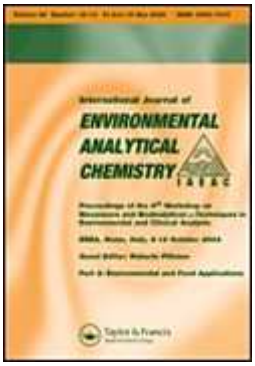




# Spectrophotometric method for manganese determination in water samples based on ion pair formation and dispersive liquid-liquid microextraction

| | |
|---|---|
| Journal: | *International Journal of Environmental Analytical Chemistry* |
| Manuscript ID: | Draft |
| Manuscript Type: | Original Paper |
| Date Submitted by the Author: | |
| Complete List of Authors: | Balogh, Ioseph; College of Nyíregyháza, Department of Chemistry<br>Rusnakova, Lenka; University of P.J. Šafárik, Department of Analytical Chemistry<br>Skrlikova, Jana; University of P.J. Šafárik, Department of Analytical Chemistry<br>Kocurova, Livia; P.J. Safarik University, Department of Analytical Chemistry<br>Torok, Marcel; P.J. Safarik University, Department of Organic Chemistry<br>Andruch, Vasil; P.J. Safarik University, Department of Analytical Chemistry |
| Keywords: | manganese, UV-VIS spectrophotometry, water, dispersive liquid-liquid microextraction, ion pair, auxiliary solvent |
| | |

# Spectrophotometric method for manganese determination in water samples based on ion pair formation and dispersive liquid-liquid microextraction

Ioseph S. Balogh[a], Lenka Rusnáková[b], Jana Škrlíková[b], Lívia Kocúrová[b], Marcel Török[c], Vasil Andruch[b,*]

[a] *Department of Chemistry, College of Nyíregyháza, HU-4400 Nyíregyháza, Hungary*

[b] *Department of Analytical Chemistry, University of P.J. Šafárik, SK-04154 Košice, Slovakia*

[c] *Department of Organic Chemistry, University of P.J. Šafárik, SK-04154 Kosice, Slovakia*



**Abstract**

A simple, inexpensive, and highly sensitive spectrophotometric method for the determination of manganese in water samples was suggested. The method is based on the formation and dispersive liquid-liquid microextraction of a violet-coloured ion pair of Mn(II) with 1,3,3-trimethyl-2-[3-(3-methyl-3*H*-benzothiazol-2-ylidene)-propenyl]-3*H*-indolium (BTIC) in the presence of 1-nitroso-2-naphtol (HL) as ligand, and subsequent UV-VIS spectrophotometric detection. The appropriate experimental conditions for DLLME procedure were found to be: a pH of 9.5; 0.12 mmol $L^{-1}$ of BTIC; extraction solvent – toluene containing 1.75 mmol $L^{-1}$ of HL; disperser solvent – methanol; auxiliary solvent – tetrachloromethane. Beer's law is obeyed in the range 0.055-0.88 mg $L^{-1}$ of Mn(II). The limit of detection (LOD), calculated based on three times of the standard deviation of the blank test (n=10), was found to be 0.004 mg $L^{-1}$ of Mn(II).

*Keywords*: manganese, UV-VIS spectrophotometry, dispersive liquid-liquid microextraction, auxiliary solvent, ion pair, water

* Corresponding author. Email: vasil.andruch@gmail.com

## 1. Introduction

The biological significance of manganese is well known [1]. Manganese is needed for mammals and birds for normal growth and the maintenance of health and is therefore considered an essential element, though manganese deficiency rarely occurs in humans, since it is commonly available in the diet. Manganese, as an essential element, is also required for the activity of many enzymes. However, excessive exposure to manganese can also adversely affect human health [2].

The conventional method for manganese determination is based on the oxidation of Mn(II) to permanganate by heating in the presence of a catalyst followed by spectrophotometric detection of Mn in the form of $MnO_4^-$ [3]. The disadvantages of this method are the need to use heat and the need to use $Ag^+$ as a catalyst ($Ag^+$ causes disruptive effects with the $Cl^-$ that is present in natural waters). Various organic and inorganic reagents [4-9] have been described for the spectrophotometric and extractive spectrophotometric determination of manganese at trace levels. In recent years, conventional liquid-liquid extraction (LLE) has been replaced by dispersive liquid-liquid microextraction (DLLME), which offers several well-known advantages.

