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SIMULTANEOUS DETERMINATION OF RUTHENIUM, OSMIUM AND PALLADIUM BY REVERSED-PHASE HPLC USING 4-(2′-THIAZOLYLAZO) RESACETOPHENONE OXIME AS CHELATING REAGENT

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Summary—The chelates of Ru, Os and Pd with 4-(2′-thiazolylazo) resacetophenone oxime were separated simultaneously by HPLC using a pre-column derivatization method, at the wavelength 560 nm, on an octadecyl-bonded silica stationary phase with a mobile phase methanol–water mixture (40–60 v/v) containing 40 m*M* of acetate buffer pH 5.0. The detection limits for Ru, Os and Pd were 2.0, 4.0 and 0.2 ng, respectively. The method has been applied successfully for the determination of metal ions in an anode slime.

Interest in the analytical applications of High Performance Liquid Chromatography for the separation and simultaneous determination of mixtures of metal ions as their chelates with organic reagents has received the attention of many analytical chemists in recent years.[1–4] HPLC of metal chelates is a promising alternative approach for overcoming the lack of selectivity of the chelating reagents and has the advantages of high sensitivity, selectivity and simultaneous detection capability. A wide variety of organic reagents such as dithiocarbamates,[5,6] 8-hydroxy quinoline,[7,8] 4-(2′-pyridylazo) resorcinol (PAR),[9–14] 4-(2′-pyridylazo) naphthol (PAN),[15] dithizone,[16] diacetyldioxime,[17] β-diketones,[18] and porphyrins[19] have been employed to complex metal ions and determined by HPLC using the methods on-column derivatization and pre-column derivatization.

Among the heterocyclic azo compounds, thiazolylazo compounds[20–22] constitute an important class of analytical reagents employed for the spectrophotometric, extraction spectrophotometric, amperometric determination of metal ions and as indicators in the complexometric titrations. However few data have been reported for the determination of metal ions by HPLC using these azo dyes.[23,24] In continuation of our earlier work[25,26] a new analytical reagent 4-(2′-thiazolylazo) resacetophenone oxime (TARPO) was reported in this paper first time as a chelating agent for the HPLC separation and simultaneous determination of metal ions Ru, Os and Pd by pre-column derivatization method.

EXPERIMENTAL

Apparatus

Liquid chromatography was performed by use of a Shimadzu Model LC-6A HPLC instrument equipped with a model SPD-6A detector and a chromatopac model C-R3 A data processor. Shimadzu UV-160A Spectrophotometer (Shimadzu, Kyoto, Japan). Systronic Mark VI digital pH meter (Systronic Instruments, Ahmadabad, India) and a Zorbax ODS column (Dupont, 250 × 4.6 mm i.d.) with a particle size of 6 μm were also used.

Preparation of 4-(2′-*thiazolylazo*) *resacetophenone oxime*

Five grams of 2-aminothiazole was dissolved in 40 ml of 6*N* HCl and cooled to 0°C, 3.5 g of sodium nitrate in 10 ml of water was well cooled and added in portion wise till there was free nitrous acid. The diazonium salt solution of 2-aminothiazole thus prepared was poured dropwise into the well cooled solution of 2,4-dihydroxy acetophenone oxime. After constant stirring for about an hour, the pH of the solution was adjusted to 6.0 with dilute NaOH solution and separated the orange–red crystals of 4-(2′-thiazolylazo)resacetophenone oxime (TARPO). TARPO was purified by dissolving in 100 ml of 0.1*N* sodium hydroxide solution followed by the extraction with diethyl ether. The extract was treated with dilute HCl to precipitation, filtered and dried in vacuum.

Molecular weight of the compound TARPO was confirmed by the presence of molecular ion peak exhibited in the mass spectra at the m/z value 278 with relative intensity 28.6%. The elemental analysis values are as follows.

	C	H	N	S	Melting point
Found	47.39	3.56	19.98	11.43	272–274°C
Calculated	47.48	3.60	20.14	11.52	

Reagents

Stock solutions of Ru(III), Os(IV) and Pd(II) in 1*M* hydrochloric acid were prepared from $RuCl_3$, $(NH_4)_2$ $OsCl_6$ and $PdCl_2$.

The mobile phase methanol–water (40 + 60, v/v) containing 40m*M* acetate buffer (pH 5.0) were prepared.

A 0.5 mg/ml stock solution of TARPO was prepared in absolute alcohol. All the other chemicals used were of analytical reagent grade.

