

Facile spectrophotometric determination of cerium using malachite green –iodide system in geological and environmental samples

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A simple and highly sensitive method is proposed for determination of trace amount of cerium. New method involves bleaching of greenish colour dye-malachite green, by the action of iodine, which is released by reaction between potassium iodide and cerium (IV) in acidic medium. Beer's law is obeyed over concentration range of 0.6 to 4.6 µg cerium (IV) in final volume of 25 ml (0.024-0.184 ppm). Molar absorptivity and Sandell's sensitivity were found to be $1.36 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 0.002 µg cm^{-2} , respectively. New method has been successfully applied for determination of cerium in silicate rocks, high purity rare earth oxides, soil, plant tissue and natural water samples.

Keywords: Ce (IV), Geological and environmental samples, Malachite Green, Spectrophotometry

Introduction

Cerium (Ce) is industrially important and is used in nuclear reactor, in alloy with nickel and chromium; and in microwave devices, lasers, masers and in television sets, besides agriculture, forestry, animal husbandry and in environment. Optimum concentration of some light rare earth elements including Ce are useful in agronomy as well as for environmental pollution assessment or in studies of biochemical processes¹⁻². Ce salts have been used to remedy from vomiting during pregnancy, depressant of central nervous system, astringents and antiseptic. Increasing industrial use and reports on Ce toxicity make it essential to have analytical procedures suitable for monitoring Ce in environmental and related fields³. Atomic absorption spectrophotometry based method lack sensitivity, while those on flame or flameless atomization or fuel rich or fuel deficient flames have proven equally ineffective⁴⁻⁶. Some of recently proposed reagents for determination of Ce (IV) are variamine blue⁷, dibromo p-methyl chloro sulphanazo⁸, propionil promazine phosphate (PPP)⁹, pyrogallol red¹⁰, TPHA¹¹, 2, 4 dihydroxy benzophenone benzoic hydrazone¹², N-p-chlorophenyl p-methoxybenzohydroxamic acid¹³, Arsenazo (III)¹⁴, 4-dimethylamino- azobenzene-42 -

arsonic acid¹⁵, and 2,6-dibromo-4 chloro carboxyarsenazo¹⁶, but method using these reagent are less sensitive and suffer from interference of various ions.

This study presents development of a simple, cost effective, and sensitive method for accurate determination of Ce at microgram level using Malachite Green-iodide system.

Experimental

Apparatus

Absorbance was measured using Systronics 104 digital spectrophotometer with 1 cm matched quartz cell and pH using Systronics 335 digital pH meter.

Reagents

Present method is based on bleaching of Malachite Green (Loba Chemie, Mumbai, India) as 0.05% aqueous dye solution by iodine, which was released by reaction of potassium iodide (KI, 1% aqueous solution) with Ce (IV) in acidic medium (1M HCl aqueous solution). Dye colour was measured at 605 nm. A standard stock (1 mg/ml) of Ce (IV) was prepared by dissolving ceric ammonium sulphate (4.25 g) in water (1 l) and standardized volumetrically²⁰. A suitable volume of this solution was diluted to get working standard Ce (IV) solution. All chemicals used were of Anal R grade. Double distilled deionized water was used throughout experiment.

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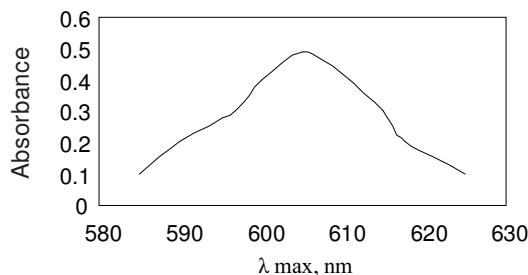


