# IODOMETRIC DETERMINATION OF 2-MERCAPTOBENZTHIAZOLE BY COULOMETRIC TITRATION

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*Dedicated to Professor Dr J. Zýka on the occasion of his 60th birthday.*

The optimum conditions were found for the determination of 2-mercaptobenzthiazole (MBT) by coulometric titration with the generated iodine using biamperometric indication of the titration end point. Use is made of the oxidation to the disulphide ($n = 1$) and to benzothiazole-2-sulphinate ($n = 4$) in the regions pH 4·5—8·5 and 10—12, respectively. Eight repeated titrations to the disulphide gave the relative standard deviations 0·27% and 1·23% in the determination of 1 675 and 33·5 μg MBT, respectively, seven repeated titrations of 419 μg MBT to benzothiazole-2-sulphinate afforded results with the relative standard deviation 0·34%.

In the determination of thiols, reactions of the —SH functional group are usually employed. The bond between the hydrogen and the sulphur atoms is weaker than that in the analogous hydroxy group of alcohols or phenols, so that hydrogen is more readily split off. The acidic properties of the thiol group proton can be utilized for alkalimetric determination of some aromatic thiols whose dissociation is characterized by the values $pK_a$ 7 to 8 (ref.[1]). Aliphatic thiols are considerably weaker acids, with the values $pK_a$ about 12 (ref.[2]). Another property of the —SH group is its ability to form low soluble salts with metal ions of the 1st and 2nd analytical groups, of which use can be made in precipitation titrations; the most important in this respect are the silver and mercury salts[3].

Of analytical utility are also the easily proceeding stepwise reactions of the —SH group with oxidants[4]. The disulphide is formed on a subtle oxidation, a more intensive oxidation leads consecutively to the thiosulphonic acid ester, disulphoxide or the isomeric thiosulphonic acid ester, sulphinic acid, disulphone; a drastic oxidation can result in the formation of sulphonic acid.

In this work, a method of iodometric determination of 2-mercaptobenzthiazole (MBT) by coulometric titration has been worked out and the medium suitable for the reaction found. The substance has been chosen as a model compound for a systematic study of the electroanalytical methods of determination of mercaptans with regard to the fact that it can be obtained in the pure state. Unlike aliphatic thiols, it is nonvolatile and is better resistant to oxidation by oxygen. It is currently used as an

analytical reagent for gravimetric or volumetric determinations of various metal ions and as a curing accelerator. The methods of determination of 2-mercaptobenz-thiazole are largely based on its reaction with silver ions leading to the low-soluble mercaptide; this is the underlying principle of the gravimetric method[5] as well as the titrimetric methods using visual[6,7], amperometric[8-10], potentiometric[11,12], or con-ductometric[13,14] indication of the titration end point. Analogous methods of de-termination of 2-mercaptobenzthiazole make use of its reaction with other metal ions such as $Hg^{2+}$ (refs[15-18]), $Cd^{2+}$ (ref.[19]), or $Cu^{2+}$ (ref.[20]). Alkalimetric[21] and iodometric[13,22,23] methods of determination and a method based on the oxidation by iodine chloride[24] have also been suggested.

## EXPERIMENTAL

### Reagents and Apparatus

2-Mercaptobenzthiazole *p.a.* was dissolved in methanol *p.a.* so as to obtain solutions of the concentrations $5 . 10^{-3}$ and $1 . 10^{-4}$ mol $l^{-1}$.

1M solution of potassium iodide, the base electrolyte for the generation of iodine, was prepared from redistilled water free from cupric ions. Its stability was ensured by adjusting the pH with a sodium carbonate solution of the concentration $1 . 10^{-3}$ mol $l^{-1}$.

The Britton–Robinson buffer (phosphoric acid, $0.2$ mol $l^{-1}$; acetic acid, $0.2$ mol $l^{-1}$; and boric acid, $0.2$ mol $l^{-1}$), 1M sodium hydroxide solution, and 0.5M phosphoric acid, potassium dihydrogenphosphate, and sodium hydrogenphosphate solutions were prepared from the *p.a.* chemicals (Lachema, Brno).

The titrations were performed in the apparatus described in[25]. A 100 ml vessel was fitted with a Teflon plug accomodating two 1 cm$^2$ generating electrodes (the cathode was separated from the titrated solution by a glass filter) and two 3 cm$^2$ electrodes for the biamperometric indication. All the electrodes were made of a platinum sheet 0.2 mm thick. The solution was stirred during the titration by means of a glass screw stirrer using a constant velocity of 2 650 r.p.m. The generat-ing electrodes were fed from a constant current supply (Prague Institute of Chemical Technology) working in the 0.01 to 100 mA region with the accuracy of 0.1%. The electrodes for the biam-perometric indication were polarized applying voltage of 50, 100, and 200 mV. The course of the titration was monitored *via* the titration curves, recorded on an EZ 2 chart recorder (Labo-ratorní přístroje, Prague) using the chart speed 1 mm s$^{-1}$. The pH values were measured on an OP 201/2 pH-meter using a combined OP-801/1 glass electrode (Radelkis, Budapest). The so-lutions of 2-mercaptobenzthiazole were proportioned by means of an E 274 hand-operated 10 ml plunger burette (Metrohm, Herisau).

