

## Combining the Extraction with Galvanostatic Coulometry for Copper Determination in the Form of Mercaptoquinolines

O. V. SHLYAMINA and G. K. BUDNIKOV

*Butlerov Institute of Chemistry, Kazan' State University,  
Ul. Kremlevskaya 18, Kazan' 420008 (Russia)*

*E-mail: Shlyamina@mail.ru*

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### Abstract

Conditions for coulometric determination of copper (II) in an extract by titration with the electrogenerated bromine have been found. 8-Mercaptoquinoline has been suggested as a complexing agent, which forms complex of composition  $\text{CuR}_2$  with copper ions. Extraction was conducted in chloroform at pH 6. The procedure is approved with synthetic mixtures and with samples of superficial waters. The lowest limit of detectable concentrations with the generating current intensity being  $1 \cdot 10^{-3}$  A and with time equal to 10 s comprises  $5 \cdot 10^{-7}$  M.

### INTRODUCTION

8-Mercaptoquinoline (MQ) or thiooxine is used widely enough as an analytical reagent. Due to heterocyclic nitrogen atom available in its structure and sulphur atom conjugated with the quinoline nucleus, the central atom can form dative  $\pi$ -bonds with sulphur atom and with  $\pi$ -electronic system of the quinoline nucleus, as well as a five-membered cycle with metals, which raises considerably the stability of MQ complexes with ions of metals [1].

A good extractability of inner-complex compounds of MQ and its derivatives with organic solvents opens broad opportunities both for collective and selective extractive concentrating of microquantities and for isolating the macroquantities of heavy metals.

Thiooxine reaction with copper is used for photometric determination of copper microquantities in various commercial and natural objects; however, it was not applied in coulometry. Meanwhile, the coulometry, as a non-calibration method, may be attractive as an alternative way for determination of individual contaminants and for estimation of their total content in the nature protection objects.

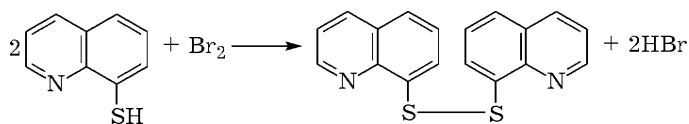
The present work investigates a potentiality to use MQ for the extractive coulometric determination of copper (II).

### EXPERIMENTAL

Electrogeneration of bromine and coulometric titration were conducted with potentiostat P-5827 M. A smooth platinum plate 432 mm<sup>2</sup> in surface area was used as a working electrode. An auxiliary electrode was made up of a platinum spiral. A cathodic chamber, where the auxiliary electrode was placed, was separated from anolyte with a semipermeable membrane. Coulometric titration was conducted in a galvanostatic regime ( $I = 5$  mA). A final point was recognized amperometrically with two polarized needle platinum electrodes ( $\Delta E = 300$  mV).

Photometric measurements were conducted with photoelectrocolorimeter KFK-2 in a sample cell with  $l = 3$  cm.

PU-2 polarograph and a cell with mercury dripping and silver-chloride electrodes were applied. The 0.1 M sulphate-ammonium buffer served as a background. The dissolved oxygen was removed by argon.



Scheme 1.

A unit AAS 1N was applied for the atomic absorption analysis of water samples.

We used the reagents of qualification "chemically pure" (kh. ch.): KBr,  $(C_4H_9)_4NBr$ ,  $H_2SO_4$ , disodium salt of EDTA,  $NaClO_4$ ,  $CaAc_2$ ,  $NH_4Ac$ , and  $CuSO_4$ . 8-Mercaptoquinoline was refined from 8,8'-diquinolyl disulphide impurity, which is formed in storage of the initial reagent, through washing it on Nutsch filter with three or four small portions of chloroform, wherein it is freely soluble. Acetonitrile was distilled over  $P_2O_5$  and then refined with absorbent carbon (5 g per 1 l of acetonitrile). Chloroform of qualification "analytically pure" (ch.d.a.) was used for extraction.

Buffer solutions with pH 7.09 (the citrate buffer) and pH 9 (the sulphate-ammonium buffer) were prepared from standard titrimetric substances.

Bromine was generated from 0.2 M KBr in a solution of 0.1 M  $H_2SO_4$  and from 0.01M  $(C_4H_9)_4NBr$  on the background of 0.05 M acetonitrile solution of  $NaClO_4$ .

The procedure of coulometric titration was as follows. 20 ml of the supporting electrolyte was introduced into a cell of capacity 50 ml; the electrodes were lowered, and a generating circuit was switched on. Upon reaching a certain magnitude of indicator current, an aliquot of a solution for investigation was input in the cell and coincidentally with this, a stopwatch was started. A final point of titration was fixed after the initial indicator current was stabilized; then the stopwatch and the generating circuit were turned off.

## RESULTS AND DISCUSSION

It is known that bromine can be generated electrically with 100 % current efficiency in water solutions of KBr in the presence of  $H_2SO_4$ . In non-aqueous solvents (acetonitrile, glacial acetic acid), a mixture of  $(C_4H_9)_4NBr$  and  $NaClO_4$  is used as a supporting electrolyte [2].