The aim of the present work is the spectrophotometric study of complex formation and the extraction of Mn(II) with 1,3,3-trimethyl-2-[3-(3-methyl-3*H*-benzothiazol-2-ylidene)-propenyl]-3*H*-indolium chloride reagent (BTIC) in the presence of 1-nitroso-2-naphtol (HL) as ligand and its application for DLLME spectrophotometric determination of manganese in water samples. The structure of the investigated reagent and numbering of the atoms are given in the Figure 1A and B, respectively. The merits of the investigated reagent include the stability of its solution over time and a high value of absorbance (molar absorptivity is $1.2\times10^5$ L $mol^{-1}$ $cm^{-1}$).

## 2. Experimental

### 2.1. Reagents

All chemicals and solvents used were of analytical grade purity, except the toluene that was used for spectroscopy. Double-distilled water was used throughout the experiment. A 0.1 mol $L^{-1}$ stock solution of Mn(II) was prepared by dissolving $MnCl_2\times4H_2O$ in water. The 1 mmol $L^{-1}$ working solution of Mn(II) was prepared by step-wise dilution of the stock solution prior to use. The acidity of the aqueous medium was

adjusted by the addition of HOAc-$NH_4OH$ buffer solution. The 1 mmol $L^{-1}$ aqueous solution of BTIC was prepared by dissolving its chloride in water.

### 2.2. Apparatus

A Cary 100 Bio UV-Visible Spectrophotometer (Varian Inc., USA) and a Spekol-11 (Carl Zeiss, Germany) spectrophotometer with matched quartz cells of appropriate path length were used for recording the absorption spectra and for routine measurements, respectively. The pH values of the solutions were measured using an ORION 720A+ pH meter with glass electrode. Centrifugation was performed using an MPW-310 centrifuge (Mechanika Precyzyjna, Poland).

Graphite furnace atomic absorption spectrometry (GFAAS) was employed as a reference method using a Varian SpectrAA-300 spectrometer (Varian Inc., CA, USA). The Mn was measured under optimised operating conditions. A Heraeus hollow-cathode lamp was utilised as a radiation source at 403.1 nm wavelength, 0.2 nm slit width, 5 mA lamp current. The 20 µL of the sample were injected, along with 5 µL of solution of Magnesium matrix modifier (Merck). The system was calibrated in the range from 0 to 0.060 mg $L^{-1}$ using certified reference material CRM B21 containing 1.000 g $L^{-1}$ Mn (Slovak Institute of Metrology, Bratislava, Slovakia).

### 2.3. General procedure

The conventional liquid–liquid extraction was carried out in graduated test tubes at room temperature. The 0.1 mL of 1 mmol $L^{-1}$ solution of Mn(II), 1.5 mL of buffer solution, 0.6 mL 1 mmol $L^{-1}$ solution of BTIC, and 0.5 mL of 1 mmol $L^{-1}$ of HL were placed into the test tubes. The volume was made up to 5 mL with water. After adding each reagent, the solution was mixed thoroughly. Next, a 5 mL portion of organic extractants was added. After extraction, the organic phase was separated and the absorbance was measured against that of the blank test.

### 2.4. Calibration of the method

*Dispersive liquid–liquid microextraction procedure*

A 5 mL sample solution containing Mn(II) up to 0.88 mg $L^{-1}$ as well as all the necessary reagents in appropriate concentrations (1.5 mL of buffer solution with pH 9.5, 0.12 mmol $L^{-1}$ of BTIC) were prepared in 10 mL conical centrifugal tubes. Then

0.5 mL of a mixture of solvents containing methanol as disperser solvent, 145 µL of toluene as extraction solvent along with dissolved 1.75 mmol $L^{-1}$ HL as ligand and 145 µL of $CCl_4$ as auxiliary solvent was vigorously injected using a 1 mL glass syringe. Afterwards, the mixture was gently shaken 3 times and centrifuged at 3000 rpm for 2 min. When finished, a layer of sediment (ca. 250 µL) containing the mixture of toluene and $CCl_4$ was found in the bottom of each tube. This was removed by an appropriate Hamilton syringe and inserted into a matched quartz cell of 2 mm path length, and the absorbance was measured at λ=560 nm.

## 3. Results and Discussion

For better understanding of the reaction mechanism, the structure and the electronic properties as well as acid-base properties of BTIC were studied, before investigation of manganese complex formation and extraction with BTIC.

