Colorimetric Determination of Bivalent Copper Using Sodium Alizarin-3-Sulfonate as a Reagent

By Anil K. MUKHERJI* and Arun K. DEY

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Sodium alizarin-3-sulfonate, commonly known as the dye Alizarin Red S (abbreviated as ARS), has been widely used in the determination of aluminum¹⁾, and has also found application in the analysis of zirconium and hafnium²⁾. Raghava Rao and coworkers³⁾ have suggested the use of the reagent in the colorimetric determination of uranium and thorium and Rinehart⁴⁾ for the estimation of rare earths. In a recent communication Mukherji and Dey⁵⁾ reported the formation of colored lakes of various metals with Alizarin Red S and suggested that the reagent might be of use in other determinations as well.

In further communications Mukherji and Dey have reported the spectrophotometric study of alizarin sulfonate chelates of cupric⁶⁾ and lead⁷⁾ and have also discussed the structure of alizarin sulfonate chelates of bivalent metals⁸⁾. It has been found that copper forms a 1 : 1 chelate with sodium alizarin-3-sulfonate with λ_{max} at 500 mμ. In this paper we are reporting our observations on the possibility of using the reagent for the colorimetric determination of bivalent copper on a micro-scale.

Experimental

Solutions of cupric sulfate (BDH Analar) and of Alizarin Red S (BDH Indicator) were prepared in carbon-dioxide free water and standardised as usual. The spectrophotometric measurements were carried out in an air conditioned room maintaining a constant temperature of 25°C.

Absorption spectra of the chelate.—The absorption spectra of the reagent using 0.0002 M solution and the chelate (1 : 1 mixture of the reagent and cupric sulfate of the same concentration) were studied at different wave lengths. The optical densities were measured with an SP 500 spectrophotometer, manufactured by Unicam Instruments Ltd. The thickness of the solution was 1 cm. in glass cells supplied with the instrument. pH of both solutions was 4.3. The results are plotted in Fig. 1.

Conformity to Beer's law.—To fixed volumes of ARS solution were added varying volumes of

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* Present address: Coates Chemical Laboratory, Louisiana State University, Baton Rouge-3, La., U. S. A.

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3) K. S. Venkataswarlu and Bh. S. V. Raghava Rao, *Anal. Chim. Acta*, **13**, 79 (1955); D. V. N. Sarma and Bh. S. V. Raghava Rao, ibid., **13**, 142. (1955).

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6) Idem., *J. Ind. Chem. Soc.*, **34**, 461 (1957).

7) Idem., *Proc. Natl. Acad. Sci., India*, **27A**, 20 (1957).

8) Idem., *Vi jñāna Pari. Anu. Patrikā*, **1**, 23 (1958).

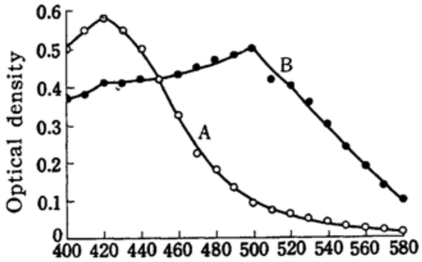


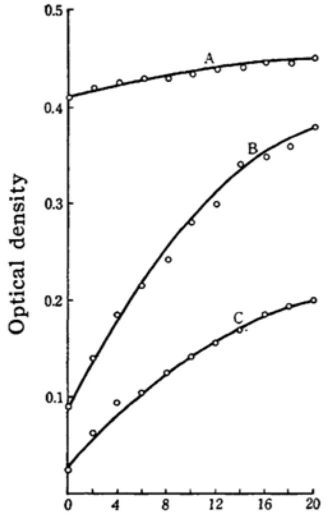
Fig. 1. Absorption spectra studies.
Curve A: Sodium alizarin-3-sulfonate 0.0002 M; Curve B: 1 : 1 mixture of sodium alizarin-3-sulfonate and cupric sulfate (0.0002 M).

cupric sulfate solution, keeping in view that the amount of the chromophoric agent remained in large excess as compared to cupric sulfate. The total volume was kept constant by the addition of water. The optical densities of 1 cm. thickness of the solutions were measured with the spectrophotometer. The observations were repeated at three wave lengths as noted in Table I:

TABLE I

Concn. of Cupric Sulfate $=1.0\times10^{-4}$ M
Concn. of ARS $=1.0\times10^{-3}$ M
Volume of ARS taken $=10$ ml.
Total Volume $=50$ ml.

