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SPECTRAL DATA FOR COPPER(II)–SUCROSE SPECIES IN AQUEOUS ALKALI SOLUTIONS

S.S.M.A. Khorasani and A.M. Shafiqul Alam

Department of Chemistry, University of Dacca, Dacca 2

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Abstract. Spectral data for copper(II)–sucrose species in aqueous NaOH solutions have been recorded over the range 200–350 nm and the influence of alkali and sucrose concentration, as also effect of sulphate and nitrate ions on the absorption behaviour have been examined. According to the proposed method, absorbance measurement at 246 nm employing 0.1N NaOH and 2% wt/vol sucrose enables one to determine 1.5–13.0 mg of copper in metallic samples, solutions and in mixtures with alkali and alkaline earth metals, chloride, nitrate, chlorate, bromide, iodide, bromate and iodate with an accuracy of ± 0.2 mg. Absorption behaviour of copper(II) sulphate and the chlorides of chromium(III) and iron(III) in alkaline sucrose solutions have also been briefly examined.

In the course of an investigation on metal–carbohydrate complexes,[1] it was observed that copper(II) chloride when dissolved in alkaline sucrose solutions strongly absorbs in the UV region. Herein are reported results of detailed measurements and attention is directed to the influence of alkali and sucrose concentrations, as also the effect of nitrate, sulphate and various metal ions on the absorption spectra. Results suggested a new simple method for rapid estimation of 1.5–13.0 mg Cu(II)/l. Absorption spectra of chromium(III)–sucrose species which interfere with copper(II) determination have also been briefly examined.

Reagents and Procedure

B.D.H. Analar grade $CuCl_2.2H_2O$, NaOH and sucrose were used to make stock solutions. All other reagents employed were E. Merck's pure grade chemicals. All stock solutions were standardised individually by conventional methods.

Experimental solutions for spectrophotometric measurements were prepared by mixing together aliquots of standard metal solutions, 1N NaOH and 20% aq sucrose in measuring flasks and diluting up to mark with distilled water and/or 1N NaOH as required. Absorbance was measured employing 1 cm fused quartz cells placed in the thermostated cell chamber (30 ± 0.1°C) of a Beckman model DU spectrophotometer.

Preliminary Investigations

Preliminary experiments showed that alkaline solutions of glucose, frucrtose, sucrose and ethylene glycol all dissolved copper(II) chloride in the same manner as alkali–glycerol,[2] but the stability of the products depended on the nature of the complexing agent used. The order of stability was copper(II)–sucrose–> copper(II)-glycerol–> copper(II)–ethylene glycol–> copper(II)–glucose–> copper(II)–fructose species. Excepting copper(II)–sucrose species all the others quickly or slowly decomposed to produce insoluble Cu_2O and therefore only the first system was taken up for detailed spectrophotometric study.

Results and Discussion

Effect of NaOH Concentration. The first series of experiments were performed to examine this effect. For this purpose copper(II) and sucrose concentrations were maintained constant throughout (2.076×10^{-4} g-atom Cu/l and 2% wt/vol sucrose) and NaOH concentration was varied between 0.01 to 1.0N. The absorption curves are reproduced in Fig. 1 and the principal data are summarised in Table 1.

It will be seen that alkali concentration has a remarkable effect on absorption behaviour and that the region of interest extends up to 350 nm. From the analysis of the results it seems that in dilute alkali solutions the absorbing species involved are somewhat different from those which exist in stronger(alkali) solutions. Progressive increase in NaOH concentration possibly affects both the nature and proportion of these species resulting in the change of absorption behaviour which is more pronounced in the concentration region 0.1–0.5N. That the above behaviour

Table 1. Spectral Data for Copper(II)–Sucrose Species in Alkaline Solutions: Influence of Alkali Concentration on the Spectra.