### 3.1. Theoretical aspects

The structure and the electronic properties of BTIC were studied using the density functional theoretical calculations with B3LYP functional and 6-31G(d) basis set using the PC version [10] of the GAMESS(US) package [11]. The structure of BTIC is almost planar (except for the methyl groups) with a very small distortion of benzothiazole moiety. The distribution of the charge in BTIC is affected by the strong delocalization through the unsaturated bridge between the two heterocyclic parts and the positive charge is located mainly on carbon atom C3 of the indole ring and on sulfur S16 of benzothiazole ring (Figure 1C). This distribution corresponds to the two possible mesomeric forms of the single charged of BTIC dye.

Negative charge is localized mainly on both nitrogen atoms N4 and N19. Analysis of the molecular orbitals showed that in the case of orbital controlled reactions of BTIC the most important places for the nucleophile attack (i.e. hydrolysis) are the bridge atom C13 and carbon atoms C15 and C3 with the highest LUMO coefficients.

### 3.2. Acid-base properties of BTIC

It is well known that the ability of basic dyes to form and extract coloured ion pairs depends substantially on their acid-base properties. Protonation and hydrolysis of the

dyes cause decreased activity of the single-charged cation. Therefore, the acid-base properties of BTIC were investigated in detail. The optimum wavelength, the molar absorptivity, the protonation constant, and the hydrolysis constant were found to be λ=552 nm, $\varepsilon_{552}=1.2\times10^5$ L mol$^{-1}$ cm$^{-1}$, $pK_{pr}=-0.68\pm0.03$, and $pK_h=12.10\pm0.06$. The absorption maximum of the protonated (λ=325 nm, $\varepsilon=3.1\times10^4$ L mol$^{-1}$ cm$^{-1}$) and hydrolysed (λ=332 nm, $\varepsilon=1.9\times10^4$ L mol$^{-1}$ cm$^{-1}$) forms shifts into the UV region of the spectrum (Figure 2) and their molar absorptivities are considerably lower in comparison to the single-charged form. The number of protons involved in the protonation of a single-charged cation of BTIC was determined graphically using the equilibrium shift method, based on the dependence of $\log\frac{A_{(H_nR)^{+(n+1)}}}{A_{(R^+)}-A_{(H_nR)^{+(n+1)}}}$ on the acidity of the medium. It was demonstrated that protonation of BTIC involves one proton. The single-charge form of the dye and the range of pH in which this form predominates have the greatest practical significance for analytical aims. We ascertained that this form predominates in a wide range, from a pH of 2 to 10 (Figure 2).

### 3.3. Investigation of the appropriate experimental conditions

Due to the finding of the appropriate experimental conditions, the influence of pH, the concentration of ligand, the concentration of BTIC, and the nature of the organic solvent were all investigated.

*Effect of pH.* Some theoretical aspects of the formation of manganese ion pair with dye reagents have been previously discussed [12]. It was presented that for the formation and extraction of manganese ion pairs with basic dye reagents, it is necessary to create in aqueous phase the conditions for the domination of the ion pair components—in our case the anionic complex of Mn(II) and the single-charged cation of the BTIC dye. For the formation of the $[ML_3]^-$ anionic complex it is necessary that there be in aqueous phase an abundance of ligand in the form of anion $L^-$. It follows from the theoretical calculations of the distribution of the species Mn, HL and BTIC that it is probable that the optimum value for the acidity of the medium will be in the range of pH 8.5 to 10.

From Figure 3 is seen that the maximum extraction of ion pair of manganese with BTIC is reached at a pH equal to 9.4-10.0, which is in close agreement with the

theoretical calculations. As a result of this, our other experiments were made directly near the values of pH 9.5. The lower absorbance at pH>10 is probably caused by the hydrolysis of Mn(II) and thus by the lower concentration of free $Mn^{2+}$ ions, which can combine with the anionic ligand $L^-$ to form the complex anion $[MnL_3]^-$. The decrease in the extraction at pH<9.4 correlates with a decrease in the concentration of the anionic form of the ligand $L^-$.

*Effect of the concentration of ligand.* The effect of the concentration of HL on the absorbance of manganese ion pairs has been studied within a range of 0.01 to 0.2 mmol $L^{-1}$ of HL. The absorbance of the extracts was highest at an HL concentration of 0.08-0.14 mmol $L^{-1}$ (Figure 3).