Procedure

In a 10 ml standard flask 2 ml of 0.5 mg/ml TARPO solution, 4 ml of buffer solution (pH 5.0) were mixed with a known volume of the sample solution containing different amounts of metal ions Ru, Os and Pd, contents were heated for 10 min in a water bath at 60°C After cooling, the volume was made up to the mark with methanol and filtered through a 0.3 μm membrane. 10 μl of the solution was injected into the column The TARPO chelates were eluted at a flow-rate of 1.0 ml/min and detected at the wave length 560 nm. The amount of each metal ion is determined by measuring the peak area.

RESULTS AND DISCUSSION

TARPO reacts with Ru, Os and Pd at pH 5.0 forming pink coloured chelates. The complexes of Ru, Os and Pd exhibit absorption maxima at 552, 560 and 555 nm, respectively. Hence normal spectrophotometric analysis of the metal ions and their simultaneous determination is difficult. To overcome the difficulty attempts were made using HPLC technique for the separation. A series of test solutions containing different known volumes of metal ions were prepared, 10 μl of the test solutions were injected into the HPLC column and eluted with the mobile phase. The detection wavelength was selected at 560 nm where the absorption of the reagent was very slight. A typical chromatogram for the separation of TARPO chelates of Ru, Os and Pd is shown in Fig. 1.

Effect of solvent and buffer compositions in the mobile phase

Several organic solvents, such as methanol, ethanol, acetonitrile, tetrahydrofuran and isopropyl alcohol combined with water were investigated as binary and ternary mobile phases. The methanol–water binary system was found to be satisfactory for the separation of the TARPO chelates of Ru, Os and Pd. However a simple methanol water mobile phase gave tailing peaks with low sensitivity. When buffer was added to the mobile phase, excellent peak shapes and high sensitivity were observed. The effect of the concentration of methanol in the mobile phase on the retention times of the chelates is shown in Fig. 2 The optimum results were obtained with 40% methanol.

The peak separation of Ru and Os is found to be dependent on the amount of buffer added (Fig. 3). It increases up to 30m*M* and latter remains almost constant. Whereas in the case of Pd no significant changes were observed. Hence 40m*M* of buffer concentration was chosen.

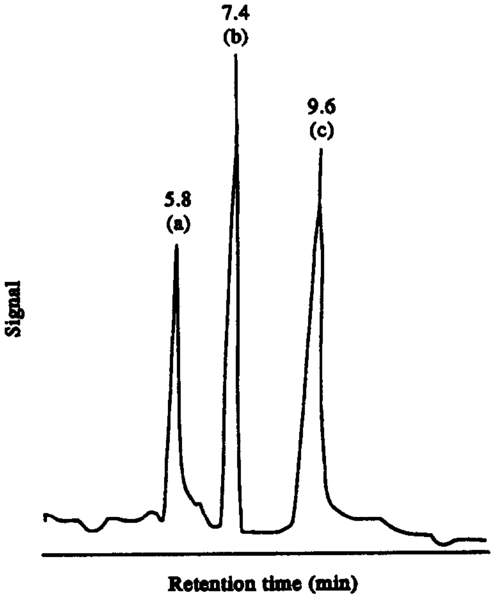

Fig 1

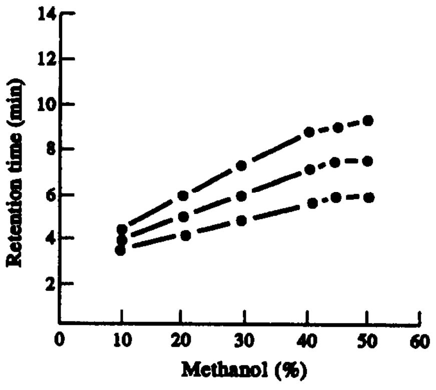

Fig 2

Optimum pH was selected as 5.0 where the TARPO chelates has maximum absorbance.

Separation and calibration of Ru, Os and Pd complexes

A series of test solutions containing different volumes of metal ions were prepared and injected into the chromatographic column. The metal ions were eluted at the flow rate 1.0 ml/min. Peak areas of the chelates Ru, Os and Pd were measured at the retention times 5.8, 7.4 and 9.6, respectively. Calibration graphs were constructed. The slopes and intercepts of the calibration graphs for the simultaneous determination of Ru, Os and Pd calculated by linear regression analysis of the peak area *vs* metal ion concentration (ppm) are presented in the Table 1. The calibration graphs were linear in the range 0.2–5.0 μg/ml for Ru and Os and for Pd it is 0.05–4.0 μg/ml. The absolute detection limits calculated as the amount injected that gave a signal to noise ratio 2:1 were 2.0, 4.0 and 0.2 ng, respectively for Ru, Os and Pd.