Fig-1—Absorption curve of Ce

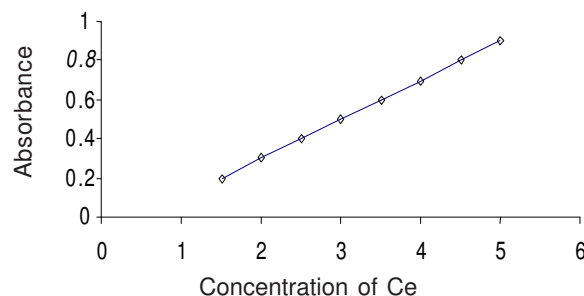


Fig-2—Calibration curve of Ce

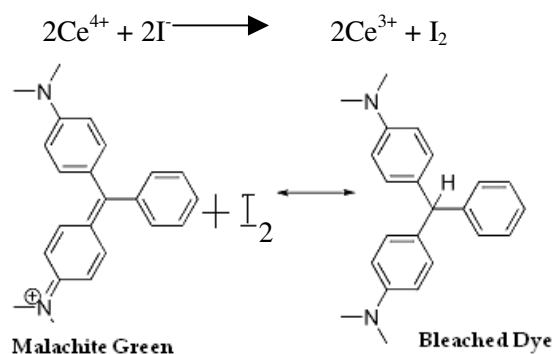
Procedure

An aliquot of a working standard solution [0.6-4.6 μg Ce (IV)] was transferred into a series of 25 ml graduated tube. In each tube, KI (1 ml) was added followed by 1M HCl (1 ml). Mixture was shaken gently till appearance of yellow colour, indicating liberation of iodine. To this, Malachite Green solution (1 ml) was added and shaken for few min and then content of tube were diluted with water up to the mark. Mixture was kept for 10-15 min for completion of reaction. Absorbance was measured at 605 nm against distilled water. A blank was prepared by replacing Ce solution in distilled water. Absorbance corresponding to bleached color, which in turn corresponds to Ce concentration, was obtained by subtracting absorbance of blank solution from that of test solution. Amount of Ce (vol) was computed from calibration graph.

Results and Discussion

Spectral Characteristics

Iodine liberated in reaction of Ce (IV) with KI in acidic medium bleaches green colour of Malachite Green dye and thereby decreases absorbance of dye at 605 nm (Fig. 1), which is directly proportional to Ce concentration. Reagent blank showed maximum absorbance at this wavelength.



Effects of Reagents Concentrations

Constant and maximum difference in absorbance was obtained when KI (1 ml) of 1M HCl and of 0.05% Malachite Green dye (1 ml) were added in described order to get optimum sensitivity. By increasing amount of KI, absorbance remains constant.

Effects of pH, Time and Temperature

Under optimum condition, constant absorbance values were obtained at pH 4.5-5.5; again, constant absorbance values were obtained instantaneously and required no heating. Therefore, determination was carried out at room temperature (30°C) and time taken for completion of reaction was found to be 10 - 15 min. Bleached colour was found to be stable for more than 6 h.

Analytical Data

Adherence to Beer's law was studied by measuring decreased absorbance value of solution by increasing Ce concentration. Straight line graph was obtained by plotting absorbance against Ce concentration. Beer's law was obeyed in concentration range of 0.6-4.6 μg Ce (IV) per 25 ml of final solution (Fig. 2). Molar absorptivity and Sandell's sensitivity for 3.0 μg Ce (IV) per 25 ml were found to be $1.36 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.002 \mu\text{g cm}^{-2}$, respectively. Reproducibility of method was checked by seven replicate measurements, each containing 3.0 μg Ce (IV) per 25 ml of final solution. Standard deviation and relative standard deviation were found to be ± 0.0059 and $\pm 1.2\%$, respectively. Lower relative standard deviation value and range of error at 95% confidence level in terms of absorbance was ± 0.0054 , indicating, good precision and accuracy of the method.

Effect of Foreign Species

Effect of various diverse ions and interfering species on Ce determination by proposed method was examined,

Table 1—Effect of foreign species [3.0 µg of Ce (IV) per 25 ml]

Foreign species	Tolerance limit* ppm	Foreign species	Tolerance limit* ppm
K ⁺ , Ba ²⁺ , Ca ²⁺ , Mn ²⁺ ,	4500	Bi ³⁺ , Ni ²⁺	1000
Cl ⁻ , Br ⁻ , F ⁻		AsO ₄ ²⁻ , Cr ₂ O ₇ ²⁻	950
Te ⁴⁺ , PO ₄ ³⁻ , SO ₄ ²⁻	2600	MoO ₄ ²⁻ , WO ₄ ²⁻	700
		As ³⁺ , Se ⁴⁺ , IO ₃ ⁻	110
Pb ²⁺ , Sn ²⁺ , Sm ³⁺ , Eu ³⁺	2000	CrO ₄ ²⁻	50
Gd ³⁺ , Ho ³⁺ , Tm ³⁺ , Lu ³⁺ ,	1500	Glucose, sucrose, fructose,	3300
Yb ³⁺ , Tl ⁺ , I ⁻		lactose	
Co ²⁺ , Cd ²⁺ , Fe ³⁺ , Cr ³⁺ ,	1150	Oxalate, tartarate	750
Al ³⁺ , Zn ²⁺		Citrate, sodium acetate	550
		Ascorbic acid	300
		Borate	250