*Effect of the concentration of BTIC.* For determining the effect of the concentration of the dye on the formation and extraction of ion pairs of Mn with BTIC, a series of experiments was carried out in which the concentration of dye was altered within the range of 0.01 to 0.2 mmol $L^{-1}$ while the concentration of the other components of the investigated system—manganese and ligand—were kept constant at $2\times10^{-5}$ mol $L^{-1}$ and at 0.1 mmol $L^{-1}$, respectively. It was determined (Figure 3) that the appropriate concentration of BTIC is 0.1-0.2 mmol $L^{-1}$.

*Effect of organic solvent.* The influence of the nature of organic solvent on the formation and extraction of ion pairs of manganese with BTIC was investigated. Aliphatic and aromatic hydrocarbons were tested as extractants, as well as their halogen derivatives, esters, ketones and alcohols. The best results were obtained by using benzene and toluene as extractants. Considering the high toxicity of benzene, for the determination it is more valuable to use toluene. The lowered molar absorptivity (from $1.42\times10^5$ to $1.37\times10^5$ L $mol^{-1}$ $cm^{-1}$) caused by changing from benzene to toluene is negligible when compared to the lower risk connected with the use of toluene. The main spectrophotometric characteristics of the extracted ion pairs are presented in Table 1. The extraction equilibrium is established in 60 s and the absorbance of the extracts is stable for 4 h. The stability constant and the extraction constant were determined to be $\beta=(1.8\pm0.1)\times10^8$, and $K_{ex}=(2.1\pm0.1)\times10^4$, respectively.

### 3.4. Reaction mechanism

The formation and the extraction of the manganese ion pair can be divided into the following steps: dissociation of the HL (formation of the $L^-$), dissociation of the reagent

(formation of $R^+$), the formation of the anionic complex of manganese, the formation of an ion pair, and its extraction. The reaction mechanism can be expressed by the following scheme:

$$HL_{(aq)} = H^+_{(aq)} + L^-_{(aq)}$$

$$RCl_{(aq)} = R^+_{(aq)} + Cl^-_{(aq)}$$

$$Mn^{2+}_{(aq)} + 3L^-_{(aq)} = [MnL_3]^-_{(aq)}$$

$$[MnL_3]^-_{(aq)} + R^+_{(aq)} = [MnL_3]^-R^+_{(aq)}$$

$$[MnL_3]^-R^+_{(aq)} + nS_{(org)} = [MnL_3]^-R^+ \times nS_{(org)}$$

or

$$Mn^{2+}_{(aq)} + R^+_{(aq)} + 3HL_{(aq)} + nS_{(org)} = [MnL_3]^-R^+ \times nS_{(org)} + 3H^+_{(aq)}$$

where $L^-$ is a ligand, $R^+$ is the cation of dye reagent, S is organic solvent, aq is the aqueous phase, and org is the organic phase.

### 3.5. Investigation of the dispersive liquid–liquid microextraction procedure

The effect of the nature of the extraction solvent, disperser solvent and auxiliary solvent used as well as extraction time were studied.

*Choice of extraction solvent.* For selection of an extraction solvent, we proceed from the assumption that the requirements for the extraction solvent in DLLME are the same as in conventional LLE [13]. Therefore, based on the results described in the *Effect of an organic solvent* section, toluene was chosen as the extraction solvent for further experiments. Since in DLLME procedure HL was dissolved in extraction solvent, the appropriate concentration of HL must again be specified and found to be 1.75 mmol $L^{-1}$.

*Choice of auxiliary solvent.* Since toluene, which was selected as the extraction solvent, has a density lower than that of water, we used not one solvent, but a mixture of two solvents, for the extraction procedure. One of these (toluene) ensures the efficient extraction of the target analyte; the second serves as an auxiliary solvent and ensures that the mixture's density is higher than that of water in order to allow for a simple phase separation by centrifugation. Solvents having a density markedly higher than that of water, such as chlorobenzene, chloroform, and tetrachloromethane, were considered as auxiliary solvents, but we excluded a priori polar solvents from this list due high absorbance of the blank test. Therefore, in this study we used tetrachloromethane as the auxiliary solvent.

*The effect of disperser solvent.* Acetone, ethanol and methanol were tested as disperser solvents. The best disperser solvent seems to be methanol due to the lowest value of the blank test among those solvents investigated.

