Analyst, July, 1974, Vol. 99, *pp*. 439–441

Polarographic Determination of Thallium, Palladium, Nickel, Zinc and Indium with Diethylenetriamine

BY A. L. J. RAO AND ASHOK KUMAR

(*Department of Chemistry, Punjabi University, Patiala, India*)

The polarographic determination of the metal ions thallium(I), palladium(II), nickel(II), zinc(II) and indium(III) is carried out in a 0·4 M solution of diethylenetriamine. Well defined and irreversible waves are obtained, which are suitable for the determination of small amounts (1 to 7 mg) of these metals. The method gives accurate and reproducible results.

MANY organic compounds, especially bases, have been used as supporting electrolytes for the polarographic determination of a number of metal ions in the presence of other auxiliary electrolytes such as hydrochloric acid, potassium chloride, phosphate, tartrate, etc., in order to increase the specificity and selectivity of the method.[1] Important reagents that have been used for this purpose are hydrazine, pyridine,[2] monoethanolamine,[3,4] triethanolamine,[5] isoquinoline formate,[6] ethylenediamine[7] and EDTA.[8] However, no attempt has been made so far to use diethylenetriamine. In this paper, a method is described for the determination of thallium(I), palladium(II), nickel(II), zinc(II) and indium(III) by using diethylenetriamine.

EXPERIMENTAL

APPARATUS—

All polarograms were recorded at 25·0 ± 0·1 °C with a manual Adept polarograph and pH values were measured with a Philips pH meter. The dissolved oxygen was removed from solutions by passing a stream of nitrogen through them for about 5 minutes. A dropping-mercury and a calomel electrode connected by a saturated potassium chloride - agar bridge were used. The values of m and t in distilled water and on open circuit were 1·85 mg s^{-1} and 3·2 s, respectively.

SOLUTIONS—

All solutions of metal salts were prepared from analytical-reagent grade materials and a 1·0 M solution of diethylenetriamine was prepared in distilled water.

EFFECT OF DIETHYLENETRIAMINE CONCENTRATION—

A number of polarograms were recorded in various concentrations of diethylenetriamine from 0·1 to 1·0 M. It was observed in all instances that with increasing diethylenetriamine concentration $E_{\frac{1}{2}}$ values become slightly more negative (Table I) and i_d values decrease slightly (about 4 to 8 per cent.). The upper plateau in the case of nickel(II) became distorted with concentrations above 0·6 M, but with this exception the concentration of diethylene-triamine has no effect on the shape of the polarograms.

TABLE I

EFFECT OF DIETHYLENETRIAMINE CONCENTRATION ON HALF-WAVE POTENTIALS OF METAL IONS

	$E_{\frac{1}{2}}$/V				
Diethylenetriamine concentration/M	Thallium (1·5 mM)	Palladium (1·2 mM)	Nickel (1·0 mM)	Zinc (1·5 mM)	Indium (0·5 mM)
0·1	−0·490	−0·640	−1·540	−1·545	−1·065
0·2	−0·493	−0·640	−1·550	−1·555	−1·075
0·4	−0·495	−0·643	−1·625	−1·565	−1·087
0·6	−0·500	−0·650	Upper plateau distorted	−1·575	−1·090
0·8	−0·505	−0·655		−1·587	−1·095

Sensitivity, 5 per cent.

EFFECT OF GELATIN—

Only with palladium(II), nickel(II) and zinc(II) were maxima observed, which were suppressed by the addition of 0·006 per cent. of gelatin for palladium(II) and 0·01 per cent. for nickel(II) and zinc(II).

EFFECT OF METAL-ION CONCENTRATION—

Polarograms were recorded for different concentrations of the metal ions thallium, palladium, zinc and indium in 0·4 M diethylenetriamine solution and nickel in 0·3 M diethylenetriamine solution at pH values higher than 10·0. Straight-line graphs that passed through the origin were obtained when values for i_d were plotted against the metal-ion concentration for all five metals. The polarographic results can therefore be used for the determination of these metal ions. The concentration ranges used for calibration are given in Table II.

PROCEDURE—

A calibration graph was prepared for each metal by recording polarograms for various known concentrations of the metal ion, and the diffusion current was plotted against the metal-ion concentration. Because the pH of the solution becomes approximately 10·0 after the addition of the diethylenetriamine, adjustment of the pH was not required. The polarograms for the solutions containing unknown amounts of the metal ions were recorded under identical conditions, the value of the diffusion current being referred to the calibration graph and the concentration of the metal ions determined. This method gave results with an error within 0·5 per cent.

