On the Study of Indirect Application of Radioactive Nuclei in Analytical Chemistry. Part IV

B. C. Purkayastha and A. K. Das

Present study deals with further extension of the work reported earler[1,2] to the determination of bismuth, palladium, and lead. The principle employed is to add excess of oxine and iodide mixture labelled with I^{131} to a slightly acidic solution containing the requisite cation and to measure the activity of a portion of the solution with a liquid counter. The loss in activity is a measure of the amount of cation present on the assumption that bismuth is precipitated as (C_9H_7ON) H (BiI_4) and divalent ions like lead and palladium have compositions like $(C_9H_7ON)HMI_3$, where M stands for a divalent cation.

Bismuth from 10 mg. to 0.05 mg. has been estimated. Lead and palladium from 10 mg. to 1.0 mg. have thus far been determined. The data lie always within statistical fluctuations.

The object of the present investigation lies in the further extension of the work[1,2] on the use of co-ordination compounds and radioactive nuclei of convenient half life for micro-estimation of the desired element in shortest possible time.

It is well known that cinchonine, oxine, quinine, etc. form sparingly soluble complex iodides of bismuth, cadmium, mercury, lead, and palladium. The estimation of bismuth by oxine as $(C_9H_7ON)H$ (BiI_4) was done by earlier workers by precipitating the requisite complex, the iodine content of which was determined by adding KIO_3 in acid solutions. The present study refers to application of I^{131} through oxine-iodide complexes in the determination of bismuth, palladium, and lead. Estimation of bismuth has been done in considerable details. Preliminary data have been recorded in cases of palladium and lead.

The principle employed is to add excess of oxine and iodide mixture labelled with Iodine-131 to slightly acidic solutions of bismuth, lead, or palladium, as the case may be, and to measure the activity of portions of the solutions with a liquid counter. The loss in activity is a measure of the amount of the cation present on the assumption that Bi is precipitated as (C_9H_7ON) $H(BiI_4)$ and divalent ions like lead and palladium have compositions like (C_9H_7ON) HMI_3, where M stands for a divalent cation.

EXPERIMENTAL

Bismuth oxide of E. Merck's extra pure quality was dissolved in HNO_3 and the acidity was adjusted by dilution with water. Bismuth was then estimated as bismuth phosphate. Oxine (8-hydroxyquinoline) was of Merck's guaranteed variety and it was dissolved in $0.1N$-HNO_3. An aqueous solution of potassium iodide of E. Merck's G.R. variety served as

1. Purkayastha and Vernekar, this *Journal*, 1957, **34**, 487.
2. Purkayastha and Chandra, *ibid.*, 1962, **39**, 231.

the stock solution. Iodine was estimated as AgI. Palladous chloride and lead nitrate used' in the investigation were of AnalaR variety. Concentration of the stock solution was checked by estimating lead and palladium in the usual way.

To a solution of bismuth a known volume of oxine and KI (labelled with I^{131}) was added. KI, 2-4 times of that required by the equation,

$$Bi^{3+} + 4\,I^- = (BiI_4)^-,$$
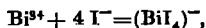
was added. It was then stirred and the volume made to the mark (vide Table I). A fraction of the solution was taken out by a pipette fitted with a filter paper cap to prevent any solid matter entering the filtrate. The activity present in the aliquot portion of the solution was measured and the total activity left in the solution was computed. In case of quantities of bismuth higher than 1 mg., about 200 mg. of oxine was added and in case of quantities below 1 mg., about 100 mg. of oxine was used. Acidity was maintained throughout at about $0.1N$. In case of quantities below 1 mg., precipitation was accelerated by cooling.

Activity was measured by a glass-wall counter meant for measuring liquids. Results for bismuth are recorded in Table I and preliminary data on the estimation of lead and palladium in Table II.

TABLE I

No.	Bi taken.	KI used.	Final vol.	Bi found.	%Error.
1	9.800 mg.	70.00 mg.	30 ml	9.500 mg.	—3.02
2	4.900	38.00	30	4.8700	—0.3
3	2.450	38.00	30	2.5200	+2.9
4	1.470	19.00	30	1.4600	—0.7
5	0.980	14.20	30	0.9560	—2.5
6	0.980	7.60	10	1.0200	+4.0
7	1.470	11.40	15	1.4300	—2.7
8	0.245	2.24	5	0.2380	—2.6
9	0.147	3.80	10	0.1500	+2.0
10	0.147	2.28	5	0.1420	—2.8
11	0.098	0.38	5	0.1010	+3.3
12	0.049	0.38	5	0.0476	—2.9

TABLE II

No.	Amount taken.	Amount of KI.	Final volume.	Amount found.	% Error.
		A. Lead in dil. HNO_3.			
1	103.00 mg.	760.0 mg.	60 ml.	101.00 mg.	—2.0
2	10.30	76.0	15	9.90	—4.0
3	5.15	76.0	10	506.00	—1.8
4	2.06	30.4	5	2.00	—3.0
5	1.03	15.0	5	1.01	—2.0
		B. Palladium in dil. HNO_3.			
6	10.30	190.0	15	10.90	—3.6
7	5.60	76.0	15	5.45	—3.0
8	1.35	19.0	10	1.32	—2.0

DISCUSSION

Table I shows that the errors in the estimation of bismuth always lie within the statistical fluctuations. Obviously, the estimation of bismuth from laboratory level to micro level can be achieved in a very short time with a fair degree of accuracy. The novelty of the procedure lies in the determination of a batch of samples, estimation of each of which does not require more than 10 mins. Another advantage is that it is free from the tedium of filtration, precautions required for washing and other necessary operations needed for quantitative estimations. It has been found that the effect of lead can be eliminated by the use of dilute H_2SO_4.

Though Borg and Wurm[3] estimated bismuth of near about the same order of magnitude by following classical methods, the use of I^{131} as a measuring indicator is a positive improvement because of simplicity and time.

Table II includes preliminary observations of possible estimation of lead and palladium. Interesting issue is that composition of the precipitate is (C_9H_7ON) HM^{II} I_3. Composition of the complex has been determined by estimating lead: iodine ratio. In this case, however, solubility of the complex in question stands in the way to extending the study towards determination of amounts in low concentrations.

It is interesting to note that with the aid of radioactive isotope simple procedures lead us to solve an analytical problem in micro and semi-micro level in a short time.

Nuclear Chemistry Division,
Saha Institute of Nuclear Physics,
Calcutta-9.

3. *Ber.*, 1927, **60B**, 1664,

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