*Tolerance limit is the amount of foreign species that causes an error of $\pm 2\%$ in absorbance value

by adding a known amount of compound to a solution containing 3.0 µg Ce (IV) per 25 ml of final solution. Tolerance limit in ppm of interfering species was established as concentration required causing an error of not more than $\pm 2.0\%$ in absorbance of Ce. Most of the common ions and other major toxicants did not interfere in the method under optimum condition (Table 1). Se⁴⁺ and As³⁺ interfere severely. Oxidizing agents (CrO₄²⁻, Fe³⁺, IO₃⁻), if present, also liberate iodine under similar conditions and interfere. However, interference of these ions could be restricted by using appropriate masking agents in analysis of samples (Table 1).

Applications

Proposed method has been successfully applied to Ce determination in geological and environmental samples. International standard rock samples (STM-1, SY-2 and MRG-1) were analyzed by this method and results are in good agreement with certified value. Further, to ensure accuracy and reliability, recovery tests were performed by standard addition of Ce (IV) to various environmental samples. Recovery values obtained were quantitative and in good agreement with reference method⁷ and this shows that method works satisfactorily.

Determination of Cerium in Rock Samples

A known amount of finally ground standard rock samples was opened out by repeated heating with concentrated nitric acid (2 ml) and HCl¹⁷⁻¹⁸. Mixture was treated with 5M sulphuric acid (2 ml) and evaporated to fumes of sulphur trioxide. Residue was leached with water, filtered and diluted to a known volume, after treating it with 5% citrate solution. Then, 10% ammonium per sulphate solution (5 ml) was added, followed by 2-3 drops of 1% silver nitrate solution. It was heated on water bath to oxidize Ce(III), present if any, to Ce(IV). Heating solution destroyed excess persulphate. An aliquot of this sample solution was analyzed by proposed method (Table 2).

Determination of Cerium in High Purity Rare Earth's Oxides

Ce content of various high purity RECs was determined by adding 1:1 HCl (10 ml) to 100 mg of samples and heating this mixture on a hot plate²⁰. After dissolution, solution was neutralized with dilute ammonia and volume was made up to 25 ml with water. Subsequently, suitable aliquots of this sample were taken and subjected to Ce determination. As concentration of Ce was below detection limits, recovery test was performed by addition of standard Ce (IV) solution (Table 3).

Table 2—Determination of cerium in rock samples

Samples	Certified cerium µg/g	Cerium found* µg/g	RSD %
STM-1, 0.1 g/2 ml	800	795 ± 0.93	0.12
SY-2, 0.1 g/5 ml	210	209 ± 0.89	0.42
MRG-1, 0.5 g/5 ml	25	24.8 ± 0.23	0.92

*Mean ± Standard deviation for five replicate

Determination of Cerium in Soil

A known amount air dried homogenized soil sample (1 g) spiked with known amount of Ce (IV) was fused with anhydrous sodium carbonate (5 g) in a silica crucible. Fused mass was dissolved in water (25 ml) and evaporated to dryness. Dried material was dissolved in water, filtered through Whatman filter paper No. 42 into 25 ml calibrated flask, neutralized with dilute ammonia, then diluted to the mark with water. An aliquot was taken and Ce content was determined (Table 3).

Determination of Cerium in Plant Tissues

Plant tissue sample were washed with water, dried at 120°C and homogenized. Sample (1.0 g) was taken and

