INDIRECT POLAROGRAPHIC DETERMINATION OF SILVER

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Summary—Conditions for the indirect polarographic determination of silver, based on the substitution reaction of silver ions with bismuth diethyldithiocarbamate dissolved in carbon tetrachloride

 $Bi(DDTC)_3 + 3Ag^+ \rightleftharpoons 3Ag(DDTC) + Bi^{3+}$

are reported. Liberated bismuth^{III} ions can be determined polarographically in the supporting electrolyte containing EDTA. Using this principle a method has been developed for the determination of silver in galenite and in silver alloys.

SILVER, being an electrolytically noble metal, produces no well-developed polarographic waves and the diffusion current of silver ions starts at zero applied e.m.f. Spálenka¹ used this phenomenon for the polarographic determination of silver in bronze and measured the shift of the lead wave above the zero current. In the present paper the substitution reaction of silver ions with bismuth diethyldithiocarbamate is studied as a possible means for the indirect polarographic determination of silver.

According to Bode² bismuth is extracted by diethyldithiocarbamate (DDTC) into carbon tetrachloride in the pH range 5–11, even in the presence of EDTA. The same applies to the extraction of silver. Because the stability constants of these carbamates differ considerably, substitution of bismuth ions by silver can occur. Eckert³ gives the sequence in the order of increasing stability for a series of carbamates of various metals as: Mn-As, Zn-Sn, Fe^{III}_Cd-Pb-Bi-Ni, Co-Cu-Ag-Hg. According to this series it is evident that, for example, mercury ions in aqueous solution displace Ag⁺, Cu²⁺, etc., from their DDTC complexes in an organic solvent. In this way Vašák and Šedivec⁴ determined mercury; similarly, Přibil *et al.*⁵ determined cobalt and Eckert⁶ manganese. The equilibrium used by these authors is illustrated by the equation:

$$\mathbf{m}[\mathrm{Me_2}^{n+}]_{aq} + \mathbf{n}[\mathrm{Me_1}(\mathrm{DDTC})_{\mathbf{m}}]_{org} \rightleftharpoons \mathbf{n}[\mathrm{Me_1}^{\mathbf{m}+}]_{aq} + \mathbf{m}[\mathrm{Me_2}(\mathrm{DDTC})_{\mathbf{n}}]_{org} \qquad (1)$$

where Me_2 is a metal, the complex of which with DDTC is more stable than that of the metal Me_1 , and org and aq are the organic and water phases, respectively.

Reagents

EXPERIMENTAL

0.01 and 0.005M silver nitrate solutions: Prepared by dissolving metallic silver in nitric acid (1:1) and standardised gravimetrically.

5% bismuth diethyldithiocarbamate in carbon tetrachloride: Prepared by precipitation of bismuth from alkaline solution containing EDTA with a 1% solution of diethyldithiocarbamate in carbon tetrachloride. The formed $Bi(DDTC)_8$ complex was washed by shaking with an alkaline solution of bismuth-EDTA complex to remove the free DDTC, then with the ammoniacal buffer solution and

finally with water. The water extract of the solution prepared in this way did not produce a polarographic wave of the bismuth^{III} ion nor of free DDTC.

Solutions of other metallic salts were prepared from reagent grade chemicals. The ammoniacal buffer solution was prepared by mixing 200 ml of 0.5M ammonia solution, 200 ml of 0.5M ammonium chloride and 200 ml of 0.5M EDTA, and diluting to 1 litre with water.

Apparatus

Polarographic curves were recorded with a polarograph of type LP55 (Laboratorní přístroje, Prague, Czechoslovakia) with a polarographic cell used in conjunction with a saturated calomel electrode.

pH was measured with an electronic pH meter, Multoscop V (Laboratorní přístroje).

DISCUSSION

Displacement of bismuth^{III} ions from $Bi(DDTC)_3$ is based on the reaction given in (1).

A 0.01*M* aqueous solution of silver nitrate was prepared so that it was 0.1M with respect to both potassium nitrate and EDTA and the pH was adjusted to 5 by addition of aqueous ammonia or hydrochloric acid. Measured amounts of this solution were shaken for 3–5 min with 25 ml of 5% bismuth diethyldithiocarbamate in carbon tetrachloride in a separating funnel. After separation of the two phases, the aqueous layer was boiled for 1 min to remove traces of carbon tetrachloride. After cooling, 20 ml of ammoniacal buffer were added, the solution diluted to 100 ml with water, and the polarographic wave of the displaced bismuth^{III} ions recorded.

These experiments, carried out in the pH range 5–11, have shown that the height of the polarographic wave corresponding to the displaced bismuth^{III} ions remains constant and is in a molar ratio of 1: 2.94 to the concentration of silver ions originally present in the solution. This ratio agrees quite satisfactorily with the theoretical value of 1: 3 and therefore it is possible to formulate the substitution reaction as

$$Bi(DDTC)_3 + 3Ag^+ \rightleftharpoons 3AgDDTC + Bi^{3+}$$
(2)

Also, the experiments have shown that equilibrium (2) is established rapidly and the conditions employed can be used as a basis for the indirect polarographic determination of silver.

Quantitative displacement of bismuth occurs over a wide pH interval, but for analytical use a relatively high pH was selected (ammoniacal buffer), where the bismuth wave is not disturbed by the waves of other metals. In Table I a series of silver determinations is given at pH values of 6 and 9.5 and the results show that the described procedure is suitable and the error of the determination does not exceed that usual error of polarographic analysis.

