

Simultaneous square wave voltammetric determination of 2-mercaptobenzothiazole and 2-mercaptobenzoxazole by partial least squares method in water samples

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Abstract

A rapid sensitive and versatile method for simultaneous determination of 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzoxazole (MBO) based on the square wave voltammetric (SWV) using mercury drop electrode (SMDE) has been presented. A three-electrode system containing SMDE working electrode, Pt auxiliary electrode and Ag/AgCl reference electrode was used throughout. The linear calibration graphs are in the concentration range of 7–40 $\mu\text{g mL}^{-1}$ and the equations are: $(\Delta i) = 1.372C_{\text{MBT}} - 9.112$ ($r = 0.9982$) and $(\Delta i) = 0.246C_{\text{MBO}} - 1.736$ ($r = 0.9985$) for MBT and MBO, respectively. Partial least squares regression (PLS) was applied to resolve the seriously overlapped voltammograms without any pre-separation step. The five level partial factorial design was used as calibration design method and the cross-validation method was used to select the number of significant factor for PLS model building. Five significant PLS components are used for MBT and MBO. A set of synthetic sample mixtures were used to validate the propose method. The root-mean-square errors of predictions (RMSEPs) and percent of relative prediction errors (RPEs) are 0.841 and 0.777 $\mu\text{g mL}^{-1}$ and ± 3.58 and $\pm 3.74\%$ for MBT and MBO, respectively. The developed method was then applied to the analysis of these two compounds in different water samples with satisfactory results.

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1. Introduction

2-Mercaptobenzoxazole (MBO) and 2-mercaptobenzothiazole (MBT) (Fig. 1) are a class of high production volume chemicals that are employed in various industrial processes and are known as widespread, toxic and poorly biodegradable pollutants [1]. Mercaptan derivatives are studied and applied for various purposes, such as corrosion inhibitor [2,3], antifungal drug in medical applications [4], coating agent of metallic surfaces [5] and predominately, as vulcanization accelerator in rubber industry [6–8]. They are frequently found in both effluents of wastewater treatment plants, surface water and they are the most important volatile organic compounds that contribute to odour problems in wastewater treatment plants [9,10].

Several methods for analyzing of MBT and/or MBO and also thiols in environmental samples can be found in the literature. The methods for simultaneous determination of them are mainly base on different chromatographic methods [11–14] which suffer from complex pre-treatments and large solvent consumption. Spectrophotometric and electrochemical method is also used for analyzing of them [15–18]. However, a sensitive methodology for the simultaneous determination of MBT and MBO using fast and reliable technique has not yet been reported in the literature.

Polarographic and voltammetric methods, generally have high sensitivity, and are widely used in many areas of analytical chemistry. However, their applicability for the determination of several components in mixtures is rather limited when the recorded polarograms or voltammograms display significant partial overlapping. So simultaneous determination of MBT and MBO by the use of the conventional voltammetric techniques in aqueous solution is difficult because of overlapping of voltammograms in this region and the superimposed curves are not suitable for quantitative evaluation.

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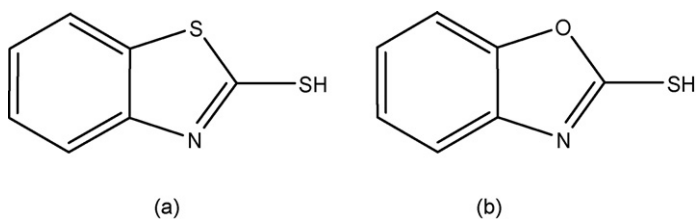


Fig. 1. Chemical structure of (a) MBT and (b) MBO.

Diverse chemometric methods have been shown to overcome this limitation successfully, and resolve the overlapping bands. Recently, these chemometric approaches have also been applied similarly to binary or ternary mixtures of organic compounds. PLS and PCR are well-known factor analysis based methods. Their basic concepts, detailed mathematical treatments and tutorials for chemical applications may be found in the referenced literature [19–22].

