Potassium Thiocarbonate—A Titrant in Amperometric Analysis

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(Received June 21, 1966)

Earlier observations from these laboratories on the polarographic characteristics of alkali xanthate[1] led to the development of an amperometric titration procedure for the estimation of a number of cations either individually or in some their typical binary mixtures.[2] Incidentally a study of the polarograms of other thio compounds suggested itself. Preliminary experiments showed that some of these thio compounds yield well defined polarographic waves under controlled operative conditions and may therefore serve as potential titrants in the amperometric determination of cations reacting to form insoluble precipitates. In this connection the behaviour of potassium thiocarbonate deserved special attention. The various limitations imposed on the use of hydrogen sulphide in chemical analysis necessitated its substitution by a more stable but equally versatile reagent for the quantitative precipitation of metals. The relative stability, ease of preparation, use over wider range of pH and especially the effectiveness for precipitation from homogeneous solution are some of the unique advantages differed by potassium thiocarbonate which has led to its extensive use as a substitute for hydrogen sulphide.[3] The field has so far been restricted to qualitative and/or semiquantitative analysis[4,5] because of the lack of adequate polarographic data of this compound.

A systematic study of the polarograms of potassium thiocarbonate under diverse conditions revealed the existance of a well defined anodic wave ($E^{1/2}$ -0.65V *vs.* SCE) in certain buffers *viz.*, ammonium tartrate + potassium nitrate, ammonium acetate + potassium nitrate, ammonium tartrate + potassium nitrate + ammonia (pH 6.8—9.2). A linear relation between the anodic diffusion current and concentration of potassium thiocarbonate over a limited range in these buffers wherein the reagent also reacted with certain cations to give characteristic precipitates paved the way to the developement of an amperometric procedure for their quantitative estimation. These observations are now described in some detail.

Experimental

The Leeds and Northrup Electro-chemograph type E was used to obtain necessary polarographic data. The characteristics of the dropping mercury electrode were $m=2.5$ mg/sec $t=3.4$ sec pH measurements were carried out with the Beckman Zeromatic pH meter.

Potassium thiocarbonate was prepared as described by Johri.[3] The method of sucessive dilution was used to obtain solutions of desired strength. Stock solution of the reagent was standardized by two procedures developed during the course of this study. In the first method, an aliquot of the reagent was treated with an execess of standard potassium ferricyanide and sufficient sodium hydroxide with an overall concentration of 3 N. The mixture was set aside for about 15—20 min and the unreacted ferricyanide was back titrated amperometrically in presence of 3—4 drops of osmium tetroxide with sodium arsenite.[6] A parallel

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1) K. Saraswathi, Ph. D. thesis (1966), Banaras Hindu University.

2) G. S. Deshmukh and K. Saraswathi, *Indian J. Chem.*, **11**, 489 (1965).

3) K. N. Johri, "Chemical Analysis without H_2S," Asia Publishing House, Bombay (1963).

4) H. H. Barber and E. Gnzeskowiak, *Anal. Chem.*, **21**, 192 (1949).

5) K. N. Johri *et al.*, *J. Sci. Ind. Res.*, **17B**, 333 (1958); **18B**, 430 (1959); *Analyst*, **96**, 487 (1961); *Indian J. Appl. Chem.*, **26**, 114 (1963); *ibid.*, **28**, 90 (1965); *Indian J. Chem.*, **3**, 158 (1965).

6) G. S. Deshmukh and M. G. Bapat, *Z. Anal. Chem.*, **156**, 105 (1957).

blank for the standardistation of potassium ferricyanide using the same arsenite solution was run to calculate the amount of ferricyanide consumed in the oxidation process. Results of these titrations showed that 8 equivalents of ferricyanide are needed by 1 mol of potassium thiocarbonate. The overall reaction may therefore be represented as follows:

$$CS_3^{2-} + 8Fe(CN)_6^{3-} + 8OH^- \rightarrow 8Fe(CN)_6^{4-} + SO_4^{2-} + 4H_2O + CS_2$$

In the second procedure, an aliquot of a standard solution of lead nitrate was titrated amperometrically in presence of ammonium acetate+potassium nitrate buffer (pH 6.8) at the dropping mercury electrode at an applied potential of -0.8 *vs.* SCE corresponding to the cathodic diffusion current of Pb^{2+}. On the addition of potassium thiocarbonate from a microburette the cathodic current of lead decreased gradually due to the precipitation of lead thiocarbonate and reached a steady state with an excess reagent. The end point obtained from the intersection of two straight lines of the L shaped curve enabled the calculation of the strength of potassium thiocarbonate. A close agreement obtained between these two observations ensured the reliability of the standardization procedures. No special precautions were taken to protect the thiocarbonate solution and since under these conditions the reagent showed a slight deterioration on standing for 24 hr or longer, its strength was checked regularly before using it as a titrant.

