absorbance of the complexes occurred only in the presence of cetylpyridinium chloride (CPC). CPC was used as a micellar forming surfactant throughout this work. Addition of CPC was accompanied by a bathochromic shift of the absorbance of the samarium–CAS complex and an increase in its molar absorptivities; 505 nm was selected as the wavelength to be measured. Reagent blank was used thereafter as a reference because it showed absorption at this wavelength.

3.2. Effect of pH

The effect of pH on the formation of the samarium–CAS complex in cetylpyridinium chloride was examined at 505 nm using various buffer solutions of different pH values. The results are given in Fig. 1. The samarium–CAS–CPC complex begins to form at approximately pH 5.5, with maximum absorbance being reached at pH values between 5.8 and 8.0. After pH 8.5, $\text{Sm}(\text{OH})_3$ was formed under experimental conditions. In the light of these findings, all subsequent studies were carried out at pH 7.5 using borax buffer.

3.3. Effect of reagent amount

The effect of chrome azurol S amounts on the formation of samarium–CAS complex in

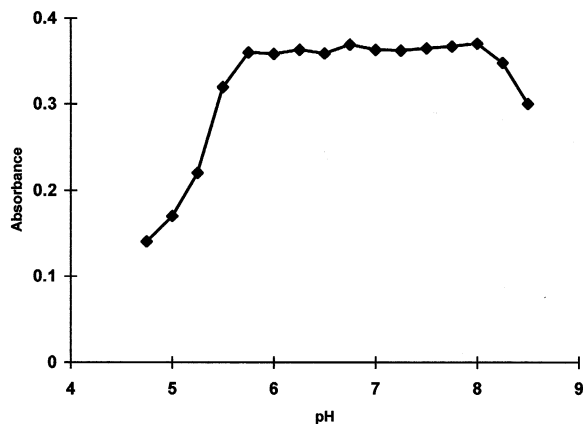


Fig. 1. Effect of pH on the formation of the samarium–chrome azurol S–cetylpyridinium chloride complex (Sm : $0.4 \mu\text{g ml}^{-1}$, 1000 μl of 0.2% CAS, 1000 μl of surfactant, pH 7.5).

cetylpyridinium chloride media was investigated at the optimum pH. It was found that maximum absorbance values were obtained for 0.2% CAS solution in the range of 800–1200 μl . In all studies, 1000 μl of reagent was used.

The effect of cetylpyridinium chloride (CPC) concentration on the absorbance of samarium–CAS complex was also studied at optimum CAS amount and optimum pH. The maximum absorbance values for the complex were obtained in the range of 750–1500 μl of 0.2% CPC solution. All subsequent studies were carried out with 1000 μl of 0.2% CPC at pH 7.5.

3.4. Effect of time on complex formation

The influence of time on the formation of the samarium–chrome azurol S–cetylpyridinium chloride complex was also studied at the optimum conditions. The color development of the complex is complete in 10 min and the color is stable for at least 48 h.

3.5. Calibration graphs and detection limit

A calibration curve was constructed for samarium according to the general procedure described above. Beer's law is obeyed from 0.05 to 2 mg l^{-1} of samarium at 505 nm as a Sm–CAS–CPC complex. The detection limits based on three times the S.D. of the blank were $30 \mu\text{g l}^{-1}$ ($N = 21$) [14]. The R.S.D. for the samarium determinations were 2% ($N = 10$) at $0.4 \mu\text{g ml}^{-1}$ Sm.

3.6. Effect of diverse ions

The interference effects of some anions, cations and metal ions were examined by measuring the absorbance of solution containing 10 μg of samarium(III) in 25 ml of distilled water and various amounts of foreign ions. The tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of samarium. The results are summarized in Table 2. The formation of the Sm–CAS–CPC complex was not influenced by alkaline, earth alkaline ions and some other anions.

Table 2
Tolerable limits of the foreign ions on the determination of samarium as CAS–CPC complex ($N = 4$)

Foreign ion	Tolerable limit [Ion]/[Sm]
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , NH ₄ ⁺	5000
SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻ , CH ₃ COO ⁻ , PO ₄ ³⁻	5000
Fe ³⁺ , Cr ³⁺ , Bi ³⁺	250
Cu ²⁺	200
Pb ²⁺ , Co ²⁺ , Al ³⁺	50
Zn ²⁺ , Cd ²⁺	25
Mn ²⁺ , Ni ²⁺	20

Table 3
Recovery of samarium added to drinking water^a from Erciyes University

Added (µg)	Found (µg)	Recovery (%)
–	N.D.	–
15	14.4	96 ± 2
30	29.4	98 ± 3
45	45.0	100 ± 1

^a Volume: 20 ml; $N = 4$.

Because many complexes were formed between metal ions and chrome azurol S, the influences of metal ions on the formation of the samarium(III)–CAS–CPC complex were also examined. The results are given in Table 2. Because the formation constants of Cr³⁺, Fe³⁺ and Bi³⁺ with EDTA are greater than the formation constants of the Sm–EDTA complex [15], prevention

Table 4
Determination of samarium in synthetic samples by the proposed method ($N = 4$)

Sample	Composition (mg l ⁻¹)	Samarium content (µg ml ⁻¹)	Samarium found (µg ml ⁻¹)
NaCl	1000	0.40	0.38 ± 0.02
EDTA	100		
NaCl	1000	0.80	0.81 ± 0.06
EDTA	100		
NaCl	1000	0.40	0.40 ± 0.03
Fe ³⁺	80		
EDTA	100		
NH ₄ Cl	1000	0.40	0.37 ± 0.03
EDTA	100		

of possible interferences from Cr³⁺, Fe³⁺ and Bi³⁺ were examined using EDTA [11,12].

The effect of EDTA on the formation of the Sm(III)–CAS–CPC complex were examined under the experimental conditions given above. Any interference effect from the addition of EDTA were not observed on the formation of the Sm(III)–CAS–CPC complex. The interference effects of the Cr³⁺, Fe³⁺ and Bi³⁺ were prevented by masking EDTA (Table 2). The interference of copper(II) ions was also prevented by the addition of thiourea [11]. The tolerable levels of Pb²⁺, Co²⁺, Zn²⁺, Cd²⁺, Mn²⁺, Ni²⁺ and Al³⁺ ions are also given in Table 2.

3.7. Accuracy of the method

The accuracy of results was verified by analyzing the concentration after addition of known amounts of samarium into the water sample from Erciyes University after filtering suspended matter by a membrane filter (pore size 0.45 µm, Millipore). As seen from Table 3, good agreement was obtained between the added and found analyte content using the recommended procedure. The recovery values calculated for the standard additions were always higher than 95%, thus confirming the accuracy of the procedure and its independence from matrix effects.

3.8. Analysis of samples

In order to highlight the utility of the proposed method, it was used for the spectrophotometric

determination of samarium contents of some synthetic samples. The results are given in Table 4. Samarium as CAS–CPC complex in the samples is successfully determined by the proposed method.

4. Conclusion

The proposed procedure is sensitive and simple for the spectrophotometric determination of trace amounts of samarium as Sm–CAS–CPC complex that has good stability. Beer's law is obeyed from 0.05 to 2 mg l⁻¹ of samarium at 505 nm as Sm–CAS–CPC complex. The proposed method was successfully applied to the samarium determination in synthetic samples.

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