

Amperometric titration of copper with ammonium dithiocarbamate and its determination in the presence of cadmium and mercury

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Abstract. Ammonium dithiocarbamate has been standardized with EDTA solution and its use for the estimation of milligram quantities of copper has been reported. Copper is titrated at +0.2 V vs SCE in ammonium tartrate-potassium nitrate-ammonia buffer using the rotating platinum micro-electrode. Copper has also been estimated in binary solutions with cadmium and mercury. The accuracy of the procedure is comparable to that obtained with other classical methods.

Keywords. Copper; ammonium dithiocarbamate; ethylenediamine tetraacetic acid; rotating platinum electrode; amperometry.

1. Introduction

Amperometric determination of copper with dichromate (Reilley *et al* 1955) and α -benzoinoxime (Langer 1942) is well-known. The use of cupferron as an analytical reagent for the amperometric determination of this cation has been investigated by Kolthoff and Liberti (1949). Usatenko and Uvarova (1960) worked out the amperometric titration of Cu^{++} with sodium pentamethylenedithiocarbamate at a rotating platinum micro-electrode. Amperometric determination of this element with various other analytical reagents are also well known (Stock 1965; Flaschka and Barnard 1972). The present study has been undertaken with a view to develop an accurate method for the amperometric determination of copper using ammonium dithiocarbamate as a titrant. Copper has also been estimated in binary solutions with cadmium and mercury.

2. Experimental

A simple form of an amperometric unit with rotating platinum micro-electrode as proposed by Kolthoff and Stricks (1953) was used. Saturated calomel electrode with Agar-KCl bridge was used as a non-polarizable reference electrode. Standard solutions of copper, cadmium and mercury were made from analar

copper sulphate, cadmium sulphate and mercuric chloride respectively and were standardized by gravimetric methods (Vogel 1964). Polarograms were recorded with an ELICO polarograph with the following characteristics of the DME : $t = 3.2$ sec, $m = 2.0$ mg/sec (in open circuit). pH adjustments were done either with ammonia solution or with dilute HCl. Synthesis of solid ammonium dithiocarbamate (ADC) is well-known (Mather 1955). However in the present investigation, an aqueous solution of ADC was synthesised (Welcher 1955) by warming 3-4 volumes of ammonia solution (28% NH_3 , sp. gr. 0.91) and one volume of carbon disulphide on water-bath for 2 hr. The rose red solution of ADC was filtered out from the unreacted carbon disulphide. pH of this solution was adjusted to ~ 8.0 with conc. HCl using a Philips pH meter. A faint turbidity which appeared at this pH was removed by the dropwise addition of ethanol. A standard solution of 2×10^{-2} M ADC was used in all these investigations.

2.1. Stability of ammonium dithiocarbamate (ADC) solution

Stability of aqueous solution of monoalkyl dithiocarbamates are entirely dependent on the pH of the medium (Joris *et al* 1970). They decompose easily below pH < 5 and above pH > 11 . In the pH range below 5, the decomposition is characterised by the existence of the two competitive reaction pathways; one leading to CS_2 and amine and other to H_2S , methylisothiocyanate and free sulphur. In alkaline medium, the decomposition is favoured by two mechanisms: (a) The first is base catalysed and is therefore favoured by a pH > 11 . (b) The second is due to an oxidation reaction of the dithiocarbamate by the oxygen content in the solution. At 0°C , the aqueous solution of ADC at pH 8.0 is stable for 3-4 months whereas at pH 10.0 this solution is stable for few weeks (Mather 1955). At room temperature ($\pm 25^\circ\text{C}$) when 2×10^{-2} M ADC solution at pH 8.0 is directly exposed to air, the solution becomes colourless within ten days. However in a tightly closed vessel the decomposition is only about 10% within the above period. Under a layer of benzene, the solution of ADC could be stored at room temperature for more than six months.

2.2. Standardization of ADC with EDTA

To an aliquot of 2.0 ml containing 2-10.0 mg ADC, an excess of copper sulphate (3×10^{-2} M) were added. Ten ml of acetate buffer (pH 5.5) was added (Welcher 1958) and the contents were diluted to 50 ml with distilled water. Ten ml of chloroform was added while gently shaking. The solution was allowed to stand for 3-4 min 3-4 drops of PAN [1-(2-pyridylazo)-2-naphthol] in methyl alcohol was added as an indicator and the excess of copper was back-titrated with 3×10^{-2} M EDTA to a sharp colour change from violet to green in aqueous layer. Blank titrations using the same amount of copper sulphate was performed to find the volume of reacted ADC.