### Working Procedure

The solutions were added to the proportioned volume of the 2-mercaptobenzthiazole solution so that after diluting with water to 25 ml the system contained iodide in the concentration 0.1 mol . $l^{-1}$ and the Britton–Robinson or phosphate buffer in the concentration 0.2 or 0.1 mol $l^{-1}$, respectively. With respect to the amount of the substance to be determined the generating current was chosen such that the determination period was about 100 to 500 s. The blank experiment period was subtracted from the titration end period. The pH of the solution was measured after the titration.

## RESULTS AND DISCUSSION

*Examination of the course of the reaction between iodine and 2-mercaptobenz-thiazole, and establishing the optimum* pH *region for the determination.* As hydrogen ions are evolved during the oxidation of 2-mercaptobenzthiazole, the oxidation-–reduction potential is dependent upon the acidity of the solution. For establishing

TABLE I

Course of oxidation of 2-mercaptobenzthiazole by iodine in dependence on pH: titration period ($t$) and the number of electrons per a molecule of 2-mercaptobenzthiazole ($n$). Titrated: $7 \cdot 528 \cdot 10^{-6}$ mol MBT; generating current: $5 \cdot 0$ mA

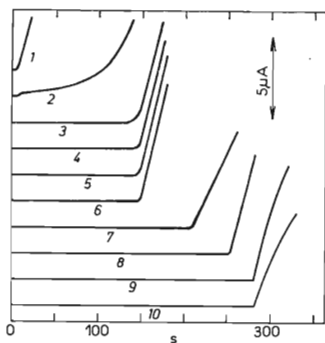| Solution pH | $t$ s | $n$ | Solution pH | $t$ s | $n$ |
|---|---|---|---|---|---|
| 1·35 | 0 | — | 9·30 | 161·0 | 1·11 |
| 3·15 | 112·0 | 0·771 | 0·75 | 208·5 | 1·44 |
| 3·70 | 136·0 | 0·936 | 9·85 | 456·5 | 3·14 |
| 4·35 | 144·0 | 0·991 | 10·22 | 552·0 | 3·80 |
| 5·20 | 145·0 | 0·998 | 10·70 | 564·0 | 3·88 |
| 6·00 | 145·0 | 0·998 | 11·15 | 577·0 | 3·97 |
| 7·00 | 145·0 | 0·998 | 11·45 | 580·0 | 3·99 |
| 7·70 | 145·0 | 0·998 | 11·56 | 575·0 | 3·96 |
| 8·65 | 147·0 | 1·01 | 11·81 | 580·0 | 3·99 |



FIG. 1

Biamperometric titration curves for titrations of 2-mercaptobenzthiazole with iodine at different pH values. pH: *1* 1·35, *2* 3·15, *3* 4·35, *4* 5·20, *5* 7·70, *6* 8·65, *7* 9·75, *8* 10·20, *9* 11·45, *10* 11·81. For the curves *8—10* the time is ($t + 300$) s

the oxidation state, the dependence of the number of exchanged electrons $(n)$ on pH was examined. For this, 1·00 ml of the MBT solution of the concentration $c(\text{MBT}) = 7·528 \cdot 10^{-3}$ mol l$^{-1}$, 5 ml of 1M-KI, and 5 ml of the Britton–Robinson buffer solution of the given value were pipetted into a vessel and diluted to volume 25 ml. The generating current was 5·0 mA, polarizing voltage for indication 200 mV, the recorded full scale deflection corresponded to 30 µA. The blank experiment periods were determined for each pH value. The titration curves for selected pH values are shown in Fig. 1, the calculated $n$ values are given in Table I.