DISCUSSION

The effect of variation of i_d with h has also been studied. The linear graphs obtained for i_d *versus* $\sqrt{h}$ and log (i/i_d-i) *versus* E in all instances indicated that the reduction wave was diffusion controlled. The values for the slope of the graphs of log (i/i_d-i) *versus* E and the values of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (as given in Table II) indicated that the waves for all five metals studied were irreversible. Because of the irreversibility of the reduction waves no deductions can be made concerning the composition of the metal complexes formed. By comparing the values of i_d with those of some reduction waves in which the electron changes involved were known, values for n were obtained and are given in Table II. The pH of the solution in the range 9·0 to 10·5 has very little effect on the diffusion current and on the shape of the polarograms.

TABLE II

POLAROGRAPHIC CHARACTERISTICS OF THALLIUM(I), PALLADIUM(II), NICKEL(II), ZINC(II) AND INDIUM(III) IN DIETHYLENETRIAMINE SOLUTION

Metal	Diethylenetriamine concentration/M	Range of metal-ion concentration/mM	$E_{\frac{1}{2}}$/V	$E_{\frac{3}{4}}$-$E_{\frac{1}{4}}$/mV (from log plot)	n	Remarks*
Thallium	0·4	0·5–3·0	−0·495	72	1	Irreversible
Palladium	0·4	0·4–2·8	−0·643	80	2	Irreversible (6G)
Nickel	0·3	0·4–1·5	−1·557	70	2	Irreversible (10G)
Zinc	0·4	0·4–2·0	−1·565	65	2	Irreversible (10G)
Indium	0·4	0·2–1·4	−1·087	62	3	Irreversible

* G represents 0·001 per cent. of gelatin.
Sensitivity, 5 per cent.

The resistance of the cell in the potential range studied remains almost constant (for a solution 1·0 mM in indium and 0·4 M in diethylenetriamine the resistance at −0·35 V is 318 Ω and at −1·8 V 320 Ω). The resistance of 0·4 M diethylenetriamine solution alone is 900 Ω and will naturally fall when metal salts are added, consequently there is no need to correct for *IR* drop.

POLAROGRAMS OF INDIUM - THALLIUM AND NICKEL - PALLADIUM MIXTURES—

The individual polarographic characteristics of the metals suggested the possibility of differentiating indium from thallium and nickel from palladium in diethylenetriamine solution.

A series of polarograms was therefore recorded on solutions of the mixed metal ions and the values for the diffusion current measured for each metal were referred to the calibration graph as before. The results observed for some mixtures are given in Tables III and IV.

TABLE III

POLAROGRAPHIC DETERMINATION OF INDIUM AND THALLIUM

Diethylenetriamine solution, 0·4 M; sensitivity, 5 per cent.; total volume, 25 ml

Amount taken /mg		Amount found/mg	
Indium	Thallium	Indium	Thallium
1·435	1·533	1·435	1·533
3·445	5·109	3·445	5·114
4·306	2·555	4·324	2·555
7·176	7·664	7·141	7·664

INTERFERENCE OF FOREIGN IONS—

The metal ions thorium, iron, bismuth, manganese, antimony, tin and uranium are precipitated from solution and thorium, iron, tin and uranium do not give a current even after precipitation. Antimony, however, gives a current in the −1·00 to −1·35-V potential range and will therefore interfere in the determination of indium. Bismuth and manganese at low concentrations do not interfere, but at higher concentrations the latter affects the diffusion current produced by nickel and zinc while bismuth affects the determinations of thallium, nickel and zinc.

TABLE IV

POLAROGRAPHIC DETERMINATION OF NICKEL AND PALLADIUM

Diethylenetriamine solution, 0·3 M; gelatin, 0·01 per cent.; sensitivity, 5 per cent.; total volume, 25 ml

Amount taken/mg		Amount found/mg	
Nickel	Palladium	Nickel	Palladium
0·587	2·128	0·587	2·128
1·174	5·320	1·174	5·346
1·468	4·256	1·460	4·256
1·761	3·192	1·765	3·192

Silver, molybdenum and tungsten do not undergo reduction and so cause no interference in the determination of thallium, palladium, nickel, zinc and indium. The advantage of diethylenetriamine as base electrolyte over others reported is that it can be used without the addition of auxiliary electrolytes and without external adjustment of the pH. The waves for the five metals are well defined and small amounts (1 to 7 mg) of these metals can be determined even in the presence of the above elements.

REFERENCES

1. Meites, L., "Polarographic Techniques," Second Edition, Interscience Publishers, New York, **1967**.
2. Grenier, J. W., and Meites, L., *Analytica Chim. Acta*, 1956, **14**, 482.
3. Rao, A. L. J., and Puri, B. K., *Analyst*, 1971, **96**, 364.
4. ——, ——, *Z. analyt. Chem.*, 1970, **252**, 376.
5. Jessop, G., *Nature, Lond.*, 1946, **158**, 59.
6. Rao, A. L. J., and Puri, B. K., *Z. analyt. Chem.*, 1971, **255**, 20.
7. Dolezal, J., *Chemické Listy*, 1955, **49**, 1237.
8. Meites, L., *op. cit.*, p. 641.

Received *November 2nd*, 1973
Accepted *December 17th*, 1973