2.3. Estimation of copper, cadmium and mercury in single component system

Preliminary studies showed that copper, cadmium and mercury were precipitated in ammonium tartrate-potassium nitrate base electrolyte. The appropriate ope-

rative conditions were established by trial experiments. It was observed that copper, cadmium and mercury are precipitated quantitatively (pH 5.5–7.5 for copper and 5.5–9.5 for cadmium and mercury) in a medium consisting of 0.02 M ammonium tartrate – 0.02 M KNO_3 to 0.1 M ammonium tartrate 0.1 M KNO_3 , pH adjustments were made with either dil. HCl. or ammonia solution. In the actual procedure, an aliquot of the metal ion solution was taken in a 50 ml pyrex beaker and 3 ml of 0.5 M ammonium tartrate – 0.5 M KNO_3 buffer was added. pH of this solution was adjusted to a desired value and then the contents were diluted to 30 ml. The titrations were carried out at +0.2 V vs SCE using the RPE. 2×10^{-2} M titrant was added from a 5 ml microburette. The galvanometer reading was noted initially as well as after each addition of the titrant. After the complete precipitation of metal ions excess reagent gave the anodic diffusion current of its own resulting in a regular rise of the current. The plot of the volume of the reagent against galvanometer reading is shown in figure 1 (curve A). The result of estimations are given in table 1.

2.4. Estimation of copper and cadmium in a binary system

An aliquot of a solution containing copper and cadmium was taken in a pyrex beaker containing the above buffer (0.1 M) of pH 6.5. The current was noted

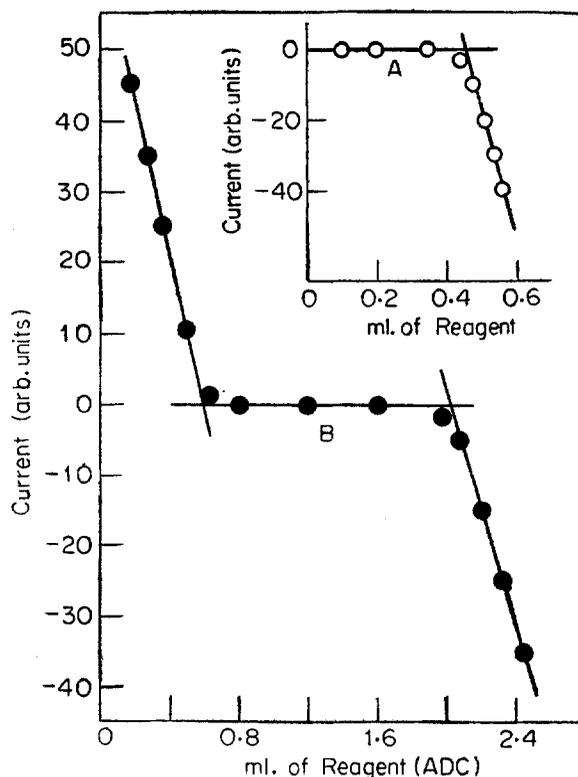


Figure 1. Typical amperometric titration curves [A] Titration curve of copper [B] Titration curve for a mixture of copper and cadmium.

Table 1. Determination of copper, cadmium and mercury in a single component system.

Metal ion	pH of the medium	Amount, mg		% Error
		taken	found	
Copper	6.5	0.5	0.498	-0.40
		1.0	1.0	..
		3.0	2.992	-0.33
Cadmium	6.5	0.25	0.25	..
		1.00	1.002	+0.20
		3.00	3.00	..
Mercury	8.0	0.50	0.498	-0.40
		1.00	0.996	-0.40
		3.50	3.50	..

Table 2. Determination of copper and cadmium in a binary system.

Sl. No.	Amount taken (mg)		Amount found (mg)		% Error	
	Cu	Cd	Cu	Cd	Cu	Cd
1.	0.5	2.0	0.5	1.998	..	-0.10
2.	2.0	0.5	2.004	0.50	+0.20	..
3.	1.5	1.0	1.508	0.998	+0.53	-0.20
4.	2.5	0.5	2.5	0.498	..	-0.40
5.	1.0	1.0	1.0	1.0

at -0.1 V vs SCE. As the addition of the reagent continued, the diffusion current to copper reduced gradually and became steady. This intersection gave the end point for copper. With further addition of titrant, cadmium started to get precipitated and when the whole of cadmium was removed, the excess of the reagent gave the anodic diffusion current of its own. The intersection at this point gave the end point for cadmium (figure 1, curve B). The results of these titrations are reported in table 2.

2.5. Estimation of copper and mercury in a binary mixture

Two titrations were performed to estimate Cu-Hg in a binary mixture. In the first titration, an aliquot of the copper and mercury was titrated at $+0.2$ V (vs SCE) in 0.1 M ammonium tartrate -0.1 M KNO_3 -ammonia buffer (pH 6.5). In the second experiment, 0.2 g of KCNS and 2 ml of pyridine were added to the same mixture and the titration was performed as above. The difference of the readings of the two experiments gave the titre value of copper. Results are shown in table 3.