As the results demonstrate, solutions up to pH 3 are unsuitable for the determination. The conditional reduction potential of the disulphide to 2-mercaptobenzthiazole is reported[24] to be $E^c = 0·475$ V in 0·01M-HCl, the standard potential of iodine

TABLE II

Determination of 2-mercaptobenzthiazole by oxidation to the disulphide. Generating current 2·0 mA

| MBT prepared µg | Solution pH | Number of determinations | MBT found µg | Relative error % |
|---|---|---|---|---|
| 418·1 | 4·8 | 4 | 404·86 | −3·16 |
| | 5·4 | 5 | 415·90 | −0·51 |
| | 6·0 | 5 | 411·89 | −1·49 |
| | 6·2 | 4 | 416·14 | −0·65 |
| | 7·0 | 4 | 414·40 | −0·89 |
| | 8·9 | 5 | 417·07 | −0·24 |
| 836·2 | 4·8 | 2 | 830·80 | −0·65 |
| | 5·4 | 2 | 831·63 | −0·55 |
| | 6·0 | 3 | 831·47 | −0·56 |
| | 6·2 | 4 | 834·64 | −0·14 |
| | 7·0 | 3 | 838·32 | +0·26 |
| | 8·9 | 3 | 836·15 | 0·00 |
| 1 254·2 | 4·8 | 2 | 1 246·4 | −0·62 |
| | 5·4 | 2 | 1 247·9 | −0·51 |
| | 6·0 | 3 | 1 248·9 | −0·43 |
| | 6·2 | 3 | 1 250·2 | −0·33 |
| | 7·0 | 3 | 1 252·7 | −0·13 |
| 1 672·3 | 4·8 | 2 | 1 657·8 | −0·87 |
| | 5·4 | 2 | 1 670·0 | −0·14 |
| | 6·0 | 2 | 1 669·8 | −0·16 |
| | 7·0 | 3 | 1 663·1 | −0·55 |

reduction to iodide is $E_{I_2, 2I^-}^0 = 0.535$ V. As can be seen from curve 2 in Fig. 1, the difference between the potentials and the reaction kinetics are insufficient to permit a direct coulometric titration. The rounded, indefinite shape of the biamperometric titration curve is unsuitable for the evaluation. Oxidation to the disulphide $(n = 1)$ proceeds in a defined way in the region pH 4 to 8·5, as is apparent from the titration curve and the calculated $n$ values. At pH above 9, further oxidation occurs without distinction between the various oxidation states, and ultimately at pH 10 to 12 the number of the exchanged electrons attains the value $n = 4$, which can be analytically utilized. We assume that this oxidation leads to benzothiazole-2-sulphinic acid:



$$+ \; 4 \, OH^- \;\; = \;\; \phantom{XXXXXX} + \; 2 \, H_2O \; + \; 4 \, e \qquad (A)$$
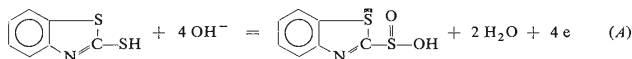
The shapes of the titration curves indicate that the oxidations to the two states are not reversible. In more basic solutions the titrations cannot be conducted because of the simultaneously occurring disproportionation of iodine[25], increasing the results of determination.

*Concentration region and evaluation of the results.* The accuracy and precision of the determination were established by carrying out a series of experiments with different quantities of 2-mercaptobenzthiazole in phosphate buffers of different pH values. The experimental and calculated data are given in Table II.

The relative error of determination is largely below 1% over a wide pH region. Titrations lasting about 100 s lead to higher errors than those lasting twice as long or more. In such cases it is convenient to choose a lower generating current, for the determination period to be prolonged to an optimum time of about 300 s.

The reproducibility of the determination was tested according to Dean and Dixon by processing the results of eight parallel titrations of 1 675 μg MBT applying a current of 5·00 mA. The data, which in the order of increasing magnitude are 1 661·5, 1 664·1, 1 670·2, 1 670·2, 1 671·0, 1 671·0, 1 676·2, and 1 677·0 μg, gave a result accurate to 99·86% with the relative standard deviation $s_r = 0.27\%$ for the coefficient of confidence 0·95. Similarly, for 33·5 μg MBT titrated applying the current of 0·14 mA, the result obtained was 100·3% with $s_r = 1.23\%$; for the fifty-fold smaller quantity of MBT the standard deviation was naturally higher.

2-Mercaptobenzthiazole can be determined also *via* its oxidation to benzthiazole-2-sulphinate in a narrower range pH 10 to 11·5. In such systems the sensitivity of determination is four times higher, owing to the value $n = 4$. The reproducibility was determined from seven parallel determinations of 418·75 μg of MBT applying the current 5·0 mA at pH 11·5; the values, 417·5, 418·6, 419·7, 420·8, 420·8, 421·9, 421·9, led to a result accurate to 100·34% with $s_r = 0.34\%$.

When low currents (below 1 mA) are used, the blank experiment period is prolonged, according to the purity of the chemicals and the competitive disproportionation of iodine, to tens of seconds, and at the same time the results increase. From a six times repeated determination of 8·35 μg of MBT using the current 0·35 mA in a buffer pH 10·90, the result of 106·8% with $s_r = 1·2\%$ was obtained.

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