The amount of bromine, which is involved in the electrochemical reaction of both the initial

mercaptoquinoline and its complex with Cu(II), was determined by coulometric titration. It was found that two electrons are required for the reaction with 8-mercaptoquinoline, and this corresponds to two bromine atoms.

8-Mercaptoquinoline most often reacts as a reducer, thus being oxidized to form typically 8,8'-diquinolyl disulphide. However, a deeper oxidation cannot be ruled out too [1], which depends on the conditions of a reaction, mainly, on the pH. An actual redox potential of 8,8'-diquinolyl disulphide/8-mercaptoquinoline pair in 1 M acid solutions comprises +0.44 V relative to normal hydrogen electrode [3]. Such oxidizers as Fe(III), V(V),  $Cr_2O_7^-$  etc. oxidize 8-mercaptoquinoline into disulphide. However, with an increase in acidity of the solution, the actual potential of the appropriate redox pair is subject to increase, whereas the oxidation of thioxine may yield alternative

TABLE 1

Results of coulometric titration of 8-mercaptoquinoline ( $n = 5$ ,  $P = 0.95$ )

It has been taken, $10^{-4}$ g	It has been found, $10^{-4}$ g	$S_r$
1.0	$0.9 \pm 0.1$	0.07
1.5	$1.4 \pm 0.2$	0.09
2.0	$1.9 \pm 0.1$	0.06

TABLE 2

Results of copper (II) coulometric determination in model solutions ( $n = 5$ ,  $P = 0.95$ )

pH	It has been taken, mg	It has been found, mg	$S_r$
5	6.4	$6.6 \pm 0.1$	0.02
5	14.0	$15.7 \pm 0.2$	0.05
5	25.3	$19.2 \pm 0.2$	0.03
5	27.6	$21.2 \pm 0.3$	0.01
6	25.3	$23.9 \pm 0.1$	0.02
6	27.6	$27.7 \pm 0.5$	0.01
9	25.3	$24.6 \pm 0.3$	0.04
9	27.6	$27.3 \pm 0.5$	0.02

TABLE 3

Results of copper (II) determination ( $\bar{X} \pm \delta$ ) in different waters of Karabash copper sulphide deposit ( $n = 0.5$ ,  $P = 0.95$ ), mg/l

Place of sampling	pH	Determination procedure			
		Coulometric	Photometric	Polarographic	AAS
Sak-Yelga River	3.25	9.7 ± 0.2	9.12 ± 0.11	9 ± 2	<5.0
Sak-Yelga River	2.50	15.6 ± 1	13.40 ± 0.09	15.0 ± 0.8	16 ± 2
Argazinskoye water reservoir	5.92	2.07 ± 0.08	1.97 ± 0.15	2.0 ± 0.5	<5.0

products. With this taken into account, it can be suggested that the electrogenerated bromine first oxidizes 8-mercaptoquinoline into disulphide (the schematic diagram 1), which then might be capable of further reacting to form dibromo derivative. The literature contains evidence on a possibility of obtaining 8,8'(4,4'-dichloro)diquinolyl disulphide [4]. It is conceivable that bromine also adds at the position 4; in so doing, two bromine atoms are required too. Eventually, two MQ molecules interact with four bromine atoms, which is in agreement with the experimental data. Alternative variants cannot be ruled out too.

The possibility is estimated to determine thiooxine through coulometric titration by the electrogenerated bromine. The results of the determination with the method "it has been taken – it has been found" for pure solutions are presented in Table 1.

Cu(II) ions form a complex of composition 1 : 2 with 8-mercaptoquinoline. In so doing, no oxidation of the reagent occurs to form diquinolyl disulphide [1]. The complex is stable both in acidic and in alkaline solutions (pH 2–12.9); it shows intensive colouring and has considerable solubility in organic solvents. Chloroform is most often used for extraction.

Coulometric titration of Cu(II) complex with MQ by the electrogenerated bromine runs with a sufficient speed and with good reproducibility. Based on the titration results, it has been determined that four bromine atoms are consumed for one complex molecule. Seemingly, the bromination reaction proceeds in this case.

A potentiality to determine Cu(II) ions by coulometric titration was checked. With this end

in view, 2 mmol of EDTA, 0.5 g  $\text{Ca}(\text{CH}_3\text{COO})_2$ , 5 ml MQ ( $1 \cdot 10^{-3}$  M), and the borate buffer (pH 7) were added to 25 ml of a sample. Copper (II) complex with MQ was extracted with two successive portions of chloroform, 2.5 ml each. Then an aliquot (0.2–0.5 ml) was taken from the extract, was put in a coulometric cell, and titrated according to the above procedure. It has been found that in the presence of EDTA, equimolar quantities of Al(III), Co(II), Fe(III), Mn(II), and Ni(II) present no hindrance.

The results of copper (II) coulometric determination in the model solutions are presented in Table 2. The minimally detectable concentration of copper (II) comprises  $5 \cdot 10^{-7}$  M at the generation current intensity of  $1 \cdot 10^{-3}$  A and with the time equal to 10 s.

The procedure has been applied to analyse the natural waters in the neighbourhood of the Karabash city (Chelyabinsk Region), where are located the mining-and-processing integrated works and the mines, on which extraction of copper ore is underway. The coulometric data acquired are comparable to the results, which have been found by means of photometry, polarography, and atomic absorption spectroscopy (Table 3).

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