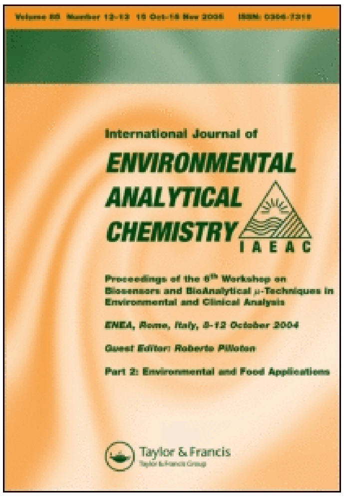

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Spectrophotometric Determination of Osmium at the PPB Level Using Pyrocatechol and Hydroxyamidine

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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM AT THE PPB LEVEL USING PYROCATECHOL AND HYDROXYAMIDINE

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A sensitive method for the spectrophotometric determination of osmium at the ppb level is described. The method is based on the formation of a brown-coloured complex by heating the reaction mixture containing Os(VIII), pyrocatechol and a hydroxyamidine at pH 8.5 over a boiling water bath, with subsequent extraction of the coloured species into chloroform. The molar absorptivity of the coloured species with N-hydroxy-*N*,*N*′-diphenylbenzamidine is 3.95×10^6 l mol^{-1} cm^{-1} at $\lambda_{max} = 410$ nm. The method is free from interferences for almost all ions tested.

KEY WORDS: Osmium(VIII), extraction, spectrophotometry, hydroxyamidine, low grade ore analysis.

INTRODUCTION

The octavalent form of osmium, osmic acid, is highly toxic and extremely irritant; it has a TLV of 0.2 pp6. Osmium tetroxide vapours enter into the environment by annealing of platinum and from pen-nib making industries.[1] Inhalation of low concentrations of osmium tetroxide vapours for a considerable period of time results in pharyngeal and laryngeal distress and digestive disturbances.[2] Detection and determination of osmium at very low concentrations in a variety of materials is therefore important. Thiourea[3] and thiocyanate[4] are the most widely used reagents for the spectrophotometric determination of osmium. However, they are not entirely suitable because ruthenium, rhodium and palladium interfere seriously. Dyes are also used for the spectrophotometric determination of the metal.[5,6] These methods are not very sensitive and, besides, separation of Os before its determination, by extraction or distillation, is needed to avoid interferences of many metal ions.

In the present investigation, *N*-hydroxy-*N*,*N*′-diphenylbenzamidine (HDPBA) and pyrocatechol were used for the extraction spectrophotometric determination of Os(VIII) at the ppb level.

EXPERIMENTAL

Materials

A standard stock solution of Os(VIII) was prepared by dissolving 1.0 g OsO_4 in 100 ml of 0.2 M NaOH and diluted to 1 litre with distilled water. Freshly prepared solutions of pyrocatechol (0.4%, w/v) in water were used. *N*-Hydroxy-*N*,*N'*-diphenylbenzamidine was synthesized according to the literature[7]; it was used in an ethanolic solution (0.4%, w/v). A $NaOH–H_3BO_3$ buffer was used for pH adjustment. All chemicals used were of analytical grade (E. Merck or BDH).

An ECIL UV–VIS GS-856 spectrophotometer with matched 1-cm quartz cells was used for absorbance measurements.

Procedure

An aliquot of the standard solution containing up to 0.35 μg of Os(VIII) is taken in a 25 ml beaker. To this solution 2 ml of pyrocatechol solution and 5 ml of the ethanolic solution of *N*-hydroxy-*N*,*N'*-diphenylbenzamidine are added. The pH of the aqueous ethanol solution is adjusted to 8.5 ± 0.2 using 0.5–2.5 ml of $NaOH–H_3BO_3$ and the volume is made up to 10 ml. The solution is heated over a boiling water bath to near dryness. The dried mass is dissolved in 5 ml of water. The cold solution is transferred to a 100 ml separatory funnel and shaken with 5 ml of chloroform. The organic layer is separated off and the aqueous phase is washed with 2 ml of freshly distilled chloroform. After drying over anhydrous sodium sulphate (1 g) in a 25 ml beaker, the combined extracts are transferred to a 10 ml volumetric flask and the volume is made up to the mark with chloroform. A reagent blank is prepared similarly. The spectrum of the coloured species is plotted against the reagent blank and its absorbance is measured at λ_{max}.

