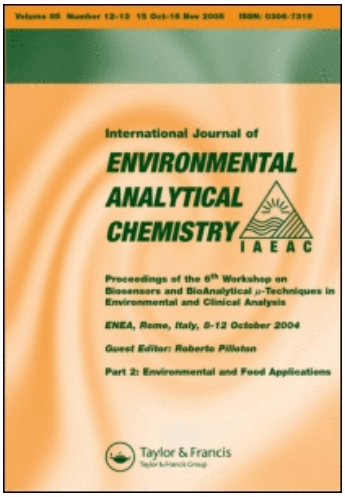

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Environmental Analysis of Cerium Using *N-p*-Chlorophenyl-2-Furylacrylohydroxamic Acid with or without 1-(2-Pyridylazo)-2-Naphthol

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A method is presented for the highly sensitive, selective, and rapid determination of cerium (IV) at trace levels in ores, animal tissues, plant tissues, and natural waters. The method is based on the chelation of cerium (IV) with a new reagent *N-p*-chlorophenyl-2-furylacrylohydroxamic acid (CFHA) and extraction into chloroform. The extract can be used directly in the spectrophotometric determination of the metal ($\varepsilon = 8.5 \times 10^3$ l mol^{-1} cm^{-1} at 470 nm) or can be converted to a ternary complex by the addition of 1-(2-pyridylazo)-2-naphthol for enhanced sensitivity ($\varepsilon = 1.8 \times 10^4$ l mol^{-1} cm^{-1} at 515 nm).

KEY WORDS: Cerium, environment, extraction, spectrophotometry, chelation.

INTRODUCTION

Cerium in environment

Cerium is traditionally referred as one of the "rare earths" but is in fact more plentiful in the earth's crust than many other elements,

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including lead.[1,2] It is also the most widely distributed of the "rare earths", averaging 22 ppm in the earth's crust. Reports on the concentration of cerium in plant material are few, while no report could be traced on this metal in animal tissues. Average cerium levels of 0.1, 0.5 and 0.005 ppm have been reported in breadfruit, taro and cassava respectively, on a dry weight basis.[2] The metal was found in only six of the 912 plant species sampled throughout the USA, in concentrations ranging from 300 to 700 ppm in ash.[3] Subsequently Connor and Shacklette[4] found 300 ppm of cerium in the ash of tomato fruits grown in Georgia, USA. Apparently cerium is absorbed profusely by some plant species while other species practically do not absorb it at all. The high levels of cerium in certain plant samples may also be due to the abnormally high concentrations of the metal in the corresponding soils, though no information is available to enable confirmation of this possibility.[5] The cerium content of sea water is of the order of 0.0015 ppb[6]; in the edible portions of oysters and clams it has been known to concentrate to levels 100 times and 1000 times higher respectively than in sea water.[7]

Cerium is industrially important and is used in nuclear reactors, in alloys with nickel and chromium, in microwave devices, lasers, masers, and in television sets.[1,2] The oxalate salt of the metal has been used to remedy vomitting during pregnancy, and other salts of the metal have been used as central nervous system depressants, astringents, and antiseptics.[2]

The percentage of oral absorption and retention of cerium is greater in neonates than in older mice.[6] Subcutaneous injection reveals slow excretion mostly by the gastrointestinal route.[6] The metal (^{144}Ce) was found to deposit in the kidneys, spleen, cartilage, and adrenal cortex.

Cerium toxicity

The signs of acute toxicity due to cerium, determined in rodents, consisted of writhing, ataxia, labored respiration, and sedation.[9] The maximum incidence of death occurred at 48 to 96 hours. There was a tendency for the females to be more sensitive than the males. Intravenous injection of various salts of the metal caused splenic and hepatic degeneration in the rodents. The intravenous administration

of cerium for its anticoagulant effect, while apparently useful, produces undesirable side effects, primarily hemolysis resulting in hemoglobinuria.[9,10].

Inhalation exposures of cerium in man have been known to cause sensitivity to heat, itching, and an increased awareness of odor and taste.[2] Intratracheal administration or inhalation exposure of experimental animals to fluorides or oxides, or a combination thereof, resulted in transient pneumonitis, subacute bronchiolitis, and regional bronchiolar stricturing. The formation of granulomas, while rare, has been reported.[2,9]

Skin damage by cerium is apparently not an important factor unless the skin is abraded.[2,9] Applications to abraded skin cause epilation and scar formation. In rabbits when the cornea was denuded, cerium caused permanent corneal opacity.[2,10]

Analysis of cerium

The increasing industrial use of cerium and the reports on cerium toxicity make it essential to have analytical procedures suitable for monitoring cerium in environment.