*Extraction time.* As was previously stated by other authors, DLLME is a very fast process. Despite this fact, we investigated the effect of extraction time in DLLME of Mn ion pair with BTIC. It was observed that the extraction time does not significantly affect the efficiency of the extraction procedure. Therefore, phase separation by centrifugation was carried out immediately after mixing the reagents by gentle manual shaking.

### 3.6. Analytical figure of merits

*Calibration range.* The calibration curve was constructed from seven data points over a range of concentrations 0.055-0.88 mg $L^{-1}$. The limit of detection (LOD), calculated based on three times of the standard deviation of the blank test (n=10), was found to be 0.004 mg $L^{-1}$ of Mn(II). A comparison of the analytical characteristics of the suggested DLLME and conventional LLE procedures is presented in Table 2.

*Precision and accuracy.* The precision and accuracy of the developed method were checked by analysing model samples spiked with known amounts of analyte and calculating the relative standard deviation percentage (RSD, %) and the recovery percentage (R, %). The inter-day and intra-day precision and accuracy results presented in Table 3 show good repeatability of the suggested method.

### 3.7. Application of the method

Based on the obtained results, a spectrophotometric method for the determination of manganese in water samples was suggested. The method is based on the formation and dispersive liquid-liquid microextraction of a violet-coloured ion pair of Mn(II) with 1,3,3-trimethyl-2-[3-(3-methyl-3*H*-benzothiazol-2-ylidene)-propenyl]-3*H*-indolium in the presence of 1-nitroso-2-naphtol as ligand, and subsequent UV-VIS spectrophotometric detection. The appropriate experimental conditions were found to be: a pH of 9.5; 0.12 mmol $L^{-1}$ of BTIC; extraction solvent – toluene containing 1.75 mmol $L^{-1}$ of HL; disperser solvent – methanol; auxiliary solvent – tetrachloromethane. According to Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption [14], the limit of manganese content in drinking

water is 50 μg $L^{-1}$. Consequently, the suggested procedure may be applicable for determination of manganese in both mineral and drinking water. The accuracy of the method was verified using the method of standard addition as well as by comparison of results obtained with GFAAS method (Table 4). Confidence limits of the results obtained by the suggested and by a reference method (GFAAS) overlap one another, proving the good precision and accuracy of the determination with no matrix interference.

**Acknowledgements**. The authors wish to thank to Dr. Veronika Jalčoviková from the Regional Office for Public Health for her help with carrying out the atomic absorption measurements.

**References**

[1] N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, (Butterworth-Heinemann, Oxford, 1997).

[2] US Environmental Protection Agency. 1993. Drinking water criteria document for manganese, http://www.epa.gov/waterscience/criteria/library/manganese.pdf (25.07.2009)

[3] W.J. Williams, *Handbook of Anion Determination*, (Butterworts and Co., London, Boston, Sidney, Wellington, Durban, Toronto, 1979).

[4] M. Alkan and D. Kara, J. Trace Microprobe Techn. **21**, 479 (2003).

[5] S.A. Barakat, Anal. Chim. Acta **393**, 223 (1999).

[6] D.T. Burns, M. Harriott and S.A. Barakat, Anal. Chim. Acta **258**, 325 (1992).

[7] M. Kamburova, Talanta **46**, 1073 (1998).

[8] P.K. Tarafder, R.K. Mondal, L. Kunkal, P. Murugan and D.P.S. Rathore, Chem. Anal. (Warsaw) **49**, 251 (2004).

[9] W. Winkler, F. Buhl, A. Arenhövel-Pacula and U. Hachula, Anal. Bioanal. Chem. **376**, 934 (2003).

[10] A.A. Granovsky, PC GAMESS ver. 6.4, http://classic.chem.msu.su/gran/gamess/ (16.12.2008)

[11] M.W: Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis and J.A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[12] I.S. Balogh, V. Andruch and M. Kovács, Anal. Bioanal. Chem. **377**, 709 (2003).

[13] P.X. Baliza, L.S.G. Teixeira and V.A. Lemos, Microchem. J. **93**, 220 (2009).