Table 3. Determination of copper and mercury in a binary system.

Sl. No.	Amount taken (mg)		Amount found (mg)		% Error	
	Cu	Hg	Cu	Hg	Cu	Hg
1.	1.00	0.50	1.002	0.498	+0.20	-0.40
2.	2.00	0.50	2.002	0.56	+0.10	..
3.	2.5	1.00	2.5	1.001	..	+0.10
4.	0.5	2.00	0.502	2.002	+0.40	+0.10
5.	0.5	1.00	0.496	1.00	-0.80	..

3. Results and discussion

Polarographic studies of ammonium dithiocarbamate in various supporting electrolytes of pH 3.0–13.0 revealed that ADC decomposes into its components at pH 5.5 and above pH 11.0. In 0.1 M sodium hydroxide solution, a white precipitate was formed, probably a disulphide resulting from auto-oxidation (Halls *et al* 1968). ADC is oxidised reversibly at the DME with an overall two-electron process between the pH range 3.0–10.0 which agrees with the behaviour of other monoalkyldithiocarbamates (Halls *et al* 1968). The main wave is split into two anodic waves, the ratio of which remains constant in the entire pH range and is practically 1:1. The constancy of $i_1 + i_2 = id/\sqrt{h}$ Hg values indicate that these waves are diffusion-controlled. A typical polarogram of ADC is shown in figure 2.

Since monoalkyldithiocarbamates decompose below pH 5 (Joris *et al* 1970), it is quite strange to observe that monoalkyldithiocarbamates (Halls *et al* 1968) and substituted dithiocarbamates (Usatenko and Tulyupa 1959) produce well-defined anodic waves in acidic medium. The height of the anodic waves remain practically the same between pH 1.0–10.0. Our results also agree with these observations. Since the anodic waves are generated mainly from the dithio-

carbamate moiety $\left(\begin{array}{c} \text{---C---} \\ || \\ \text{S} \end{array} \right)$, it is highly probable that despite their decompositions

in acidic medium, $\begin{array}{c} \text{---C---} \\ || \\ \text{S} \end{array}$ moiety remains undisturbed and hence well-defined anodic waves are obtained.

The anodic wave of ADC extends over a wide span of applied potential (+0.4 to -0.6 V vs SCE) and this observation finds an immediate application in the amperometric determination of metals precipitated by ADC. The applied potential for these determinants was so chosen that the metal ions were not reduced but the reagent had an oxidation step at that potential. As long as the precipitate occurred, the current readings remained steady and after the end point the anodic current of the excess reagent increased (curve A).

The combined use of the cathodic wave of metal ions and the anodic current of ADC under controlled pH conditions for the amperometric titration of metal ions was envisaged. By selecting the combinations of such metals out of which

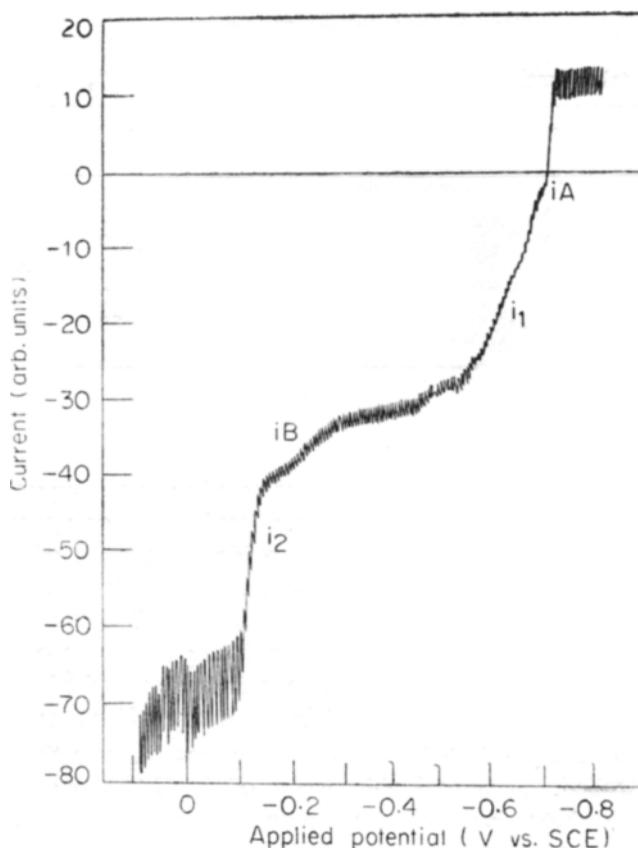


Figure 2. A typical polarogram of 6.0 m M/ADC in 0.05 M ammonium tartrate + 0.05 M KNO_3 + ammonia medium of pH 8.0. i_A and i_B are adsorption prewaves.