Several organic reagents have been tried in the past for extraction —determination of cerium, such as β-diketones, cupferon, organophosphorus compounds, high molecular weight amines and diethyl ether.[11] The general drawbacks of these reagents are:[11] slow or incomplete extraction of the metal, inadequate selectivity, and lack of sensitivity. The spectrophotometric method based on Alizarin Red S is commonly used, but is sensitive to pH changes.[12] In general, the available spectrophotometric methods cannot be applied directly in the analysis of cerium in environmental samples which normally contain iron, calcium, magnesium, phosphate, etc. in quantities large enough to interfere with the analysis.[13] The methods based on atomic absorption spectrometry have lacked sensitivity; the methods based on flame or flameless atomisation, or fuel-rich or fuel deficient flames, proving equally ineffective.[14] Recently a sensitive method has been reported using tantalum-lined graphite furnace atomic absorption spectrometry[14] for the analysis of cerium in geological materials but the method has not been tried on other environmental samples such as biological tissues and natural waters. We had introduced[15] *N*-*p*-chlorophenyl-2-furohydroxamic acid as a reagent

for rapid extraction and simultaneous spectrophotometric determination of cerium (IV). During attempts at further enhancement of the sensitivity of cerium determinations, we synthesised a series of hydroxamic acids introducing conjugation in the form of $-CH=CH-$ group between the furan ring and the carboxy coordination site. The resulting *N*-phenyl-2-furylacrylohydroxamic acid and its nine analogues (Table 1) were explored for extraction-determination of cerium. As expected, these reagents had significantly higher sensitivity (Table 1) than their 2-furo- counterpart ($\varepsilon = 6.5 \times 10^3$ l mol^{-1} cm^{-1} at 465 nm)[15] and the sensitivity was further enhanced by forming a ternary complex with 1-(2-pyridylazo)-2-naphthol (PAN).

Table 1 Spectral characteristics of binary cerium-hydroxamic acid and ternary cerium-hydroxamic acid-PAN systems[a]

Hydroxamic acid	*Binary system*		*Ternary system*	
	Wavelength of maximum absorbance λ_{max}, *nm*	*Molar absorptivity at* λ_{max}, *l mol*$^{-1}$ *cm*$^{-1}$	*Wavelength of maximum absorbance,* λ_{max}, *nm*	*Molar absorptivity at* λ_{max}, *l mol*$^{-1}$ *cm*$^{-1}$
N-p-Methoxyphenyl-2-furylacrylo-	450	7.1×10^3	505	1.3×10^4
N-m-Methoxyphenyl-2-furylacrylo-	450	6.9×10^3	502	1.1×10^4
N-p-Tolyl-2-furylacrylo-	455	7.2×10^3	505	1.2×10^4
N-m-Tolyl-2-furylacrylo-	455	7.0×10^3	505	1.2×10^4
N-Phenyl-2-furylacrylo-	460	7.2×10^3	505	1.1×10^4
N-p-Chlorophenyl-2-furylacrylo-	470	8.5×10^3	515	1.8×10^4
N-m-Chlorophenyl-2-furylacrylo-	470	8.1×10^3	515	1.5×10^4
N-p-Bromophenyl-2-furylacrylo-	465	8.2×10^3	512	1.5×10^4
N-p-Iodophenyl-2-furylacrylo-	465	8.0×10^3	510	1.4×10^4
N-p-Nitrophenyl-2-furylacrylo-	460	7.1×10^3	508	1.2×10^4

[a]Against reagent blanks; the reagents had negligible absorbance at these wavelengths.

EXPERIMENTAL

Reagents and apparatus

All chemicals were analytical reagent grade unless otherwise stated. The water was deionised and double distilled.

The reagent *N*-*p*-chlorophenyl-2-furylacrylohydroxamic acid (CFHA) and its analogues were prepared and purified employing the general method of Tandon and Bhattacharyya.[16] They were crystallised repeatedly from benzene to sharp, constant, melting points and were characterised by UV, IR and NMR spectroscopy, as detailed elsewhere.[17] A 0.5% (5 g l^{-1}) reagent solution in ethanol was used for chelaton-separation of cerium. PAN and tartaric acid aqueous solutions were 0.1 g l^{-1} and 0.2 g l^{-1} respectively.