Partial least squares modeling is one of the powerful multivariate statistical tool that has been applied to the quantitative analysis. The theory and application of partial least squares methods have been discussed by several workers [23–30]. PLS is a technique that is closely related to principal component regression (PCR). However, in PLS, the decomposition is performed in a slightly different fashion. Instead of first decomposing the spectral matrix into a set of eigenvectors and scores, and regressing them against the concentration as a separate step, PLS actually uses the concentration information during the decomposition process. There are several algorithms for PLS and one well-recognized algorithm for computing PLS regression components is nonlinear iterative partial least squares (NIPALS) [31]. Sijmen de Jong introduced SIMPLS algorithm estimation method for PLS regression [26]. It gives the same result as NIPALS by the PLS1 algorithm for the prediction of c (or concentrations) when this is a single vector, but a slightly different solution for multivariate C (PLS2). In this work, we used NIPALS algorithm for simultaneous square wave voltammetric determination of MBT and MBO in water samples. We used the PLS1 method and so a concentration vector, c , for each individual compound.

2. Experimental

2.1. Apparatus

The voltammetric measurements were carried out with a SMDE working electrode in a three-electrode arrangement. A platinum wire was used as auxiliary electrode together with a silver—silver chloride reference electrode (Ag/AgCl), using 3 M KCl as electrolyte with a porous membrane. Nitrogen purge is needed for oxygen removal from the test solutions.

Measurements were carried out on a Princeton Applied Research (EG&G 273 A) electrochemical device. Electrodes and electrochemical vessels were parts of SMDE 303A EG&G PARC which were controlled by the mentioned device. A Pentium IV computer controlled all settings and data processing of the system.

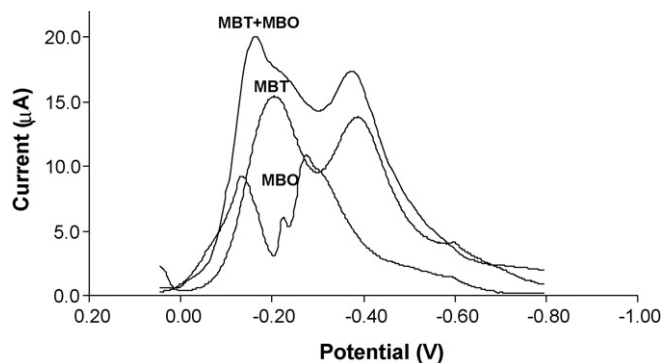


Fig. 2. The square wave voltammograms of MBT, MBO ($20 \mu\text{g mL}^{-1}$ for both compounds) and their mixture at the SMDE electrode.

The SW voltammogram data were collected and transferred to a Pentium IV computer for subsequent data manipulation. Data analysis was performed in MATLAB (Mathworks, version 7.0) and Microsoft[®] Excel (2002).

2.2. Reagents

All chemicals were of analytical grade and obtained from Merck. Pure MBT and MBO were purchased from (Merck). Double distilled water was used throughout. MBO and MBR stock solutions ($1000 \mu\text{g mL}^{-1}$) were prepared by dissolving 0.1000 g of MBO and/or MBT in 10 mL of methanol and diluting it to 100 mL with a mixture of 60:40 of MeOH to H₂O. Working solutions were prepared by appropriate dilution of the stock solution with distilled water. Britton–Robinson buffer solutions (pH 3–10) were prepared by adding appropriate amounts of 1 M sodium hydroxide solution into 100 mL mixture solution containing 0.2 M of boric, acetic and phosphoric acids in the mixture.

2.3. Procedure

The general procedure for obtaining voltammograms (square wave method) was as follows: into a 10 mL volumetric flask, 2.0 mL of Britton–Robinson buffer solution and appropriate amount of standard MBT and MBO solutions ($200 \mu\text{g mL}^{-1}$) were added and then the solutions were diluted to the mark with distilled water (the final concentrations of MBT and MBO were in range of $7\text{--}40 \mu\text{g mL}^{-1}$). At first, the solutions were purged with nitrogen for 2.5 min. After 5 s, as equilibrium time, the SW voltammograms were recorded by applying a negative-going scan over the potential range from +0.05 to -0.80 V. The obtained voltammograms were used for further calculations. All measurements were made at 25°C . Typical SW voltammograms of MBT, MBO and a mixture is shown in Fig. 2. These voltammograms were used for chemometrics interpretation.

