Table 1 — Photometric Determination of Selenium(IV) with Iron(II)

Amount of selenium (μg)		Error %
Taken	Found	
157·9	156·4	−0·9
236·9	238·4	+0·6
331·6	333·2	+0·5
394·8	391·6	−0·8
511·6	516·2	+0·9
631·7	635·9	+0·7
789·5	791·6	+0·3

solution was then titrated with iron(II). Stirring was provided by passing a stream of carbon dioxide. The passage of the gas was stopped before taking the absorbance readings. The titration was continued this way till the dial reading became constant. To get stable dial readings it required about 3 min in the beginning of the titration and about 9 min before the equivalence point. After the end-point was reached the absorbance values became constant within 1 min. Upon drawing a graph between the volume of the titrant and corrected absorbance two linear plots were obtained and the point of intersection of these lines corresponded to the end-point. Some representative results were presented in Table 1.

Selenium(IV), iron(III) and iron(II) have negligible absorbance in the region 350-750 nm in 80% (v/v) phosphoric acid medium. Elemental selenium in the presence of gum arabic is present in the form of an orange-red colloidal solution. The absorbance of this colloidal solution (in 80% phosphoric acid medium in the presence of 1% gum arabic) is maximum at 350 nm and gradually decreases with increase in wavelength. Since a filter corresponding to a wavelength of 350 nm was not available, the titration was monitored using a blue-violet filter (380-430 nm).

Beer's law was found to be obeyed up to a concentration of 15·79 μg/ml using a cell of 2 cm path length. The accuracy of the method is ±0·9%. The precision of the method was determined by titrating ten samples, each containing 473·7 μg of selenium, a value approximately in the middle of the optimum range. The mean value was found to be 472·4 μg with a standard deviation of 3 μg.

Chloride, sulphate, perchlorate and acetate ions do not interfere. A 10-fold excess of Te(IV) and a 100-fold excess of Te(VI) do not interfere. Selenium(VI) does not interfere up to a 10-fold excess; above this concentration it interferes by slowly getting reduced to elemental selenium. Copper(II) interferes.

Two of us (K.V.R. and D.S.N.) are grateful to the UGC and CSIR, New Delhi, for the award of research fellowships.

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Complexes of Salicylidene-*o*-aminothiophenol with Pd(II), Hg(I & II) & Ag(I) & Its Use as a New Analytical Reagent for Their Amperometric Determination

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Received 2 *February* 1976; *accepted* 28 *May* 1976

Salicylidene-*o*-aminothiophenol, the Schiff base derived from *o*-aminothiophenol and salicylaldehyde, has been used for the amperometric determination of Pd(II) (at an applied voltage of −0·44 V vs SCE), Hg(I and II) and Ag(I) (at −0·55 V vs SCE) using dropping mercury electrode as the indicator electrode. 12-21·3 ppm of Pd(II), 60-100 ppm of Hg(II), 120-200 ppm of Hg(I) and 50-108 ppm of Ag(I) can be determined with an accuracy of ±0·5%. A number of foreign ions including Pt(IV), Ir(III), Au(III) and Bi(III) do not interfere even if present in 5-10 fold excess while traces of Ru(III) and Rh(III) interfere. The solid metal complexes have also been isolated and characterized.

We report here the amperometric determination of Pd(II), Hg(II), Hg(I) and Ag(I) using salicylidene-*o*-aminothrophenol as a new analytical reagent. Structures of the solid complexes formed have also been investigated using analytical, conductance and IR data.

All physical measurements were carried out as reported[1] previously. The stock solutions of palladium chloride and mercurous nitrate were prepared in 0·2*M* hydrochloric acid and dilute nitric acid respectively while those of others were prepared in doubly distilled water. All the reagents were of AR (BDH) quality. The ligand (m.p. 136° ± 1°) was synthesized by the condensation of salicylaldehyde and *o*-aminothiophenol as described earlier[2].

The pK_1 and pK_2 values of the ligand as determined by potentiometric half-titration method[3] were 7·1 and 9·8 respectively. Pd(II) was found to form 1:1 and 1:2 metal-ligand complex in the concentration ranges 0·0005/0·0002*M* and 0·1-0·0005*M*

TABLE 1 — ANALYTICAL AND CONDUCTANCE DATA FOR THE LIGAND AND ITS COMPLEXES

Compound	Molar conductance in EtOH (ohm^{-1} cm^2 mole^{-1})	Calc. (%)			Found (%)		
		M	C	H	M	C	H
$C_{13}H_{11}NOS$*	—	—	68·12	4·80	—	67·82	4·69
$H[Pd(C_{13}H_{10}NOS)Cl_2]$†	82‡	26·17	38·38	2·70	26·00	37·96	2·62
$[Pd(C_{13}H_{10}NOS)_2]$	0·0	18·91	55·47	3·55	18·60	55·32	3·27
$[Hg(C_{13}H_{10}NOS_2]$	0·0	30·55	47·51	3·04	30·23	47·21	2·92
$[Hg(C_{13}H_{10}NOS)]$	0·0	46·80	36·39	2·33	46·39	36·08	2·30
$[Ag(C_{13}H_{10}NOS)]$	0·0	32·11	46·44	2·97	32·00	46·06	2·88