[14] *The European Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption,* http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:330:0032:0054:EN:PDF (16.12.2008)

## Legends

**Figure 1.** Structure of BTIC (A), numbering of the atoms (B), and Mulliken charges on heavy atoms summed with charges on hydrogen (C)

**Figure 2.** The absorption spectra of BTIC: single-charged (1), protonated (2), and hydrolysed (3) forms and the effect of the acidity of the medium on the absorbance of single-charged form of BTIC

$1\times10^{-5}$ mol $L^{-1}$ BTIC, $l$ = 5 mm

**Figure 3.** Effect of the pH of the aqueous phase (1), concentration of HL (2), concentration of BTIC (3) on the extraction by toluene of manganese ion pairs with BTIC

$2\times10^{-5}$ mol $L^{-1}$ $Mn^{2+}$; $l$ = 3 mm; 1 - ion pair; 1' - blank test

(1): 0.1 mmol $L^{-1}$ HL, 0.12 mmol $L^{-1}$ BTIC

(2): 0.12 mmol $L^{-1}$ BTIC, 1.5 mL of buffer solution with a pH of 9.5

(3): 0.1 mmol $L^{-1}$ HL, 1.5 mL of buffer solution with a pH 9.5

**Table 1.** Spectrophotometric characteristics of extracted manganese ion pairs

$2\times10^{-5}$ mol $L^{-1}$ Mn(II), 0.12 mmol $L^{-1}$ BTIC, 0.1 mmol $L^{-1}$ HL, pH = 9.5

**Table 2.** Comparison of analytical characteristics of the suggested DLLME and conventional LLE procedures

**Table 3.** Intra-day and inter-day precision and accuracy data for the determination of Mn (n = 5)

**Table 4.** Determination of manganese in real water samples (n = 5, average)

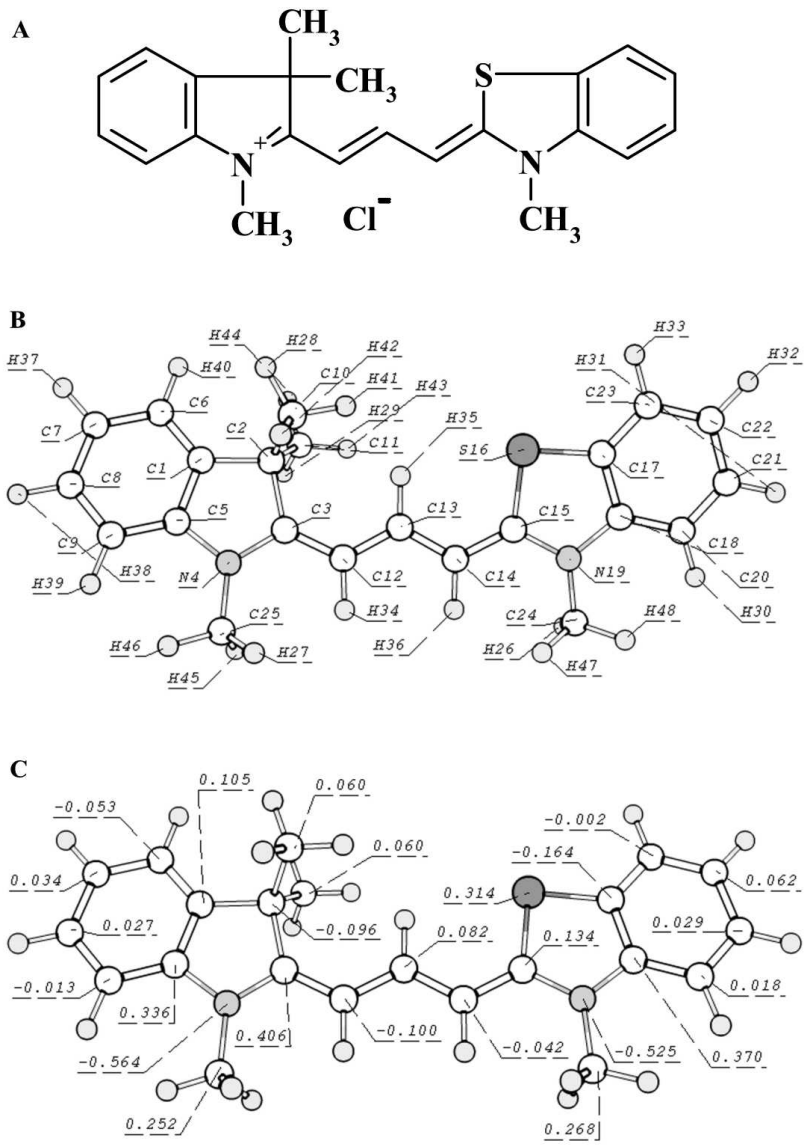


Figure 1. Structure of BTIC (A), numbering of the atoms (B), and Mulliken charges on heavy atoms summed with charges on hydrogen (C)
185x271mm (150 x 150 DPI)