Sucrose concn % wt/vol		2.0	2.0	2.0	2.0	0.0
NaOH concn N		0.01	0.10	0.50	1.00	1.00
λ max primary	nm	204–206	219	—	—	—
λ min primary	nm	210	222	—	—	—
λ max main	nm	258	246	240	240	224
	ε	1890, 1460, 3650.	2650, 2520, 4860.	5150	5150	5650

is not due to formation of only copper(II)–hydroxy complexes[3] was shown by recording the spectrum of a clear solution of copper(II) chloride in 1.0N NaOH. This absorption curve is substantially different from those in presence of sucrose in respect of nature, number and position of the maxima as also the value of molar extinction coefficient. We, however, believe that the copper(II)–hydroxy species may affect the absorption behaviour of the copper(II)–sucrose complexes in the lower (<220 nm) wavelength regions. Thus the peak at around 246 nm appears to be more fundamental.

The small chloride content of experimental solution can have little effect on the spectra, especially because this influence can be significant only at high concentrations and up to around 210 nm only.[4]

As strong alkali solution may attack fused quartz on long contact, it was decided to limit the NaOH concentration to 0.1N in subsequent experiments.

Effect of Sucrose Concentration. In these set of experiments, designed to show the above influence, copper(II), and alkali concentrations were kept constant (1.557×10^{-4} g–atom Cu/l and 0.1N NaOH) and sugar concentration was varied between 0.1 and 3.0% wt/vol. The spectra are recorded in Fig. 2 and the main data are included in Table 2. It will be seen that in 0.1% sucrose solutions the absorption behaviour is entirely different from those

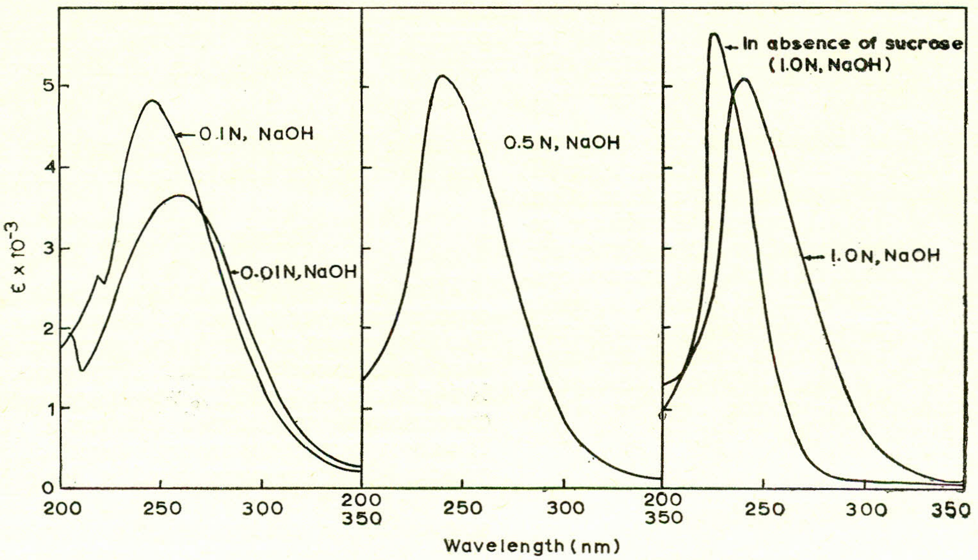

Fig. 1. Absorption spectra of copper(II)—sucrose species in alkaline solutions: influence of alkaline concentration.