*[S: Calc. 13·97. Found: 14·06%]. †[Cl: Calc.: 17·22. Found: 17·10%]. ‡In nitromethane.

respectively as revealed by amperometric titrations. The titrations were carried out at the plateau of the polarogram of Pd(II) chloride (−0·44 V). In the case of 1:1 Hg(I) and Ag(I) complexes and 1:2 Hg(II) complex the titrations were carried out at the plateau of the polarogram of the ligand (−0·55 V). These stoichiometries were confirmed by conductometric titrations

Procedure for the determination — 50 ml of 1*M* KCl or KNO_3 were added to a known volume of standard metal ion solution and the volume made up to 100 ml by adding doubly distilled water. An aliquot (20 ml) of this solution was transferred to a polarographic cell and deaerated by bubbling pure nitrogen gas. A potential of −0·44 V in the determination of Pd(II) and −0·55 V in the determination of other metals (vs SCE) was applied, using dme as an indicator electrode. Measured volumes of the reagent solution were added and after each addition, the solution was stirred by bubbling nitrogen gas and the current was measured after an interval of a few seconds.

12-/21·3 ppm of Pd(II), 60-/100 ppm of Hg(II), 120-/200 ppm of Hg(I) and 50-/108 ppm of Ag(I) can be determined with an accuracy of ±0·5%.

Interference by the presence of external ions was studied by taking an aliquot of the metal ion solution, adding 5-10-fold excess of the foreign ion and carrying out the titrations as described above Li(I), Na(I), K(I), Rb(I), Tl(1), Mg(II), Ca(II), Sr(II), Ba(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II), Mn(II), Sn(II), UO_2(II), Al(III), Cr(III), Fe(III), Tl(III), As(III), Sb(III), Bi(III), In(III), Ga(III), La(III), Ir(III), Au(III), Sn(IV), Th(IV), Zr(IV), Ce(IV), Pt(IV), Mo(VI), W(VI) do not interfere while even the traces of Ru(III) and Rh(III) interfere.

However, Pd(II), Hg(I and II) and Ag(I) interfere in each other's estimation.

Preparation of the solid complexes and their IR studies — 1:2 (metal-ligand) complexes of Hg(II) and Pd(II) and 1:1 complexes of Hg(I), Ag(I) and Pd(II) were prepared by mixing the calculated amounts of reactants containing a little excess of the latter. The precipitates were filtered, washed several times with distilled water and then dried *in vacuo* over anhydrous H_2SO_4. The separation and washings of the suspended precipitates of 1:19 Pd(II) complex were carried out by centrifuging. The silver complex was not photosensitive. The analytical and conductance data of the complexes are given in Table 1. All the complexes, except the 1:1 Pd(II) complex, are non-electrolytes in ethanol.

The νOH band observed at 3240 cm^{-1} in the IR spectrum of the ligand disappeared in the spectra of the palladium complexes while a very weak band at 2590 cm^{-1} in the spectrum of the ligand due to νSH disappeared in the spectra Hg(II), Hg(I) and Ag(I) complexes. There was a shift in the position of ν—C=N— band from 1580 cm^{-1} in the ligand to 1560 cm^{-1} in the spectra of Pd(II) and Hg(II) complexes. This indicates the coordination of Pd(II) through oxygen and nitrogen and of Hg(II) through sulphur and nitrogen.

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N-Phenyl-N-(2-benzothiazolylazo)hydroxylamine as an Analytical Reagent for Pd(II), Cu(II) & Ni(II)

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Received 25 *October* 1976; *accepted* 21 *December* 1976

N-Phenyl-N-(2-benzothiazolylazo)hydroxylamine has been successfully used as an analytical reagent for the gravimetric determination of Pd(II), Cu(II), and Ni(II). The solid complexes of the general formula, $(C_{13}H_9N_4SO)_2M$, have been isolated at *p*H 2·5-3·0 for Pd(II) and Cu(II) and at *p*H 4·5-5·5 for Ni(II). The stability constants of chelates have also been determined *p*H-metrically in aq. dioxane.

MUKERJI in a comparative study of the efficacy of various hydroxamic acids for the determination of metal ions, established the superiority of the title reagent[1] over N-phenyl-N-(phenylazo)-hydroxylamine and its analogues[2,3]. The analytical