A standard cerium (IV) solution was prepared from ceric nitrate and was standardised volumetrically.

The absorption spectra were recorded on Perkin–Elmer model 402 and Hitachi model 220 spectrophotometers. Spectral measurements at constant wavelengths were done with SF-4 (USSR) spectrophotometer employing matched quartz cells of 10 cm path length unless otherwise stated. The pH measurements were done on Industrial Electronics Corporation Model 092 and Elico Model PE 132 pH meters.

Procedure for extraction and determination

Extraction: The pH of a cerium solution containing 4–40 μg of Ce(IV) was adjusted to 9 ± 0.5 using 0.1 M solutions of HCl and NaOH and 5 ml of reagent solution (5 g l^{-1}) in ethanol was added with stirring. The resulting precipitate was equilibrated with 5 ml of chloroform for 2 min and the chloroform extract was separated. The extraction was repeated with a fresh 5 ml of chloroform, and the mother liquor was washed with two 2 ml portions of chloroform to recover any trapped droplets of the extract.

Direct determination: For the direct determination the extracts and washings were transferred to a 25 ml calibrated flask. They were diluted up to the mark with chloroform and the absorbance was measured at 470 nm against the blank prepared in the same manner as the sample solution but without cerium.

Determination as a ternary complex with PAN: The chloroform-CFHA extracts and washings were transferred to a 100 ml separatory funnel containing a 10 ml mixture of PAN ($0.1\,g\,l^{-1}$), and tartaric acid ($0.2\,g\,l^{-1}$) in water, adjusted to pH 6.4. The contents were equilibrated for 5 minutes and the phases were allowed to separate. The red coloured organic phase containing the cerium (IV)-CFHA-PAR ternary system was transferred to a 25 ml calibrated flask. It was diluted to the mark with chloroform and measured against the reagent blank prepared in the same way as the cerium extract but without the metal ion.

RESULTS AND DISCUSSION

Absorption characteristics and sensitivity

The binary cerium (IV)-MFHA extract has absorbance maxima at 470 nm ($\varepsilon = 8.5 \times 10^3\,l\,mol^{-1}\,cm^{-1}$). Beer's law is obeyed in the range 1–15 ppm of Ce(IV). The sensitivity of the method, defined by Sandall[18] as the minimum concentration achieving an absorbance of 0.001, is 0.1 ppm cerium. The sensitivity was further enhanced by forming a ternary complex with PAN. For this, cerium needs to be reduced to trivalent state for which tartaric acid is employed as described in the experimental section. The ternary Cerium (III)-MFHA-PAN extract has λ_{max} at 515 nm ($\varepsilon = 1.8 \times 10^4\,l\,mol^{-1}\,cm^{-1}$). The system obeys Beer's law in the range 0.25–8.5 ppm of cerium (IV); the Sandell sensitivity being 0.05 ppm. A two-fold enhancement in the sensitivity is thus achieved in the ternary system compared to the binary system.

Effect of pH and reagent concentration

Extraction of Cerium (IV) with CFHA commences at pH 6.5 and becomes quantitative in the range 7.8–10. It is recommended to set the pH of the sample to 9 ± 0.5 before CFHA addition. A 0.5% ($5\,g\,l^{-1}$) CFHA solution in ethanol was adequate for complete precipitation of cerium and rapid extraction of the precipitated chelate into chloroform. Concentrations of CFHA lower than 0.4% slowed down the precipitation and subsequent extraction while

concentrations higher than 0.5% had no beneficial effect. Therefore 0.5% CFHA solution is recommended as safe and adequate reagent concentration. Likewise the PAN and ascorbic acid concentrations of 0.01% and 0.02% were found to be optimal.

Effect of diverse ions

The method tolerates Au(III), Zn(II), and Hg(II) when present in 200-fold the amount of Ce(IV). Mg(II), Li(I), K(I), and Na(I) are tolerated when present in 50000-fold the amount of Ce(IV). Halides, nitrate, sulfate, acetate, and carbonate are tolerated in more than 50000-fold excess. Tartrate, oxalate, and citrate, which tend to reduce Ce(IV) to Ce(III), have the potential to interfere but their interference is eliminated by oxidizing them with nitric acid prior to precipitation of Ce(IV). These acids are likely to be encountered in significant concentrations only in the analysis of certain plant tissues—for example oxalic acid in cabbage and citric acid in lemon. However, the acid treatment used in solubilising the plant tissues[19,20] automatically destroys these acids. Likewise, drying and digestion of animal tissues[19,20] eliminates the likely interference from these acids.