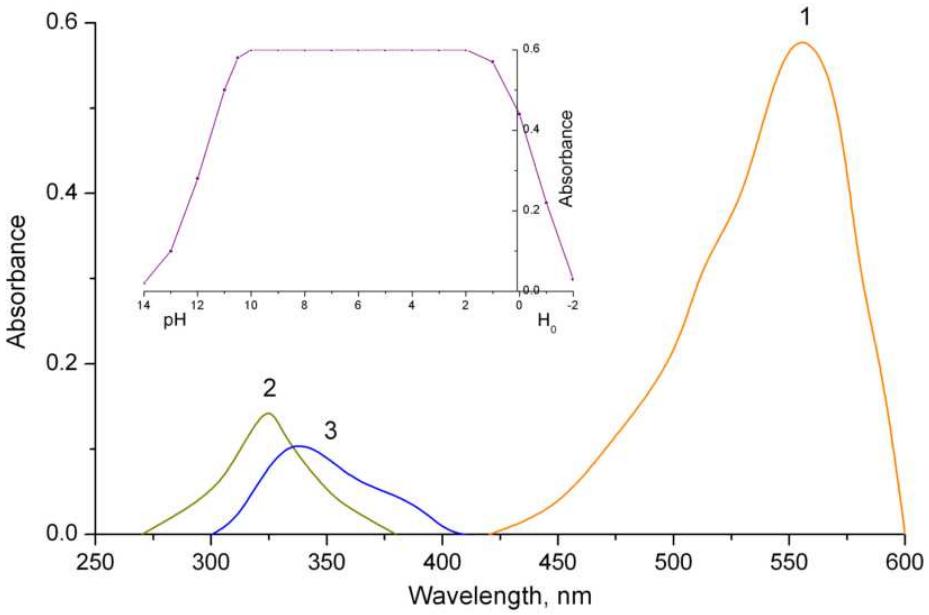


Figure 2. The absorption spectra of BTIC: single-charged (1), protonated (2), and hydrolysed (3) forms and the effect of the acidity of the medium on the absorbance of single-charged form of BTIC
1×10-5 mol L-1 BTIC, l = 5 mm
279x199mm (81 x 81 DPI)