Results and Discussion

The choice of an appropriate medium in which the cation to be estimated reacted quantitatively with thiocarbonate required the performance of trial experiments. Two alternatives were available. A supporting electrolyte wherein the titrant and titrand yielded well defined waves was evidently to be preferred. However, in the absence of such a medium advantage could still be taken of a wave produced by either of the reactants. Since under favourable conditions of pH and ionic strength, the anodic wave of thiocarbonate extended upto -0.5 V *vs.* SCE, the first of the above two alternatives was restricted to such cations like Cu^{2+} whose cathodic current plateau covered an identical span of the applied potential. On the other hand titrations could be performed at an applied potential corresponding to the anodic diffusion current of potassium thiocarbonate or the cathodic wave of the cation. All these possibilities have been experimentally realized and form therefore the basis of the amperometric determination of a few cations described in this communication.

Data obtained so far show that Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+} react quantitatively with thiocarbonate in a pH range 6.8—9.2. The polarograms of these cations in various buffers within the above pH range facilitated the choice of a suitable medium and an applied potential for their titrations against thiocarbonate. Among these buffers -0.1 M ammonium acetate $+0.1$ M potassium nitrate (pH 6.8) was found to be the most appropriate for these titrations. In this medium the $E^{1/2}$ of Cd^{2+} and Pb^{2+} was found to be -0.66 and -0.47 V *vs.* SCE respectively. In a series of experiments an aliquot of the unknown solution of the cation was taken in a 100 m*l* pyrex beaker containing buffer and was deaerated by bubbling pure nitrogen. The Fisher Electropode with DME and SCE was used and titrations were carried out at an applied potential corresponding either to the cathodic diffusion current plateau of the cation or the anodic current of K_2CS_3 (-0.4 V *vs.* SCE). The end point was located by the graphical method as described in the standardization of thiocarbonate against lead nitrate. Data obtained under these conditions showed that 0.2 to 1.5 mg of the above cations could thus be estimated accurately. A typical set of results for the estimation of Pb^{2+} and Cd^{2+} in 0.1 M ammonium acetate $+0.1$ M potassium nitrate (pH 6.8) is returned in Table 1.

It may be noted that the procedure is simple, less time consuming and easily adoptable in routine analysis. The possibility of applying this technique to the estimation of other cations either individually or in their binary mixtures has been envisaged to widen the utility of potassium thiocarbonate as a potential reagent in electrometric titrations. Thus the determination of Cu^{2+} and Zn^{2+} individually and also in a mixed solution has been accomplished and communicated elsewhere for publication.

TABLE 1. AMPEROMETRIC DETERMINATION OF Cd^{2+} AND Pb^{2+} WITH POTASSIUM THIOCARBONATE

S. No.	Amount taken, mg		Amount found, mg		Difference, mg	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
1	0.198	0.21	0.20	0.21	+0.002	—
2	0.35	0.42	0.36	0.43	+0.01	+0.01
3	0.52	0.52	0.52	0.526	—	+0.006
4	1.06	0.63	1.08	0.62	+0.02	−0.01
5	1.35	1.05	1.33	1.06	−0.02	+0.01
6	2.08	1.48	2.00	1.46	−0.08	−0.02
7	—	1.74	—	1.64	—	−0.10

Summary

A procedure for the standardization of potassium thiocarbonate and its use in amperometric analysis is described. Polarographic characteristics of thiocarbonate indicated some interesting possibilities for its use in the estimation of metal ions forming insoluble precipitates in certain buffers. Data obtained for Pb^{2+} and Cd^{2+} show that 0.2 to 2 mg of these cations may be determined accurately by the above procedure. Extention of these observations to the estimation of other cations is envisaged.

Sincere thanks of the authors are due to Dr. G. B. Singh for facilities and to the Government of India for an award of a research training scholarship to one of them (P. G).