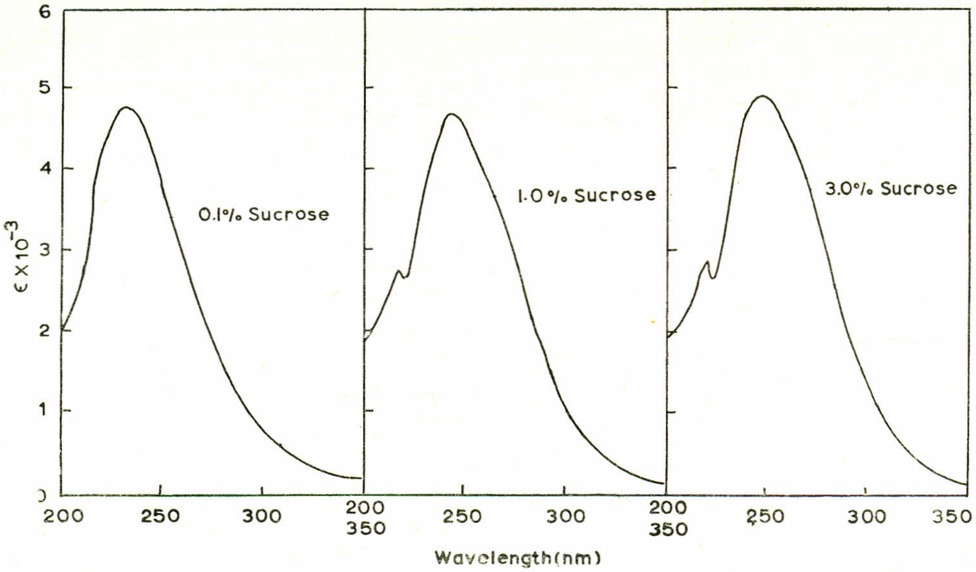

Fig 2. Absorption spectra of copper(II)—sucrose species in alkaline solutions: influence of sucrose concentration.

in 1–3% solutions. Thus concentration dependence is almost of the same nature as in the case of alkali. It seems that a sucrose concentration of at least 1% is to be maintained in the medium in order that significant amounts of the copper(II)–sucrose species of interest may be formed. Results once again indicate that the primary peak is possibly less fundamental than the main peak and the optimal concentration of sucrose, chosen should be around 2% wt/vol.

Effect of Copper II Concentration. This series of experiments were performed to see whether the system in presence of optimal amounts of alkali and sucrose obeys Beer–Lambert's law. Results are graphically represented in Figs. 3 and 4. It will be seen that Beer' law is valid up to a copper(II) concentration of about 13.2 mg/l, if absorbance data are recorded at 219, 222, 240 and 346 nm. However, from a practical point of view, we recommend that a wavelength of 240 or 246 nm should be used for estimation of 1.5–13.0 mg Cu/l.

TABLE 2. SPECTRAL DATA FOR COPPER(II)–SUCROSE SPECIES IN ALKALINE SOLUTIONS: INFLUENCE OF SUCROSE CONCENTRATION ON THE SPECTRA.

Sucrose concn % wt/vol NaOH concn 0.1N		0.1	1.0	2.0	3.0
λ max main	nm	232	242	246	244–246
λ max primary	nm	—	216	219	220
λ main primary	nm	—	220	222	222-224
	ε	4750	4670, 2740, 2650.	4860, 2650, 2520.	4910, 2900, 2660.

TABLE 3. STABILITY OF ABSORBANCE READINGS AT 246 nm.

(NaOH concn 0.1N; sucrose concn 2% wt/vol; copper (II) concn 1.557×10^{-4} g-atom/l)

Time in min	0.0	20.0	31.0	50.0	61.0	72.0
Absorbance	0.768	0.768	0.767	0.766	0.765	0.755

Stability of the Spectra. After ascertaining the optimum concentrations, effect of time on the stability of the absorbance readings at 246 nm was examined. Results indicate (Table 3) that there is no significant change in the extinction coefficient for at least one hour, a time interval sufficient for multiple determinations.

Since there was no evidence for formation of Cu_2O in this system, we can assume that cupric ion is not reduced easily by sucrose and the slow change in absorbance with time may be due to some other reasons.

Effect of Sulphate and Nitrate Ions. In presence of added sodium sulphate (2% wt/vol), the absorbance reading at 246 nm increased somewhat (~2.5%) but the spectrum remained undisturbed while in presence of sodium nitrate (2% wt/vol) absorbance was infinite at the same wavelength. The behaviour in the latter case can be easily attributed to the strong characteristic absorption for nitrate ions at the wavelength used.[5] In separate experiments copper(II)–sulphate was dissolved in 0.1N aqueous NaOH containing 2% wt/vol sucrose and the spectrum of the solution was scanned. It can be seen from the results (Fig. 5) that there is an unmistakable resemblance between the spectra for chloride and sulphate of copper(II), the only difference being in the lower wavelength region. This on the one hand substantiates our previous contention that the main peak is more fundamental and is possibly characteristic of the