Table 3—Determination of cerium in various environmental samples

Samples	Ce (IV) added µg	Cerium found					
		Proposed* method, µg	RSD %	Recovery %	Reference* method ¹⁰ µg	RSD %	Recovery %
Gd ₂ O ₃ , 0.5g/5 ml	3.0	2.99 ± 0.030	1.0	99.66	2.98 ± 0.040	1.3	99.33
	7.0	7.01 ± 0.050	0.7	100.14	6.99 ± 0.070	1.0	99.85
La ₂ O ₃ , 0.5g/5 ml	3.0	2.98 ± 0.025	0.8	99.33	2.97 ± 0.030	1.0	99.00
	7.0	6.99 ± 0.080	1.1	99.85	6.96 ± 0.060	0.86	99.42
Dy ₂ O ₃ , 0.5 g/5ml	3.0	3.01 ± 0.042	1.3	100.23	2.98 ± 0.050	1.6	99.33
	7.0	7.02 ± 0.074	1.0	100.28	6.98 ± 0.081	1.16	99.71
Plant ^b tissue, 1 g/ 5 ml	3.0	2.98 ± 0.046	1.5	99.33	2.96 ± 0.030	1.1	98.66
	7.0	6.99 ± 0.087	1.2	99.85	6.97 ± 0.058	0.83	99.57
Soil, 1g/5ml	3.0	2.97 ± 0.037	1.2	99.00	2.95 ± 0.037	1.25	98.33
	7.0	6.98 ± 0.065	0.9	99.71	6.96 ± 0.051	0.7	99.42
Human hair, 0.1g/5ml	3.0	2.99 ± 0.049	1.6	99.66	2.97 ± 0.022	0.74	99.00
	6.0	5.98 ± 0.070	1.1	99.66	5.96 ± 0.130	2.2	99.33
Tap water, 50ml/5ml	3.0	2.98 ± 0.024	0.8	99.33	2.95 ± 0.058	1.9	98.33
	6.0	5.97 ± 0.068	1.1	99.50	5.95 ± 0.081	1.34	99.16

*Mean ± standard deviation for five replicate analyses

Table 4—Comparison of proposed method with other reported spectrophotometric methods

Reagents	Medium/pH	λ max nm	Sensitivity (µ) l mol ⁻¹ cm ⁻¹	Remarks
Variamine blue ¹⁰	2 M HCl	560	1.65x10 ⁴	CrO ₄ ²⁻ , Fe ³⁺ , Cu ²⁺ , IO ₃ ⁻ interfere, colour system is less stable
Propionyl promazine phosphate (PPP) ¹²	1 M H ₃ PO ₄	513	2.11x10 ⁴	Ni ²⁺ , Cu ²⁺ , Fe ³⁺ , Th ⁴⁺ interfere, less sensitive
Tetraethylene pentaamine hepta acetic acid (TPHA) ¹⁷	-	304	4.5x10 ⁴	Absorbance is in UV region, Fe ³⁺ interfere (Less sensitive)
2,4 Dihydroxy benzophenone benzoic hydrazone ¹⁸	pH - 10	400	2.0x10 ⁴	Many metal ions interfere, less sensitive and selective
N-p-Chlorophenyl p-methoxybenzohydroxamic acid ¹⁹	pH 8-10	460	7.2x10 ³	Extractive and less sensitive
Malachite Green (Present work)	1 M HCl	605	1.36x10 ⁵	Simple, highly sensitive, cost effective, higher stability of colour.

heated along with conc. sulphuric acid (5 ml) on a hot plate at 70°C for 5 min; conc. nitric acid was added drop wise until all visible reaction ceased, after which temperature was raised to 100°C and heating was continued for 15 min. Reactant were taken off the plate, and water (25 ml) was added; resultant solution was cooled and made up to a known volume with water in calibrated flask after being neutralized with dilute ammonia. An aliquot of sample solution was analyzed by proposed method. Since Ce content in sample was negligible, synthetic samples were prepared by addition of standard Ce (IV) solution to sample prior to being dissolved (Table 3)

Determination of Cerium in Tap Water

Drinking tap water sample (50 ml) from laboratory was taken and analyzed for Ce. Since all tested negative, known amounts of Ce (IV) were added to sample and Ce content were analysed. Recovery values obtained were close to 100% (Table 3).

Determination of Cerium in Hair

A known amount of human hair was digested with 10 ml mixture of HCl and HNO₃ (3:2 v/v) for 10 min. Contents were cooled, neutralized with dilute ammonia and diluted to 25 ml with water. An aliquot of sample solution was analyzed for Ce by general procedure (Table 3).

In all above cases (Table 3), parallel determinations were carried out making use of reference method⁷ and data of results of various analyses showed no significant difference between proposed and reference method, indicating that proposed method is very accurate (Table 4).

Conclusions

A new, simple, and highly sensitive method for determination of Ce in various geological and environmental samples has been developed. New method needs neither heating nor extraction to organic phase, works satisfactorily and found superior to spectrophotometric methods.

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