RESULTS AND DISCUSSION

The absorption spectra of the brown coloured complex formed by the reaction between Os(VIII), pyrocatechol and HDPBA shows maximum absorption at 410 nm. The reagent blank has some absorption at this wavelength; hence, it was used as a reference for all spectral measurements. Of the various polar and non-polar organic solvents tested, chloroform was chosen for the extraction of the coloured species because of the high colour intensity.

The optimum pH range of the aqueous ethanol solution for the colour development of the species in chloroform was found to be pH 7.7–9.3. The pH of the aqueous phase for the extraction of the coloured species into chloroform should be between 3.0 and 9.5. The maximum colour is attained only when the reaction mixture containing Os(VIII), pyrocatechol and HDPBA is heated to near-dryness over a water bath at 80 ± 5°C. However, heating the dried mass for more than 3 min results in thermal decomposition of the species. At least 0.0036 M pyrocatechol and 0.0035 M

HDPBA in ethanol–water (50:50) are required for full and constant colour development in chloroform and no adverse effect was seen up to 0.013 M pyrocatechol and 0.01 M HDPBA. The volume ratio of ethanol to water can be varied from 1:4 to 4:1 ($V_{aq}:V_{eth}$) without any adverse effect. For the extraction of the coloured species into chloroform, the aqueous to organic volume ratio should be between 1:2 and 3:2. In chloroform the brown coloured species is stable for at least 24 h at room temperature (25 ± 2°C). Its molar absorptivity is 3.95×10^6 l mol^{-1} cm^{-1} at 410 nm. The RSD of the method for 10 replicate measurements at a level of 25 ppb of Os(VIII) was ±2.0%. The system followed Beer's law up to 0.35 μg Os/10 ml of final organic solution with a correlation coefficient of 0.9.

The stoichiometry of the colour reaction between Os(VIII), pyrocatechol and HDPBA was studied by plotting *log* distribution ratio of the coloured species versus *log* molar concentration of the reagents taken. The results showed the reaction ratio Os(VIII): pyrocatechol: HDPBA to be 1:2:2. The coloured species may either be the oxidized product of the reagents or the ternary complex of the metal with pyrocatechol and HDPBA; its exact nature is not known.

The effect of diverse ions on the determination of 0.25 μg of osmium per 10 ml of aqueous ethanol solution as studied following the above procedure. Considerable amounts of platinum metals and a large amount of other ions are tolerated. The tolerance limit of various ions (in μg in parentheses) causing an error of less than 2% are as follows: V^{5+}(0.5); Ru^{3+}(2.8); Ti^{4+} (6); Ni^{2+}(15); Pd^{2+}(25); Fe^{3+}(50); Cu^{2+}, Ir^{3+}, Pt^{4+} and Mo^{6+} (75); Sb^{3+}(100); Cd^{2+}(150); W^{6+}(175); Sr^{2+}, CH_3COO^-, NO_3^- and SCN^- (200); Pb^{2+}, Sn^{4+}, Re^{7+} and $C_2O_4^{2-}$(300); Zn^{2+}, Bi^{3+}, Th^{4+}, I^- and F^-(400); Al^{3+} and As^{5+}(450); EDTA(5000).

Table 1 Determination of osmium in a standard ore sample and synthetic mixtures.

Sample	*Osmium present*	*Osmium found*	*RSD (±%)**
Ore sample USBM-Pt-A Reference Pt ore US Bureau of Mines	Osmium reported, 103 ± 7 ppb	113 ppb	1.8
Synthetic mixtures (% Composition of osmiridium, reported)	μg Os taken		—
(1) South Africa Ru(8.9), Ir(17) Pt(0.2), Os(69.9)	Os, 0.25 μg	0.248 μg	2.0
(2) Australia Ru(5.22), Ir(58.13), Pd(3.04), Os(33.46)	Os, 0.3 μg	0.302 μg	1.8

* n = 5.

Because no relevant environmental samples were available, the present method was applied to the determination of osmium in a standard low-grade ore and synthetic mixtures. Synthetic mixtures were prepared by mixing appropriate amounts of platinum metals in the ratios given in Table 1. For the determination of osmium in ore, an accurately weighed amount is digested by acid.[8] The residue is dissolved in 1% (w/v) tartaric acid and diluted to 50 ml with tartaric acid; 5–10 ml of this solution are taken for analysis. The metal content in the synthetic mixtures was determined by following the recommended procedure. The data obtained are summarized in Table 1. They indicate that the present method yields highly satisfactory results.

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