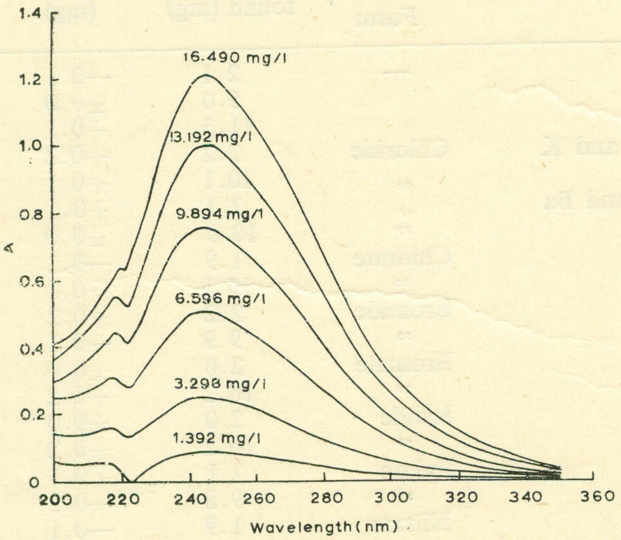

Fig. 3. Absorption spectra of copper(II)—sucrose species in alkaline solution: Effect of copper(II) concentration.

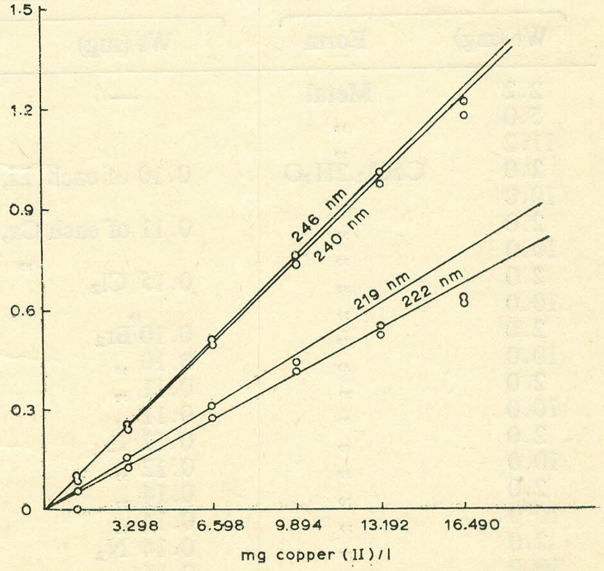

Fig. 4. Beer's laws plots for copper(II)—sucrose species in alkaline solution.

copper(II)-sucrose species, and on the other indicate possibility of applying the proposed method for determination of copper(II) in presence of sulphate as well. However, this has not been fully established.

Effect of Metal Ions. Chromium(III) and iron(III) hydroxides showed behaviour similar to copper(II) hydroxide in sucrose–alkali solutions. These also affected the absorption spectrum of copper(II) tremendously.

We, therefore, briefly examined the individual spectra for these metal ions in aqueous sucrose–alkali and results are given in Fig. 6. It is obvious that in presence of these metals, copper(II) cannot be estimated by the proposed method.

Alkali and alkaline earth metals do not influence the spectra of copper(II) in these systems but nickel(II) and manganese(II) form products which although sparingly soluble do affect the copper(II) spectrum.

Results indicated that chromium(III), iron(III) and possibly nickel(II) and manganese(II) as well, react with sucrose in alkaline solutions in the same manner as copper(II).

Determination of Copper Alone or in Presence of Other Elements. Determination of copper in samples of electrolytic copper and in synthetic mixtures with other elements was carried out using the technique developed. Results are given in Table 4, it indicate that the method is quite suitable for rapid determina-

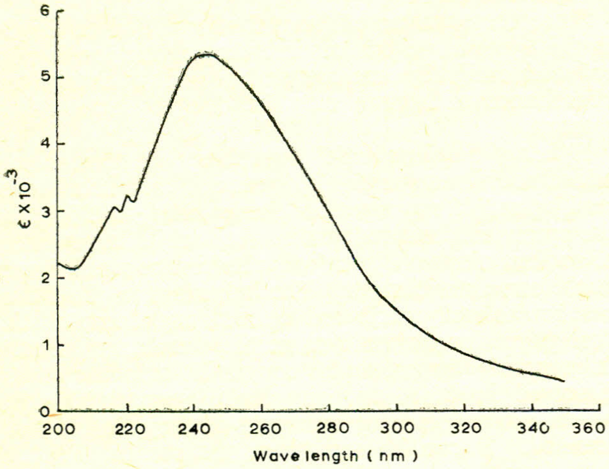

Fig. 5. Absorption spectra of copper(II)–sulphate in alkaline sucrose soltuion.