Volume of $CuSO_4$ ml.	Optical density		
	450 mμ	500 mμ	550 mμ
0	0.410	0.080	0.025
2	0.420	0.140	0.065
4	0.425	0.186	0.095
6	0.430	0.215	0.105
8	0.430	0.245	0.125
10	0.435	0.280	0.145
12	0.440	0.300	0.155
14	0.440	0.340	0.170
16	0.445	0.350	0.185
18	0.445	0.360	0.195
20	0.450	0.380	0.200



Volume of $CuSO_4$ ml.

Fig. 2. Conformity to Beer's law.
Curve A, 450 mμ; Curve B, 500 mμ; Curve C, 550 mμ.

The results in Table I are represented graphically in Fig. 2. It may be seen that the calibration curves have a curvature, which is probably due to the colloidal nature of the reagent[9].

Stability of the color at room temperature.—A mixture of solutions of 0.0002 M of cupric sulfate and 0.001 M of ARS (pH of mixture 4.0) gave the same optical density even after 72 hours of standing at room temperature, showing that the color is stable enough for colorimetric measurements.

Influence of temperature.—The color intensity remains constant over a temperature range 20° to 35°C, as may been in Table II:

Influence of pH.—The intensity of color is stable between pH 3.20 to 7.50, as may be seen in Table III:

Sensitivity of the reagent.—The smallest amount of cupric ion that can be detected with Alizarin Red S is 6.4 p. p. m., when absorbance measurements are done in 1 cm. cells.

TABLE II

Concn. of cupric sulfate $=0.0002$ M
Concn. of ARS $=0.001$ M
pH of mixture $=4.00$

Temperature °C	20	25	30	35	40	45
Optical density per cm. (500 mμ)	0.680	0.680	0.680	0.680	0.685	0.685

TABLE III

Concn. of cupric sulfate $=0.00005$ M
Concn. of ARS $=0.0002$ M
Temperature $=25$°C

pH	2.80	3.20	4.00	5.30	6.20	7.50	8.10
Optical density per cm. (500 mμ)	0.420	0.740	0.740	0.740	0.740	0.740	0.440

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[9] Idem., *Kolloid-Z.*, in press.

TABLE IV

Concn. of cupric sulfate = 0.0002 M (12.7 p. p. m.)
Concn. of ARS = 0.001 M
pH of the mixture = 4.00 ± 0.50
Temperature = 25°C

Ion	Added as	Concn. of ion p. p. m.	Observed change in optical density %	Tolerance limit p. p. m.
Ag^+	$AgNO_3$	9	+ 5	0
Tl^+	Tl_2SO_4	96 32	+ 3 + 1	32
Pb^{2+}	$Pb(NO_3)_2$	16	+20	0
Hg_2^{2+}	$Hg_2(NO_3)_2$	32 2	−11 − 1	2
Hg^{2+}	$HgCl_2$	16 6	− 3 − 1.5	6
Bi^{3+}	Bi-oxalate	80	Turbid	0
Cd^{2+}	$CdCl_2$	45 30	+ 3 + 2	30
AsO_3^{3-}	H_3AsO_3	82 41	− 4 − 2	41
Sb^{3+}	$Sb_2(SO_4)_3$	76	Turbid	0
Fe^{3+}	$FeCl_3$	Interferes at all concn.		0
Fe^{2+}	Ferrous ammonium sulfate	Interferes at all concn.		0
Al^{3+}	$Al(NO_3)_3$	Interferes at all concn.		0
Cr^{3+}	$CrCl_3$	16 8	+ 3 + 1.5	8
Mn^{2+}	$MnSO_4$	80 40	+ 4 + 2	40
Zn^{2+}	$ZnSO_4$	11 6	+ 3 + 2	6
Ni^{2+}	$NiSO_4$	80 40	+ 4 + 2	40
Co^{2+}	$CoSO_4$	50 30	+ 3 + 2	30
Ba^{2+}	$BaCl_2$	55	+20	0
Sr^{2+}	$SrCl_2$	21 10	+ 3 + 2	10
Ca^{2+}	$Ca(NO_3)_2$	32 18	+ 3 + 2	18
Mg^{2+}	$MgSO_4$	10 6	+ 3 + 2	6
Be^{2+}	$BeSO_4$	20 8	+ 4 + 2	8
Zr^{4+}	$ZrO(NO_3)_2$	Interferes at all concn.		0
UO_2^{2+}	UO_2SO_4	Interferes at all concn.		0
Th^{4+}	$ThCl_4$	19 10	+ 3 + 2	10
Ce^{3+}	Cerous ammonium sulfate	22 11	− 3 − 1.5	11
Ce^{4+}	$Ce(SO_4)_2$	12 2	− 4 − 1	2

