Spectrophotometric Determination of Amines by Cu(II)

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Received 5 *June* 1975; *accepted* 15 *September* 1975

A spectrophotometric method for the determination of amines using Cu(II) has been developed. Job's method and mole-ratio method have been used to determine the metal-amine ratio in the coloured complex formed.

A SENSITIVE method for the spectrophotometric determination of amines using acetyl chloride and ferric salts has been described in our earlier report[1]. Recently copper sulphate has been used for the determination of ethylene diamine[2]. We report here a method for the spectrophotometric determination of some amines using Cu(II).

Following amines were used: Ethylamine, ethanolamine, isopropylamine, *o*-phenylenediamine, isoquinoline and pipridine (Riedel); dimethylamine, trimethylamine, 1,3-diaminopropane, aniline, *p*-toluidine, pyridine (BDH); methyl amine and morpholine (Koch-Light) $CuSO_4$ was a BDH (AR) product.

In most cases, 1*M* solution of amines was prepared in conductivity water. Those insoluble in water were dissolved in methanol. Copper sulphate solution was prepared in conductivity water.

Determination of amines — A small amount of amine (4-60 mg) was mixed with 1 ml of 0·5*M* copper sulphate solution. The solution was shaken well and volume made up to 10 ml by the addition of a solution of ammonium acetate buffer. The absorbance of the coloured complex against blank (1 ml of 0·5*M* copper sulphate and 9 ml ammonium acetate solution) was recorded at the specified wavelength.

It was observed that the increase in temperature brought about a slight decrease in the absorbance. However, for the sake of convenience all determinations were carried out at 25°. The optimum *p*H for the Cu-amine complex was between 6 and 7 and, therefore, buffer of *p*H 6·5 was used. The effect of chloride, nitrate, sulphate and acetate anions was negligible in this procedure of determination of amines. It was found that benzamide, acetamide, chlorobenzene, bromobenzene, nitrobenzene, phenol, methyl cyanide, acetone, benzophenone and propyl alcohol did not affect the absorbance. Pyrogallol and catechol increased the absorbance while acetic acid and aldehydes decreased the absorbance.

Determination of 1,3-*diaminopropane in the presence of aniline, p-toluidine, pyrrole, diphenylamine, isoquinoline, pyridine and* β-*naphthylamine* — 1 ml of the sample containing 1-8 mg of 1,3-diaminopropane was taken in an Erlenmeyer flask and heated on a water-bath for a few min to remove the solvent (particularly if the sample is dissolved in ethanol). To this was added 1 ml of 0·1*M* copper sulphate solution. The reaction mixture was shaken and volume made up to 10 ml by the addition of 1 ml of saturated sodium thiosulphate and formate buffer (*p*H 7). It was again shaken well and kept for 10 min. The contents were centrifuged to remove precipitate if any. The clean solution was decanted and the absorbance measured at 590 nm. The % error in the determination of 1,3-diaminopropane in the presence of other amines was ±2·8%. The standard deviation was 0·08.

Determination of o-phenylenediamine — To 0·5 ml of solution containing 50-250 μg of *o*-phenylenediamine, 1 ml of 0·01*M* copper sulphate and 0·1 ml acetyl chloride were added and reaction mixture heated on a water-bath at 80° for 30 min. Reddish-brown coloured complex thus formed was shaken with 20 ml of isobutanol for 2-3 min. The coloured complex was extracted in butanol layer. The absorbance was noted at 460 nm. Determination of unknown samples of *o*-phenylenediamine showed an error of ±4%.

The optimum temperature for the determination of *o*-phenylenediamine is 80°. It was found that the reaction is unaffected within *p*H range 1-7 while at higher *p*H the colour of the complex changes to green. Benzamide, acetamide, chlorobenzene, nitrobenzene, phenol, acetone, acetic acid and benzophenone did not interfere in the determination of this amine while aldehydes interfere.

The results of determination reveal that amines can be determined using Cu(II). Extraction in isobutanol in the presence of acetyl chloride increases the sensitivity and selectivity in the determination of *o*-phenylenediamine. Job's method of continuous variation and mole-ratio method showed that with *o*-phenylenediamine, a 1 : 1 complex is formed while a 1 : 2 complex is formed in the case of 1,3-diaminopropane.

The authors are grateful to Prof. Wasiur Rehman for providing research facilities.

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Sodium Phenobarbitone as a New Titrant for Microdetermination of Aspartic & Glutamic Acids

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Received 1 *September* 1975; *accepted* 27 *October* 1975

Aspartic and glutamic acids have been determined titrimetrically in micro amounts (67-294 μg) employing sodium phenobarbitone as titrant and bromocresol purple as indicator. The end point is marked by the appearance of a faint pink colour. Only one carboxylic group of the acids reacts with sodium phenobarbitone.