3. Results and discussion

3.1. Influence of pH on peak current and peak potential

In general, pH is one of the variables that commonly and strongly influence the shapes of voltammograms, and it is impor-

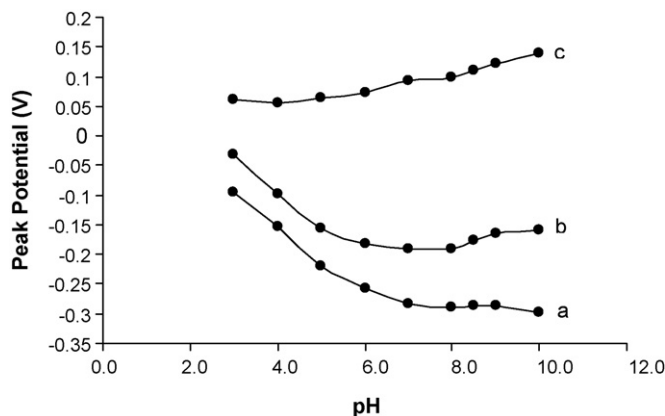


Fig. 3. Influence of pH on the (a) MBT, (b) MBO and (c) peak potential difference ($\Delta E = E_{MBO} - E_{MBT}$). The concentrations of the MBT and MBO are the same and equal to $30 \mu\text{g mL}^{-1}$.

tant to investigate the effects of pH on the electrochemical systems. The effect of pH on the peak current and peak potential of MBT and MBO over the pH range of 3–10 were monitored individually in the same conditions. The main factor that affecting the differences between MBT and MBO is the number of S atoms (softer base than nitrogen) presented in these compounds. Because of differences in the structure of two components (MBT is a softer complexing agent than MBO), the pH changes of the medium will affect the adsorption of thiols on the mercury drop. So the peak potential of components is separated (shifted) based on the pH of the test solution (Fig. 3). Both compounds show almost the same current changes (Fig. 4). As it is seen from Fig. 3 by increasing the pH of medium the difference of peak potentials increased, but the summation of the peak currents reach to maximum value at pH 8. So the optimum pH value for subsequent analysis was chosen 8. The amount of buffer added to solutions was also optimized and optimum value was determined to be 2 mL.

3.2. Selection of electrochemical parameters

The influence of electrochemical parameters known to affect the SWV, viz. pulse height, frequency and scan increment were studied. In the investigation process, each variable was changed

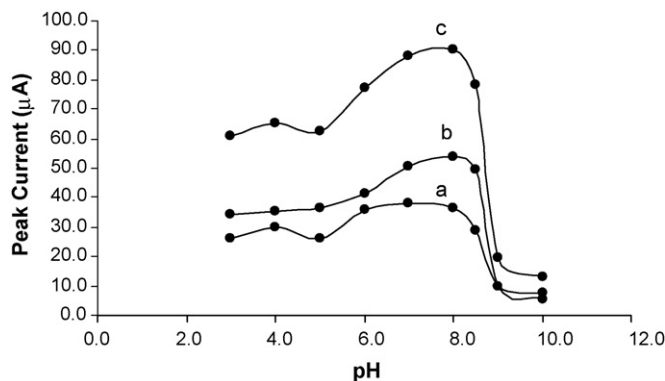


Fig. 4. Influence of pH on summation of (a) MBO, (b) MBT and (c) sum of the peak currents. The concentrations of the compounds are as in Fig. 3.

while the other two were kept constant. The variables of interest were studied over the ranges of 10–150 mV for pulse height, 10–250 Hz for frequency and 1–10 mV for scan increment. It was found the scan increment has no significant effect on peak currents, however, the peak sensitivity increased with increasing pulse height and frequency. It must be mentioned that the higher values of pulse height and frequency cause more broadening of individual compounds voltammograms which cause more overlapping of the voltammograms of mixture components. To acquire voltammograms of relatively high sensitivity and well-shaped waves with relatively narrow peak width, values of 100 mV, 60 Hz and 3 mV were chosen as optimum values for pulse height, frequency and scan increment, respectively.