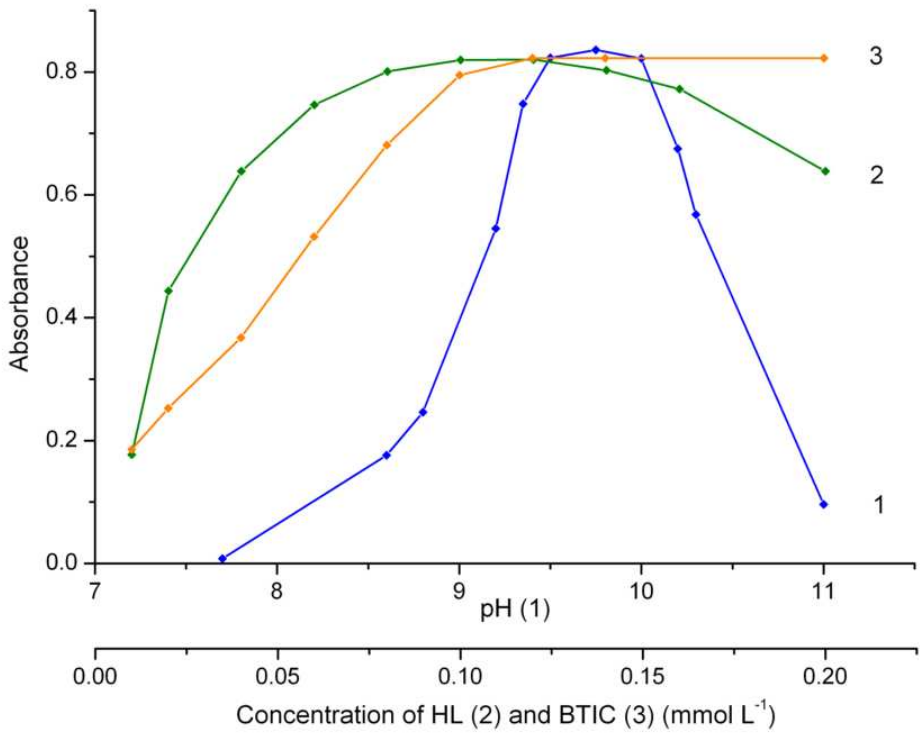


Figure 3. Effect of the pH of the aqueous phase (1), concentration of HL (2), concentration of BTIC (3) on the extraction by toluene of manganese ion pairs with BTIC
2×10-5 mol L-1 Mn2+; l = 3 mm; 1 - ion pair; 1' - blank test
(1): 0.1 mmol L-1 HL, 0.12 mmol L-1 BTIC
(2): 0.12 mmol L-1 BTIC, 1.5 mL of buffer solution with a pH of 9.5
(3): 0.1 mmol L-1 HL, 1.5 mL of buffer solution with a pH 9.5
279x215mm (81 x 81 DPI)

**Table 1.** Spectrophotometric characteristics of extracted manganese ion pairs $2\times10^{-5}$ mol $L^{-1}$ Mn(II), 0.12 mmol $L^{-1}$ BTIC, 0.1 mmol $L^{-1}$ HL, pH = 9.5

| Extractant | λ, nm | $\varepsilon\times10^{-5}$, L $mol^{-1}$ $cm^{-1}$ |
|---|---|---|
| Benzene | 560 | 1.42 |
| Toluene | 560 | 1.37 |
| *p*-Xylene | 560 | 0.90 |
| *o*-Xylene | 560 | 0.57 |

**Table 2.** Comparison of analytical characteristics of the suggested DLLME and conventional LLE procedures

| Parameters | DLLME-UV-VIS | LLE-UV-VIS |
|---|---|---|
| Wavelength, nm | 560 | 560 |
| Linear range, mg $L^{-1}$ | 0.055-0.88 | 0.11-2.75 |
| Regression equation [a] | | |
| Intercept, *a* | 0.0021 | 0.0043 |
| Slope, *b* | 1.7949 | 0.3027 |
| Correlation coefficient, *r* | 0.9997 | 0.9996 |
| LOD, mg $L^{-1}$ | 0.004 | 0.012 |

[a] $A = a + bC$, where $A$ means the absorbance, $a$ the intercept, $b$ the slope and $C$ the concentration of Mn in mg $L^{-1}$

**Table 3.** Intra-day and inter-day precision and accuracy data for the determination of Mn (n = 5)

| Taken, mg $L^{-1}$ | Intra-day | | | Inter-day | | |
|---|---|---|---|---|---|---|
| | Determined[a], mg $L^{-1}$ | RSD, % | R, % | Determined[a], mg $L^{-1}$ | RSD, % | R, % |
| 0.22 | 0.22±0.01 | 3.7 | 100.0 | 0.23±0.01 | 3.6 | 100.0 |
| 0.44 | 0.45±0.01 | 1.8 | 102.3 | 0.43±0.02 | 3.8 | 100.0 |
| 0.66 | 0.65±0.01 | 1.2 | 98.5 | 0.68±0.02 | 2.4 | 100.0 |
| 0.99 | 1.01±0.03 | 2.4 | 102.0 | 1.00±0.02 | 1.6 | 101.0 |

[a] $\bar{x} \pm \Delta x = \bar{x} \pm s\frac{t}{\sqrt{n}}$ ($t$ = 2.77, $P$ = 0.95), $t$ - Student coefficient for n-1 degrees of freedom

**Table 4.** Determination of manganese in real water samples (n = 5, average)

| Sample | Mn added, mg $L^{-1}$ | Mn found, mg $L^{-1}$ | RSD, % | R, % |
|---|---|---|---|---|
| Mineral water[a] | 0 | 1.21±0.08 | 5.3 | 104.3 |
| | 0.22 | 1.31±0.08 | 4.9 | 94.9 |
| | 0.33 | 1.45±0.06 | 3.3 | 97.3 |
| | 0.55 | 1.59±0.13 | 6.6 | 93.0 |
| Natural water[b] | 0 | 0.91±0.03 | 2.6 | 96.8 |
| | 0.22 | 1.19±0.10 | 6.8 | 102.6 |
| | 0.33 | 1.27±0.09 | 5.7 | 100.0 |
| | 0.55 | 1.49±0.07 | 3.8 | 99.3 |

[a] Labelled concentration is 1.16 mg $L^{-1}$.

[b] Concentration determined by AAS is 0.94±0.10 mg $L^{-1}$