Ion	Added as	Concn. of ion p. p. m.	Observed change in opitcal density %	Tolerance limit p. p. m.
WO_4^{2-}	Na_2WO_4	20	−11	0
MoO_4^{2-}	$(NH_4)_2MoO_4$	Interferes at all concn.		0
VO_3^-	NH_4VO_3	Interferes at all concn.		0
SeO_4^{2-}	K_2SeO_4	12 6	− 3 − 2	6
TeO_3^{2-}	K_2TeO_3	Interferes at all concn.		0
CO_3^{2-}	Na_2CO_3	20 5	+ 3 + 1	5
SO_4^{2-}	K_2SO_4	152	− 0.5	Large excess
Cl^-	KCl	100	− 1	Large excess
Br^-	KBr	128 64	− 3 − 2	64
I^-	KI	50 30	− 3 − 2	30
ClO_3^-	$KClO_3$	34 20	− 3 − 2	20
BrO_3^-	$KBrO_3$	51 16	− 3 − 1	16
IO_3^-	KIO_3	70 20	+ 3 + 1	20
F^-	NaF	8	− 6	0
SiO_3^{2-}	Na_2SiO_3	31 20	− 3 − 2	20
Citrate	Sodium citrate	76 40	− 3 − 2	40
Tartrate	Potassium tartrate	60 20	− 5 − 2	20
Oxalate	Ammonium oxalate	34 9	− 4 − 1	9
NO_3^-	KNO_3	80 60	− 2.5 − 1.5	60
CNS^-	KCNS	48 24	− 3 − 1.5	24
PO_4^{-3}	Na_2HPO_4	38 8	+ 8 + 2	8
$S_2O_8^{-2}$	$K_2S_2O_8$	80 60	− 3 − 2	60
HCO_3^-	$NaHCO_3$	10 4	− 2.5 − 1	4
$S_2O_3^{2-}$	$Na_2S_2O_3$	45 25	− 3 − 2	25
Acetate	Sodium acetate	Interferes at all concn.		0
$B_4O_7^{2-}$	$Na_2B_4O_7$	13	+ 8	0

Influence of foreign ions.—The effect of a large number of cations and anions on the color intensity was studied with the help of the spectrophotometer. The tolerance limits were quantitatively determined. The tolerance limit represents the concentration of a foreign ion, which would affect the optical density of the solution under investigation by less than ±2%. The results are given in Table IV.

Recommended Procedure

For the determination of copper, a solution is prepared and treated to separate the interfering substances as usual[1,10]. The pure copper salt solution thus obtained, is treated directly or with an aliquot portion with a ten-fold molar excess of a freshly prepared aqueous solution, of the reagent. The pH of the solution is adjusted between 4 and 6. The optical density of the solution is then read at 500 mμ, in an absorption cell of suitable thickness. The color intensity can also be measured with a photoelectric colorimeter with an appropriate filter. The temperature of observation should preferably be 20∼30°C.

Summary

The formation of a 1:1 copper chelate with sodium alizarin-3-sulfonate, having λ_{max} at 500 mμ has been reported. The color formation has been applied to the colorimetric determination of copper on a micro-scale. The color has been found to be stable between pH 3.20 and 7.50, at temperatures 20∼30°C. The sensitivity of the reagent is 6.4 p.p.m. of the copper ion. The interference by a large number of cations and anions has been studied and the tolerance limits are quantitatively determined spectrophotometrically. It has been recommended that the reagent is suitable for the colorimetric determination of copper(II) on a micro-scale and the conditions have been prescribed.

Chemical Laboratories
University of Allahabad
Allahabad, India

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[10] E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed., Interscience Publishers, Inc., New York (1950), 295.