TABLE I

Analytical data and physical characeristics of phenolic derivatives of $(\eta^5\text{–}CH_3 . C_5H_4)_2 TiCl_2$

Compound	Colour	M.wt. found (calc.)	Analysis (Found/Calc.) C	H	Ti
$(\eta^5\text{–}CH_3 . C_5H_4)_2 Ti(OC_6H_5)_2$ Phenol	Reddish	375 (392)	73·39 (73·47)	6·08 (6·12)	12·18 (12·25)
$(\eta^5\text{–}CH_3 . C_5H_4)_2 Ti(OC_{10}H_7)_2$ –Naphthol	Reddish brown	478 (492)	77·95 (78·03)	5·61 (5·69)	9·70 (9·75)
$(\eta^5\text{–}CH_3 . C_5H_4)_2 Ti(O_2C_6H_4)$ Resorcinol	Green	302 (314)	68·72 (68·80)	5·65 (5·73)	15·21 (15·29)
$(\eta^5\text{–}CH_3 . C_5H_4)_2 Ti(O_2C_6H_4)$ Catechol	Green	300 (314)	68·70 (68·80)	5·68 (5·73)	15·20 (15·29)
$(\eta^5\text{–}CH_3C_5H_4)_2 Ti(O_3C_6H_4)$ Phloroglucinol	Greenish blue	310 (330)	65·40 (65·46)	5·38 (5·45)	14·47 (14·54)

bands at 1410 cm^{-1} are due to M-O–C stretching frequencies[5].

Various phenoxy groups in these are attached to the metal atom by covalent bonds.

January 20, 1981.

1. Reynold, L. T. and Wilkinson, G. J., *Inorg. Nucl. Chem.*, 1959, 9, 86.
2. Fritz, H. P., *Adv. Organometal. Chem.*, 1964, 1, 279.
3. Thompson, H. W., *J. Chem. Soc.*, 1948, p. 328.
4. Hadzi, D. and Sheppard, N., *Trans. Faraday Soc.*, 1954, 50, 911.
5. Davies, M. and Jones, R. L., *J. Chem. Soc.*, 1954, p. 120.

RAPID SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM WITH PERAZINE

H. SANKE GOWDA, J. B. RAJ AND K. S. JAGADEESH*

Department of Post-Graduate Studies and Research in Chemistry, Manasa Gangotri Mysore 570 006, India

*S.J. College of Engineering Mysore 570 006, India

Introduction

THE coloured reaction between selenium(IV) and perazine (PZ), 10-[3-(4-methyl-1-piperazinyl)propyl] phenothiazine dimalonate has not been previously studied. The authors have now developed PZ as a *selective and sensitive reagent for the spectrophotometric* determination of selenium(IV). The proposed method offers the advantages of simplicity, sensitivity, selectivity, rapidity and determination at room temperature without the need for extraction.

Experimental

Reagents

The stock solution of selenium(IV) was prepared by dissolving a known amount of selenium dioxide in 500 ml of doubly distilled water containing 5 ml of conc. hydrochloric acid and standardised by the gravimetric method[1]. The stock solution was further diluted as needed. A 0·2% (w/v) aqueous solution of PZ was preapared and stored in an amber coloured bottle in a refrigerator. Beckman model DB spectrophotometer with matched 1 cm silica cells was used for absorbance measurements.

Procedure

1 ml of the stock solution, contaning 1·2–45 μg of selenium(IV), 5–15 ml of 10 M hydrochloric acid and 1 ml of 0·2% PZ solution were transferred to a 25 ml volumetric flask. The solution was mixed thoroughly and diluted to the mark with doubly distilled water. The absorbance was measured at 514 nm against a corresponding reagent blank. The amount of selenium in the sample was deduced from the standard calibration curve.

Results and Discussion

PZ reacts with selenium(IV) to form a pink coloured species in hydrochloric, sulphuric or phosphoric acid

medium at room temperature (27 ± 1° C). The study of the species in sulphuric or phosphoric acid medium is not recommended because the reaction is slow and less sensitive.

The maximum colour intensity is observed instantaneously in 7–9 M hydrochloric acid. Below and above this acid range the absorbance is not maximum. A 15-fold molar excess of the reagent is necessary for the full development of colour intensity. The pink coloured species which is assumed to be a radical cation exhibits absorption maximum at 512–516 nm at which the reagent does not absorb. The absorbance readings remained constant for 2 hours and were insensitive to temperature in the range 5–45° C. The order of addition of the reagents was not critical.