one produces reduction current and the other does not at the same potential, their determination in a mixture is accomplished with the addition of the reagent to the mixed solution. With the addition of the reagent at first the titration curve descends (cathodic current of the first metal decreases), then stays close to horizontal (the second metal which does not produce cathodic wave is reacting) and finally ascends beyond the second end point (curve B). Since the half wave potential of cadmium is more negative than that of copper, the latter may be determined cathodically while cadmium is determined anodically. In tartrate buffer (pH 6.5) at -0.1 V (vs SCE) cadmium reacts only after all copper has been precipitated.

A slight modification of the above procedure is adopted for the Cu-Hg binary mixture. Since the polarograms of copper and mercury overlap with each other in tartrate buffer the above procedure could not be applied to estimate this binary mixture. The volume of the reagent consumed by both the metal ions is first determined at pH 6.5. Then a second titration is performed after masking copper with KCNS and pyridene. With a pre-determined molarity of the reagent, it is

then a simple matter to estimate the concentration of the two cations constituting the mixture.

In the standardization of ADC with EDTA it was found that the deep brown Cu-ADC complex interfere with the colour change of the indicator. So chloroform is used to extract the Cu-ADC complex in the organic phase. Under these conditions the copper complex of PAN is not extractable. Chloroform does not interfere with the titrations and the colour change of the indicator is quite sharp in its presence. The colorimetric experiments with 1-5 mg of copper ions have revealed that if EDTA is added to the Cu-ADC complex solution in acetone, the Cu-ADC complex remains unaffected. Hence the removal of the precipitate is not necessary. A close agreement between the results of estimation of ADC with EDTA and various metal ion solutions amperometrically ensured the reliability of the standardization procedures.

Metal-to-ligand molar ratio has been found to be 1 : 2 for divalent ions and 1 : 3 for trivalent ions respectively. Microanalysis of the precipitates proved that they are actually pure metal sulphides. X-ray (powder diffraction) and TGA studies of the same precipitates also revealed the same facts. Reactions of ADC with Cu^{++} ions showed that a brown precipitate appears when Cu^{++} ions are in excess. But a black precipitate appears when ADC solution is in excess in the system. This behaviour can be tentatively explained by the assumption that the brown precipitate initially formed is the compound $\text{Cu}(\text{dithiocarbamate})_2$. The black precipitate is attributed to copper sulphide. Excess addition of ADC results in the cleavage of the monothiocarbamate with the formation of copper sulphide (Halls *et al* 1968). It has been found that only the transitional elements form stable dithiocarbamate salts with ADC. Capacchi *et al* (1966) reported the crystal structure of $(\text{NH}_2\text{CS}_2)_2 \text{Ni}^{II}$ and $(\text{NH}_2\text{CS}_2)_3 \text{Co}^{III}$. Metal dithiocarbamate bonds of the nontransitional elements are too weak in aqueous medium and hence they decompose immediately to form only the metal sulphides.

The data presented in tables 1-3 are reproducible and within limits of experimental errors ($\pm 0.5\%$). Its accuracy is comparable with that obtained with other classical methods. The anodic waves of monoalkyldithiocarbamates corresponding to a two-electron overall process differ in principle from a vast majority of organic sulphur compounds, which give one-electron anodic waves (Heyrovsky and Kuta 1965). The $E_{1/2}$ of the anodic waves of most of these thio compounds lies at the positive side of the zero value (applied potential). The thio compound whose polarogram extends over a wide span of potential both in the positive and negative directions of the zero value would be the most suitable analytical reagent for the amperometric separation of metal ions. Fortunately, the anodic wave of ADC extends over a wide span of applied potential (+0.4 to -0.6 V vs SCE). Therefore, ADC is preferred over many monothiocarbamates and dithiocarbamates (Trorn and Ludwig 1962). The presence of -OH and -COOH group in dithiocarbamates enhances formation of water soluble complexes (Tulyupa *et al* 1974) whereas, ADC forms insoluble complexes in aqueous medium with a large number of metal ions at a particular pH. Analytical separation of various metal ions without change in pH of the medium with ADC is thus feasible. Amperometric separations of metal ions through the change of pH of the medium are tedious and time-consuming. Therefore, it may be claimed that the delineation

of the operative conditions through a series of trial experiments to introduce and also to widen the scope of this reagent (ADC) as a titrant in amperometry is perhaps the most noteworthy feature of these investigations.

Further work on the similar line is in progress.

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