The interference from V(V), Ti(IV), Fe(III), Cu(II), Ni(II), Co(II), and U(VI) can be eliminated by prior extraction of these ions by 0.1 M solutions of CFHA in chloroform from solutions maintained at 4–8 M HCl for Ti(IV) and V(VI); pH = 0.1 for Fe(III); pH = 4.2 for Cu(II); pH = 5.0 for U(VI); and pH = 5.5 for Ni(II) and Co(II). Samples containing 0.5 or 5 ppm cerium and 25 ppm of each of these interfering ions were subjected to prior extractions as above and analysed for cerium. The recoveries of cerium were quantitative, within a relative error of $\pm 2\%$.

ENVIRONMENTAL ANALYSIS

Determination of cerium in lanthanum oxide

Lanthanum oxide, 100 mg, containing 0.5% cerium dioxide was dissolved in 1 M sulfuric acid (25 ml). A 25% w/v ammonium chloride solution (5 ml) was added, followed by the reagent solution (2 ml). The contents were diluted to 50 ml and, after adjusting the pH

to 4.5 ± 0.5, were transferred to a 100 ml separatory funnel. The contents were twice equilibrated with 10 ml portions of chloroform. The organic phase was discarded. The pH of the aqueous phase was raised to $9(\pm 0.5)$ and CFHA dissolved in ethanol (5 ml) was added. Cerium was then determined as detailed above.

Determination of cerium in certified samples of bastnasite unleached concentrate, monazite and vehicle exhaust particulates

Certified samples of bastnasite unleached concentrate (IGS-41) and monazite (IGS-36) from British Geological Survey (Institute of Geological Sciences), UK, were analysed for cerium after decompo-

Table 2 Analysis of cerium in lanthanum oxide, certified reference materials, animal tissues, plant tissues and natural waters

Sample	*Cerium present (certified value)*	*Cerium added*	*Cerium found (average of six determinations)*	*Standard deviation*
Lanthanum oxide ore	—	Nil	0.496%	0.006
	—	0.2%	0.694%	0.008
Bastanasite ore concentrate (IGS-41)	26.25%	Nil	25.91%	1.33
	26.25%	5.00%	31.77%	1.94
Monazite (IGS-36)	19.4%	Nil	18.98%	1.65
	19.4%	5.00%	24.84%	1.39
Vehicle exhaust particulates (NIES-8)	3.1 ppm	Nil	2.98 ppm	0.11
	3.1 ppm	2.50 ppm	5.71 ppm	0.17
Muscle of frog *Rana tigrina*	—	Nil	Nil	—
	—	2.00 ppm	1.98 ppm[a,b]	0.06
	—	5.00 ppm	4.97 ppm[a]	0.07
Fodder plant *Melilotus indica*	—	Nil	0.29 ppm[a,b]	0.04
	—	1.00 ppm	1.30 ppm[a,b]	0.06
	—	2.00 ppm	2.28 ppm	0.09
Lake water	—	Nil	Nil	
	—	1.00 ppm	0.98 ppm[b]	0.02
	—	5.00 ppm	4.96 ppm	0.08

[a]Dry weight basis.
[b]Cells with 10 cm path length were used for absorbance measurements.

sition, coprecipitation, and dissolution in 0.1 M nitric acid.[14] The vehicle exhaust particulates samples (NIES-8) from National Institute for Environmental Studies were dissolved by treatment with perchloric and hydrofluoric acids.[21] The results of replicate analyses are presented in Table 2.

Determination of cerium in plant tissues, animal tissues and natural waters

The samples of plant and animal tissues were washed with 5% V/V EDTA solution and physiological saline solution respectively, followed by deionised distilled water to free them from adhering soil or blood. They were carefully wiped with filter paper before taking their wet weight. They were then dried at 120 °C to a constant weight and brought into solutions by acid treatment as detailed elsewhere.[19,20] Water samples were filtered on-site, immediately after being drawn, through 0.45 μm membrane filter and made 0.05 M in HNO_3 as recommended in standard methods.[22]

To make sure that matrix effects are not influencing the analysis, cerium was determined with and without standard addition. The reliability of the method is reflected in the results (Table 2).

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