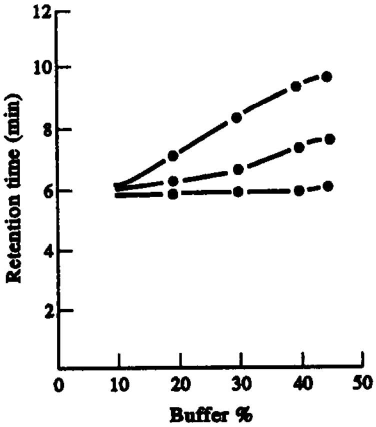

Fig. 3

Table 1. Coefficients of linear regression analysis

	Metal ion		
Parameter	Ru	Os	Pd
Concentration (ppm)	0.2–5.0	0.2–5.0	0.05–4.0
Amount injected (ng)	20–100	20–100	20–100
Slope/area (*ml*/*μg*)	1978	2768	2034
Intercept (area)	368	657	−441
Correlation coefficient	0.9994	0.9988	0.9991

Effect of foreign ions

The effect of various foreign ions in the determination of known amounts of (2 μg) Ru, Os and Pd was studied by adding each foreign ion in turn to the sample before pre-column derivatization of the metal–TARPO chelates. The maximum level (μg) of foreign ion, which gives a change of less than ±5% in the peak area of the TARPO chelates of Ru, Os and Pd, that could be tolerated in the simultaneous determination were as follows:

Ti(IV), Bi(III): 200, Cd(II), Al(III): 150, Zn(II), Mn(II), Cr(VI), Li(I): 100, Ag(II), Hg(II), Pb(II): 60, Pt(IV), Mo(VI), V(IV), Cu(II), Fe(III): 20, Co(II): 10

Applications

An anode mud sample from a copper smelter spiked with Ru, Os and Pd was analysed for the metal ions. The spiked slime was ground to fine particles and was dissolved in concentrated hydrochloric–nitric acid mixture (1:1 v/v) by heating on a hot plate. The solution was cooled, 1 ml of 100 mg/ml sodium chloride solution was added, and the mixture was evaporated to near dryness, washed into a 25 ml standard flask diluted to the volume with distilled water. An aliquot of the solution was taken and the Ru, Os and Pd TARPO chelates were formed by reaction with TARPO and determined by HPLC as described earlier. The results are presented in the Table 2.

DISCUSSION

Comparison of the results with the reports published for other compounds[5–19] clearly shows that the present method does not require any difficult procedures or the use of ionic solvents, surfactants or on-column derivatization methods. In the case of TAR clear separation was obtained only in presence of tetrabutylammonium ion as counterion. Further the detection limits (2 ng and 4 ng/ml for Ru and Os or 0.02 and 0.04 ng injected) obtained with TARPO are substantially lower

Table 2. Results of anode slime analysis

Amount added (μg)			Amount found* (μg)			Relative standard deviation (%)		
Ru	Os	Pd	Ru	Os	Pd	Ru	Os	Pd
0.5	0.5	0.2	0.48	0.47	0.495	3.21	2.85	2.71
1.0	1.0	1.0	0.97	0.96	1.01	1.68	1.87	1.25
2.0	2.0	2.0	1.98	1.94	1.93	0.86	0.67	0.42
3.0	3.0	3.0	2.97	2.99	2.94	0.42	0.22	0.34
4.0	4.0	4.0	3.92	3.90	3.98	0.28	0.32	0.21

*Average of six determinations

than those obtained with TAR (6 ng and 17 ng/ml or 0.15 ng and 0.42 ng injected). The molar absorptivities calculated for the TARPO complexes of Ru and Os are 0.54×10^4 and 0.81×10^4, whereas the TAR complexes shows 0.93×10^4 and 4.4×10^4. The value calculated for Pd with TARPO is 0.22×10^4. The smaller molar absorptivities for the TARPO complexes suggest that the lower detection limits here are due at least in part to improved instrumentation.

Similarly TARPO exhibits more sensitivity than TAR and Arsenazo (III) in the spectrophotometric determination of uranium and the simultaneous determination of uranium and thorium by derivative spectrophotometry.[25,26]

All the observations illustrate that TARPO is a new analytical reagent with distinct advantage over TAR and other classes of thiazolylazo compounds.

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