The effect of equilibration time (ET) that controls a variable delay during the cell performance and then the application of an initial potential to the electrodes were studied. Equilibration times of 0–45 s were applied to the electrodes and the corresponding voltammograms were recorded. The results showed that ET values greater than 5 s have no considerable effect on increasing the peak current and so 5 s was chosen as optimum ET value.

Optimized chemical and instrumental parameters were as follows: equilibrium time; 5 s, scan increment; 3 mV, pulse height; 100 mV, frequency; 60 Hz, SMDE size; large, and 2 mL of Britton–Robinson buffer solution of pH 8.

3.3. Linear calibration plot of single components

To ensure of linear behavior and to obtain the linear dynamic range of each compound two sets of samples for MBT and MBO in different concentrations were prepared and under the optimum conditions SWV was carried out. The individual calibration curve was constructed with several points at peak potential of each compound (at -0.21 V for MBT and -0.14 V for MBO in the concentration range of $7\text{--}40 \mu\text{g mL}^{-1}$). Calibration graph equations are: $(\Delta i) = 1.372C_{MBT} - 9.112$ ($r = 0.9982$, $n = 15$) and $(\Delta i) = 0.246C_{MBO} - 1.736$ ($r = 0.9985$, $n = 15$) for MBT and MBO, respectively, where C is the concentration of analyte in $\mu\text{g mL}^{-1}$ and $\Delta(i)$ is the difference between voltammogram peak currents of sample and blank solutions in μA . R.S.D. for 15 replicate measurements for determination of 10 and $30 \mu\text{g mL}^{-1}$ are 2.30 and 1.22% for MBT and 2.36 and 1.18% for MBO. The LOD's are 0.14 and $0.80 \mu\text{g mL}^{-1}$ for MBT and MBO, respectively.

3.4. Mixture design

Multivariate calibration methods, such as PLS require a suitable experimental design of the standards to span entire sample space to guarantee the prediction ability of the established multivariate model. The designed calibration matrix used allows maximizing statistically the information content of the recorded voltammograms. A five level partial factorial mixture design was used for two-component mixtures concentration range of $7\text{--}40 \mu\text{g mL}^{-1}$ for both MBT and MBO [34]. The composition of the calibration set mixtures is represented in Table 1. The voltammograms in the potential range of $+0.05$ to -0.8 V with

Table 1
The composition of the calibration set mixtures

Mixtures	Concentration $\mu\text{g mL}^{-1}$		Mixtures	Concentration $\mu\text{g mL}^{-1}$	
	MBT	MBO		MBT	MBO
M1	23	23	M14	23	40
M2	23	7	M15	40	40
M3	7	7	M16	40	7
M4	7	40	M17	7	30
M5	40	15	M18	30	7
M6	15	40	M19	7	23
M7	40	23	M20	23	30
M8	23	15	M21	30	30
M9	15	15	M22	30	15
M10	15	30	M23	15	7
M11	30	40	M24	7	15
M12	40	30	M25	15	23
M13	30	23			

250 experimental data points per voltammogram was selected for analysis. Five further samples, coded as M26–M30, were chosen as test set to check the prediction ability of the calibration model.

3.5. Statistical parameters

It is useful to introduce several measures of a model's fit to the data and its predictive power. The root-mean-square error of calibration (RMSEC) tells us about the fit of the model to the calibration data. It is defined as:

$$\text{RMSEC} = \sqrt{\frac{\sum_{i=1}^n (\hat{C}_i - C_i)^2}{n - A - 1}} \quad (1)$$

where \hat{C}_i are the values of the predicted concentrations when all samples are included in the model, n the number of calibration samples and A is the number of PLS components.

The root-mean-square error of cross-validation (RMSECV) is a measure of a model's ability to predict new samples and is defined as:

$$\text{RMSECV} = \sqrt{\frac{\sum_{i=1}^n (\hat{C}_i - C_i)^2}{n}} \quad (2)$$

where the \hat{C}_i are predictions for samples not included in the model formation. Note that in Eq. (1), denominator is $n - A - 1$ and in Eq. (2) is n .