Influence of other metals on the determination of silver

The selectivity of the indirect procedure described above for the determination of silver depends on the nature of the complexes of other metals with DDTC. According to the sequence of stabilities previously given, it is evident, for example, that Mn, As, Zn, Cd, Pb, Sn and Fe^{III} are not able to influence equilibrium (1), and because the polarographic determination of displaced bismuth^{III} ions is carried out in the presence of EDTA, all of these elements (with the exception of a large concentration of iron) do not interfere in this determination. On the other hand, mercury interferes because, like silver, it displaces bismuth^{III} from Bi(DDTC)₃. Up to a ratio of Cu: Ag = 2:1, substitution of copper for silver does not occur, but copper^{II} ions remain in the aqueous layer and produce a polarographic wave with a more negative half-wave

potential than that of bismuth^{III}. This could be eliminated by the addition of potassium cyanide to the supporting electrolyte. Employing 0.1M EDTA which contains 0.1M potassium cyanide and 10% (v/v) ethanol, bismuth can be determined even in the presence of a one hundred-fold excess of copper.^{7,8} It is, however, impossible to add potassium cyanide before the substitution reaction, because cyanide ions influence equilibrium (2) and considerable displacement of bismuth ions occurs.

Ag taken, mg/25 ml	Displacement pH	Ag found, mg/25 ml	Δ, %
0.20	6	0.48	-4
	9.5	0.53	+6
1.00	6	0.95	-5
	9.5	1.03	+3
1.50	6	1.46	-3
1.20	9.5	1.46	-3
2.00	6	2.08	+4
2.00	9.5	2.00	0
2.50	6	2.60	+4
2.30	9.5	2.42	-3

TABLE I—DETERMINATION OF SILVER BY DISPLACEMENT OF BISMUTH FROM $Bi(DDTC)_3$

APPLICATION

Experimental results indicated that the procedure could be used for the indirect polarographic determination of silver present in amount from 0.005% upwards and it has been applied to the analysis of silver bronze and galenite.

Determination of silver in materials containing large amounts of copper

Dissolve 1 g of sample (silver bronze) in 10 ml of nitric acid (1:1) and evaporate the solution to a small volume. Dilute to 100 ml with water, neutralise with ammonia solution (1:1) and acidify once more by adding 5 drops of nitric acid (1:1). Add dil. hydrochloric acid to precipitate silver chloride quantitatively, then stand for about 0.5 hr. Filter and wash in the usual way. Dissolve the precipitate on the filter with 10 ml of ammonia solution (1:1), wash the filter-paper with 25 ml of the ammoniacal buffer and add to the resulting solution 0.5 g of ammonium chloride and 10 ml of 1M EDTA. Dilute to about 100 ml with water. Shake for 3 min with 50 ml of 5% bismuth diethyldithiocarbamate in carbon tetrachloride. After separation of the two phases, boil the aqueous layer for 1 min, then transfer it to a 100-ml volumetric flask and dilute to the mark with water. After removing oxygen with nitrogen, record the polarographic curve of bismuth from -0.2 to -1.0 V (saturated calomel electrode).

Determination of silver in galenite

Dissolve 1 g of sample in 25 ml of nitric acid (1:1), evaporate the solution to about 5 ml and, after cooling, dilute to 50 ml with water. Add 10 ml of 1M EDTA, neutralise with ammonia solution (1:1) to phenolphthalein indicator and add 10 ml of a solution 1M with respect to ammonia and 1M with respect to ammonium chloride. Shake 3 min with 50 ml of 5% bismuth diethyldithiocarbamate

in carbon tetrachloride. After separation of the two phases, boil the aqueous phase for about 1 min, transfer to a 100-ml volumetric flask, add 10 ml of 1M potassium cyanide, 10 ml of ethanol and finally dilute to the mark with water. Record the bismuth wave as described above.

The procedures described have been used for samples of bronze with 3.40% of silver, and for galenites which contained 75-85% of lead, and up to 0.1% of copper and silver in the range 0.35-0.55%. Results of these analyses are summarised in Table II, and the corresponding polarographic curves are shown in Fig. 1.

IN VARIOUS MATERIALS				
Sample	Ag present,	Ag found,	Δ,	
	%	%	%	
Galenite 1	0·52	0·49	-6	
	0·52	0·56	+7	
Galenite 2	0·35	0·35	0	
	0·35	0·33	-6	
Silver bronze	3·40 3·40	3·31 3·45	-2.5 + 1.5	

TABLE II—INDIRECT POLAROGRAPHIC DETERMINATION OF SILVER IN VARIOUS MATERIALS



(3) standard solution corresponding to 0.27% of silver.

Zusammenfassung-Bedingungen für die indirekte polarographische Bestimmung von Silber wurden gefunden, die auf einer Verdrängungsreaktion von Silber und Wismut-diäthyldithiocarbamate in Tetrachlorkohlenstoff beruht. Das chemische Gleichgewicht kann wie folgt beschrieben werden

$$Bi(DDTC)_3 + 3Ag^+ \rightleftharpoons 3Ag(DDTC) + Bi^{+3}$$

Das freigesetzte Wismut wird polarographisch in einer ÄDTE enthaltenden Grundlösung bestimmt. Mit der Methode wird Silber in Galena und Silberlegierungen ermittelt.

Résumé-Les auteurs ont mis au point le dosage polarographique indirect de l'argent, fondé sur la réaction d'échange entre les ions argent et le diéthyldithiocarbamate de bismuth dissous dans le tétrachlorure de carbone. La réaction d'échange est:

$$Bi(DDTC)_{s} + 3Ag^{+} \rightleftharpoons 3Ag(DDTC) + Bi^{s+}$$

Les ions Bi^{s+} libérés peuvent être dosés par polarographie dans un électrolyte support contenant de l'E.D.T.A. La méthode a permis le dosage de l'argent dans la gallène et différents alliages.

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