SEVERAL titrants have been used earlier[1-3] for the microdetermination of aspartic and glutamic acids. We have now found that these acids can also be determined titrimetrically in micro amounts (67-294 μg) utilizing a new titrant, sodium phenobarbitone, in the presence of bromocresol purple as indicator. The results of such a

Table 1 — Microdetermination of Aspartic and Glutamic Acids

Aspartic acid (μg)		Glutamic acid (μg)	
Taken	Found	Taken	Found
266	269	294	300
	271		297
	274		300
133	136	147	150
	138		153
	138		153
67	69	74	77
	67		79
	69		77

study are presented in this note. Only one carboxylic group of the aspartic and glutamic acids was found to react with sodium phenobarbitone. Further, the potentiometric titrations of hydrochloric acid by sodium phenobarbitone gave sharp inflexions at one equivalence between *p*H 4·5 and 7·0. The method described is accurate, less time consuming and gives reproducible results (Table 1). However the determination of the individual acid in their binary mixture is not feasible because of interference.

The reagents used were aspartic acid (E. Merck), glutamic acid (E. Merck), sodium phenobarbitone (K. Light), and bromocresol purple (BDH).

Procedure — An aliquot (0·5 ml) of 0·001*M* aspartic or glutamic acid was diluted with distilled water to about 15 ml, and 1 or 2 drops of 0·0053% solution of bromocresol purple added to it. The resulting yellow solution was titrated against 0·001*M* sodium phenobarbitone to the first faint pink colour. The results are given in Table 1.

The author is grateful to Prof. R. C. Mehrotra for his guidance, and to the CSIR, New Delhi, for financial assistance.

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Phenylazoacetaldoxime, a New Reagent for the Estimation of Co(II or III)

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Received 30 *June* 1975; *accepted* 6 *October* 1975

The title reagent has been successfully used for the gravimetric determination of Co(II or III). Co(III)-oxime complex absorbs strongly in UV-visible region in benzene. This has led to the development of a spectrophotometric method for the determination of microquantities of Co(III). Phenylazo-*p*-tolualdoxime is equally effective for the determination of cobalt.

THE commonly used reagents for the estimation of cobalt are oximes[1-7]. A new class of azooximes (A, R=alkyl or aryl) found to have a very high affinity for Co^{2+} and Co^{3+} was synthesized by Bamberger *et al.*[8]. In this paper some of the analytical applications of this class of azooximes are reported. These compounds, commonly known as C-nitrosohydrazones (B), actually exist as oximes (A)[9].

The reaction between cobalt (II or III) salts and arylazooximes (A), leads to the formation of complexes of the type tris(arylazooximato)cobalt (III) (C)[9] which have a dark red colour, show intense absorption bands in UV and visible region and are completely insoluble in aqueous medium. The precipitation of cobalt with arylazooximes in the aqueous medium is quantitative.

The arylazooximes (A) were prepared by the revised procedure of Bamberger *et al.*[8,9]. Phenylazoacetaldoxime (A, $R=CH_3$, $Ar=C_6H_5$, m.p. 117°), phenylazobenzaldoxime (A, $R=Ar=C_6H_5$, m.p. 133°) and phenylazo-*p*-tolualdoxime (A, $R=C_6H_4CH_3$, $Ar=C_6H_5$, m.p. 132°) were used for the estimation of Co(III). A slight excess of arylazooxime (A), dissolved in aq. ammonia (1: 1) was added dropwise with continuous shaking to Co(II) salt solution in water and *p*H of the solution adjusted to ~8 by adding aq. ammonia. The dark brown precipitates were digested on a water-bath for 30 min, the precipitates filtered, heated to a constant weight and washed with 5% ammoniacal solution till these were completely free of the precipitating reagent. The precipitates were finally washed with doubly distilled water and dried overnight at 140° and cobalt estimated from the weight of the precipitated complex (C).

$RC(=NOH)N=N\text{-}Ar$
A

$RC(NO)=N\text{-}NH\text{-}Ar$
B

$[RC(NO)N=N\text{-}Ar]_3Co$
C

The anions NO_3^-, SO_4^{2-}, CH_3COO^-, Cl^-, ClO_4^- do not interfere with the estimation of Co(III). However, the transition metals like Fe, Mn, Ni, Cu do interfere. The method is particularly useful for the determination of Co(II) and Co(III) in their coordination complexes. The aqueous solution of the Co^{3+} or Co^{2+} was obtained from the complex of cobalt (II or III) after digesting several times with an acid mixture containing conc. HNO_3, conc. H_2SO_4 and conc. $HClO_4$. This solution was then used for the estimation of the metal gravimetrically by arylazooximes as described above. The estimation of cobalt by this method was successfully carried out from its complexes of hydroxyazophenols, salicylaldimines and *o*-hydroxyacetophenimines. The % error was always less than 0·5. This method gives better results than α-nitroso-β-naphthol method for the gravimetric estimation of cobalt[10]. The tris(phenylazoacetaldoximato) Co(III) chelate (C, $R=CH_3$) gives intense red purple colour in benzene; λ_{max} 490, 390, 315 (ε 11300, 14000, 41500). These solutions obey the Lambert-Beer's law over a wide range of concentrations. All these three bands were successfully employed for the estimation of cobalt spectrophotometrically.

Co^{2+} in aqueous solution was precipitated by aq. ammoniacal solution of phenylazoacetal-