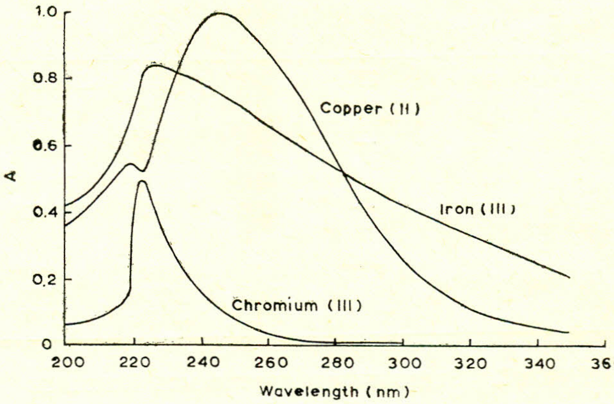

Fig. 6. Absorption spectra of copper(II)–, iron(III)– and chromium(III)—sucrose species in alkaline solution.

TABLE 4. RESULTS FOR COPPER METAL AND SYNTHETIC MIXTURES WITH OTHER ELEMENTS.

Copper taken		Element added		Copper found (mg)	Difference (mg)
Wt (mg)	Form	Wt (mg)	Form		
2.2	Metal	—	—	2.1	—0.1
5.0	,,			5.0	±0.0
11.2	,,			11.3	+0.1
2.0	$CuCl_2.2H_2O$	0.10 of each Li, Na and K	Chloride	2.2	+0.2
10.0	,,	,,	,,	10.1	+0.1
2.0	,,	0.11 of each Ca, Sr and Ba	,,	2.1	+0.1
10.0	,,	,,	,,	10.0	±0.0
2.0	,,	0.15 Cl_2	Chlorate	1.9	—0.1
10.0	,,	,,	,,	10.1	+0.1
2.0	,,	0.10 Br_2	Bromide	2.2	+0.2
10.0	,,	0.10 ,,	,,	9.9	—0.1
2.0	,,	0.11 ,,	Bromate	2.0	±0.0
10.0	,,	0.11 ,,	,,	10.2	+0.2
2.0	,,	0.12 I_2	Iodide	2.0	±0.0
10.0	,,	0.12 ,,	,,	10.2	+0.2
2.0	,,	0.14 ,,	Iodate	2.1	+0.1
10.0	,,	0.14 ,,	,,	9.8	—0.2
2.0	,,	0.14 N_2	Nitrate	1.9	—0.1
10.0	,,	0.14 ,,	,,	10.0	±0.0

tion of the element. Maximum deviation is within ±0.2 mg/l, for 2.0 to 10.0 mg/vol of copper taken.

Proposed Method

Dissolve a weighed amount of the solid sample (copper metal, or copper salts) containing 1.5 to 13.0 mg of the metal, in minimum amount of conc HNO_3 and heat to eliminate oxides of nitrogen (and bromide, iodide, chlorate, bromate, iodate etc., if present). Finally, evaporate repeatedly with concd HCl to almost dryness to remove all traces of nitrate. Treat the chloride (with traces of HCl) with 100 ml of a 1N NaOH solution containing 20 g of dissolved sucrose. Transfer the mixture to a 1-litre measuring flask and dilute up to mark with distilled water. Use this solution for measurement of absorbance against a reagent blank of 0.1N NaOH containing 2% wt/vol sucrose, in the manner described earlier.

Samples containing nitrate may be directly given the HCl treatment and worked up into experimental solutions.

Solutions containing Cu(II) may be analysed by preliminary evaporation to dryness followed by the treatment described above.

Amount of copper(II) may be calculated with reference to a Beer's law plot to be constructed beforehand using 1.5–15.0 mg Cu/l.

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