Table 2
Concentration data for prediction set mixtures of MBT and MBO and their predicted and recovery values

Mixtures	MBT concentration $\mu\text{g mL}^{-1}$			MBO concentration $\mu\text{g mL}^{-1}$		
	True	Predicted	Recovery (%)	True	Predicted	Recovery (%)
M26	40	38.94	97.35	20	20.75	103.75
M27	35	34.78	99.37	15	14.46	96.40
M28	23	23.75	103.28	7	8.04	114.86
M29	7	6.26	89.43	40	39.71	99.27
M30	15	13.88	92.53	20	21.00	105.00

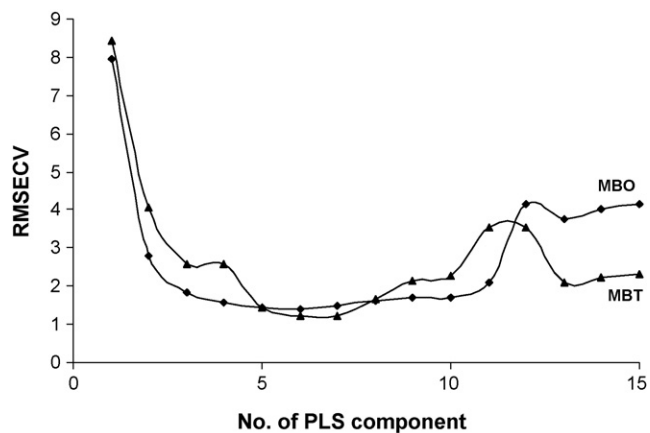


Fig. 5. RMSECV vs. number of PLS components.

RMSECV is related to the PRESS (or predicted residual sum of squares) value for the number of principal components included in the model, i.e.

$$\text{RMSECV}_K = \sqrt{\frac{\text{PRESS}_K}{n}} \quad (3)$$

where PRESS_K includes K components in the data, which it is common to calculate PRESS, and thus RMSECV, by leaving out one cross-validation, i.e. where each sample is left out of the model formulation and predicted once [32].

It is possible to calculate a relative error of prediction (REP) for the new data that the reference values are known.

$$\text{REP}(\%) = \frac{100}{\bar{C}} \sqrt{\frac{\sum_{i=1}^n (\hat{C}_i - C_i)^2}{n}} \quad (4)$$

In this equation, C_i are the true concentration of the analyte in the samples not included in the model formation, \hat{C}_i represents the estimated concentration of the analyte in the samples, \bar{C} the mean of true concentration in the prediction set and n is the total number of samples used in the prediction sets [33].

It is also possible to calculate a root-mean-square error of prediction (RMSEP) when the model is applied to new data provided that the reference values for the new data are known. RMSEP is calculated exactly as in Eq. (2) except that the estimates \hat{C}_i are based on a previously developed model but are used to predict an independent test set.

In this work, in order to select the number of significant PLS components for modeling the system without over-fitting the concentration data, the cross-validation method was used leav-

Table 3
Statistical parameters of the optimized matrix using SIMPLS model

Analyte	No. of PLS components	RMSEC	RMSECV	RMSEP	RPE (%)
MBT	5	0.79	1.22	0.84	3.58
MBO	5	0.83	1.39	0.78	3.74

Table 4
Influence of foreign ions on the simultaneous determination of MBT and MBO at the 20 $\mu\text{g mL}^{-1}$ concentration for both compounds

Ion	Tolerance limit $\mu\text{g mL}^{-1}$
^a Na ⁺ , ^a K ⁺ , ^b CO ₃ ²⁻ , ^b HCO ₃ ⁻ , ^b ClO ₄ ⁻ , ^b NO ₃ ⁻ , ^b PO ₄ ³⁻ , sucrose, glucose,	2000
^b SO ₄ ²⁻ , ^b WO ₄ ²⁻ , ^b F ⁻ , ^b NO ₂ ⁻	1500
^c Mg ²⁺ , ^d Ba ²⁺ , ^b Cl ⁻ , ^a Ca ²⁺ , ^a Co ²⁺ , ^c Ni ²⁺ , phenol, resorcinol, benzoic acid,	1000
^a Cr ³⁺ , ^c Mn ²⁺ , ^a Al ³⁺ , ^c Cd ²⁺ , ^a Zn ²⁺ ,	500
^a Fe ³⁺ , ^a Bi ³⁺	400
^a Pb ²⁺ , ^e Sn ²⁺	300
^f SCN ⁻ ,	100
^a Hg ₂ ²⁺ , ^a Cu ²⁺ , ^g MBIM, ^h MP	Interfere

^a Nitrate salt.