Beer's law is valid over the concentration range 0·05–1·8 ppm of selenium. The optimum concentration range evaluated by Ringbom's method[2,3] is 0·4–1·6 ppm. The sensitivity of the reaction is 2 ng/cm² and the molar absorptivity is $3·84 \times 10^4$ litre $mole^{-1}$ cm^{-1}.

Effect of Diverse Ions

The following amounts (ppm) of diverse ions are found to give less than 2% error in the determination of 1 ppm of selenium: Ba(II) and Zn(II) 4,000; Al(III) and Ti(IV) 1,000; Bi (III) 1,600; Cd(II) 2,200; Ca(II) 1,400; Co(II) and Rh(III) 40; Cr(III) 200; Hg(II) 20; Mn(II) and Ni(II) 600; Mg(II) 4,250; Sn(II) 2,000; Sr(II) and Pb(II) 2,800; Fe(III) and Cu(II) 1; Ag(I) 8; Te(IV) 3,500; U(VI) 800; fluoride 600; chloride 2,800; bromide and EDTA 4,000; acetate, sulphate and citrate 5,000; nitrate 50; oxalate 200; phosphate 1,600; and tartrate 8,000. The tolerance limits of Fe(III) and Cu(II) can be raised to 8 and 10 ppm in presence of 1,500 ppm of phosphate and 4,000 ppm of EDTA and 4,000 ppm of EDTA respectively. The major advantage of the method is that PZ can be used as a selective reagent for the determination of selenium in the presence of tellurium. The sensitivity of the proposed method is found to be more than that of 3,3′-diaminobenzidine[4], 2,3-diaminonaphthalene[5], 2-mercaptobenzimidazole[6], tributyl phosphate[7], 2-hydroxythiobenzohydrazide[8], and mercapto acetic acids[9]. PZ is superior to diamino chryazin[10] and thioacetamide[11] which require high temperature and very long time for maximum colour development.

Determination of Selenium in its Alloys

Synthetic mixtures corresponding to the alloys of Se–Fe (42·6–51·8% Fe), Se–Ba (63·49% Ba), Se–Hg (71·76% Hg), Se–Pb (72 41% Pb) and Se–Rh (28·6–60% Rh) were prepared and the selenium content determined following the standard procedure. The results are given in Table I.

TABLE I

Determination of selenium in synthetic mixtures

Alloy	Selenium (ppm)	
	Taken	Found*
Fe–Se	0·20	0·21**
	1·00	1·00**
	1·64	1·64**
Ba–Se	0·50	0·50
	1·00	0·99
	1·51	1·51
Hg–Se	0·31	0·30
	1·30	1·30
	1·61	1·61
Pb–Se	0·25	0·25
	1·22	1·22
	1·68	1·67
Rh–Se	0·50	0·49
	1·11	1·11
	1·71	1·71

* Average of four determinations.
** In the presence of 4000 ppm of EDTA.

J. B. R. thanks the University of Mysore for the award of Post-Graduate University Fellowship and K. S. J. is grateful to U.G.C., New Delhi, for the award of Teacher Assistantship.

April 2, 1981.

1. Sanke Gowda, H. and Narayana Achar, B., *Indian J. Chem.*, 1978, **16 A**, 537.
2. Ringbom, A., *Z. Anal. Chem.*, 1938, **115**, 332.
3. Ayres, G. H., *Anal. Chem.*, 1949, **21**, 652.
4. Hoste, J. and Gills, J., *Analyt. Chim. Acta*, 1955, **12**, 158.
5. Lott, P. F., Cucor, P., Moriber, G. and Solga, J., *Analyt. Chem.*, 1963, **35**, 1159.
6. Busev, A. I. and Huang, M. T., *Zh. Analyt. Khim.*, 1962, **17**, 1091.
7. Yadav, A. A. and Khopkar, Shripad M., *Chemia Analit.*, 1971, **16**, 299.
8. Gangopadhyay, P. K. and Shome, S. C., *J. Indian Chem. Soc.*, 1976, **53**, 1134.
9. Busev, A. I. and Min-T'iao Huang, *Z. Anal. Chem.*, 1963, **18**, 360.
10. Brown, R. S., *Anal. Chim. Acta*, 1975, **74**, 441.
11. Futekov, L. and Shocherev, G., *Nauch. Trudy Plovdiv. Univ.*, 1972, **10**, 81.