^b Sodium salt.

^c Sulfate salt.

^d Acetate salt.

^e Chloride salt.

^f Potassium salt.

^g 2-Mercaptobenzimidazole.

^h Mercaptopyrimidine.

ing out one sample at a time [32]. A good rule for choosing the number of PLS components to retain is to use the cross-validation, so the optimum numbers of components retained are 5 for both MBT and MBO. In Fig. 5, the obtained RMSECV versus number of PLS components is shown. The results obtained by PLS (the model) for the five test samples are summarized in Table 2. It also shows the recoveries of prediction set samples containing MBT and MBO. The recoveries were also quite acceptable as they were between 89.43 and 114.86%. Table 3 summarizes RMSEC, RMSEP, RMSECV, RPE and the optimum number of PLS components for each analyte.

The method was used for the analysis of both components in synthetic samples with complex matrixes (mixtures of MBT and MBO are spiked in to power plant utility and heat exchanger cooling waters), with satisfactory results (Table 5).

Table 5
Determination of MBT and MBO spiked in to power plant utility and heat exchanger cooling water samples

Sample	Added $\mu\text{g mL}^{-1}$		Found $\mu\text{g mL}^{-1}$		Recovery (%)	
	MBT	MBO	MBT	MBO	MBT	MBO
Power plant	23	40	24.15	39.17	105.0 \pm 2.8 ^a	97.9 \pm 2.1
Utility water	30	15	29.57	15.75	98.5 \pm 2.6	105.0 \pm 2.7
Heat exchanger	23	40	24.64	38.75	107.1 \pm 2.7	98.9 \pm 2.6
Cooling water	30	15	28.37	16.38	94.6 \pm 2.5	109.2 \pm 2.7

^a Standard deviation based on four replicate analyses.

3.6. Effect of foreign ions

One of the striking points of any new method is its interfering limit of the potential interferences. So to check and evaluate the tolerance limit of different interferences for the proposed method, the interferences due to several cations and anions were studied in detail. For this study, different amounts of some common ionic species and some organic compounds were added to a mixture of MBT and MBO. The starting point was 2000 ppm of interfering ions in the presence of MBT and MBO. The tolerated limits were taken as those concentrations causing changing not greater than $\pm 5\%$ of the concentration of each analyte in the mixtures [34]. The interfering effect of different cations and anions are listed in Table 4. Under the experimental conditions (Britton–Robinson buffer, pH 8) some ions, such as Zn²⁺, Mg²⁺, Ba²⁺, Ca²⁺, Ni²⁺, Co²⁺, Cr³⁺, Mn²⁺, Al³⁺, Cd²⁺, Fe³⁺, Pb²⁺, Sn²⁺ and Bi³⁺ were precipitated and after centrifugation of solutions and separation of precipitate the clear sample solutions voltammogram were recorded. The analyte signal decrease by increasing the concentration of some interfering ions, because of co-precipitating (adsorption) of MBT and MBO with precipitate but in lower concentration of interfering ion the amount of precipitate decrease and analyte signal dose not decrease significantly.

4. Conclusion

Partial least square calibration was successfully applied to the resolution of SWV peaks of MBT and MBO in different mixtures. The recorded voltammograms from mixtures overlapped seriously because of the similarities in the chemical structures of the two compounds. The proposed method is simple, inexpensive and precise which does not require any complex pre-treatment. It enables the joint determination of the two compounds without the need for any prior separation or special conditions. The method is applied successfully for the determination of the two analytes in the spiked sample of the real matrix samples.

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