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Short communication

Determination of low thiourea concentrations in industrial process water and natural samples using reversed-phase high-performance liquid chromatography

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Abstract

A rapid LC method was developed to determine thiourea in natural samples and freshly prepared as well as used tin-baths from the galvanic industry, with LC on a C₁₈-bonded silica column and with doubly distilled water as eluent. The retention time of thiourea is 1.35 min ± 5%. UV detection is at 236 nm. Small sample volumes of 10–50 µl allow detection down to 2 µg/l thiourea without any interference by heavy metals or organic compounds and in the case of marine samples by mineral salts. The presented technique should be highly useful for industrial purposes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thiourea [(NH₂)₂CS] is of great importance for various industrial applications such as rubber vulcanization, electrodeposition of metals, cleaning and polishing compositions, and also in the agricultural industry [1].

Thiourea can be present in tin-baths at up to 60 g/l (average 1 g/l) used in the galvanic industry.

Thiourea and related compounds are known to be toxic [2], for example, thiourea inhibits nitrification in the soil and hydrosphere. Therefore, release into the environment should be avoided [1]. At present, no limiting value for thiourea concentrations in waste water exists, but – because of environmental pollution problems – the aim of producers of thiourea-containing waste water is to reduce its concentration to <1 mg/l.

Thiourea is insufficiently volatile and stable to permit the use of gas chromatography without prior derivatization. Other chromatographic techniques such as thin-layer and liquid chromatography (LC) are more commonly used. Because of the polarity of

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thiourea, normal-phase LC should be the preferred method of analysis.

Moreover, different LC methods to detect thiourea can be utilized, but most of them require organic eluents (e.g., methanol, acetonitrile or tetrabutylammonium hydrogensulfate) [3–6] or have the disadvantage of long retention times for thiourea, which reduces the practicability benefits for industrial purposes and especially the use as online measuring system.

As an alternative, colorimetric or chemical methods for the detection of thiourea [methods using sodium dichromate or $\text{NaAg}(\text{CN})_2$, spot and colour tests] are available, but most of these are time-consuming, need large-scale sample preparation steps or require toxic chemicals, and cannot be used to design online measuring systems for, e.g., waste water. The introduction of a method with high detectability of thiourea in the presence of heavy metals and organic compounds is of great importance for monitoring thiourea fluxes during industrial processes.

The reversed-phase (RP) LC method presented in this study minimizes the requirements for the equipment to the lowest level (e.g., by using a simple C_{18} phase and doubly distilled water as eluent), so that a high sample throughput with minimal costs is possible. A sample preparation is not necessary, thiourea is detected directly in tin bath samples, industrial waste water and samples of marine sediments and seawater.

2. Experimental

2.1. Chemicals

Thiourea was purchased from Fluka (Neu-Ulm, Germany) and served as standard compound for calibration. Doubly distilled water was filtered through a $0.2\ \mu\text{m}$ cellulose acetate filter (Sartorius; 1110747 N) and purged with helium for 15 min.

Chlorobenzene originated from Merck Eurolab (Darmstadt, Germany) and was added to the samples as control substance.

2.2. LC

LC was performed on a Merck–Hitachi system

using a LiChrospher 100, RP-18 column ($125 \times 4.6\ \text{mm}$, $5\ \mu\text{m}$) and an isocratic elution with doubly distilled water (100%). Flow-rate was 1 ml/min (Merck–Hitachi L-7120 intelligent pump), and the detection of thiourea was realized at 236 nm using a Merck–Hitachi L-7420 UV–Vis detector. The column was heated to 35°C in an L-7350 LaChrom column oven (Merck). Total injection volume was 10 to $50\ \mu\text{l}$ (volume of the sample-loop: $25\ \mu\text{l}$), using a Rheodyne valve.

Different waste water samples (tin-bath samples) originated from producers of printed circuit boards. One of the industrial waste waters tested contained 10% methanesulfonic acid, 10% polyethylene glycol (PEG-400), 5 g/l tin and 2 g/l copper. All samples were diluted with doubly distilled water depending on the concentration of thiourea.

Chlorobenzene resembles thiourea in its absorption spectrum. This substance additionally shows a short retention time on the RP-18 column similar to thiourea. For these reasons, chlorobenzene (final concentration in the samples: 1 mg/l) was used as control substance to prove that the early elution of thiourea is not the effect of a major stumbling block. Additionally, sediment samples from the North Sea, Jadebusen near the Refinery of Wilhelmshaven, Germany, were used to study the influence of different organic and anorganic compounds on the elution and retention of thiourea in LC. Samples from the marine sediment were filled into petri-dishes. Regarding their content of solid compounds, the samples were centrifuged for 5 min at $4000\ \text{g}$ (Universal 1200, Hettich, Tuttlingen, Germany). The supernatant was used for thiourea analysis.

To see the effect of heavy metals on the thiourea detection, solutions of heavy metals (copper and tin, 0–50 mg/l each) were added to thiourea containing samples and to standard solutions.

3. Results and discussion

Waste water treatment in galvanic industry and process control, e.g., to see the pollution level of tin baths require the continuous measurement of thiourea concentrations. Different techniques are in use, but most of them are time consuming, so that an improvement is necessary. The use of LC in combination with UV detection brings advantages, because

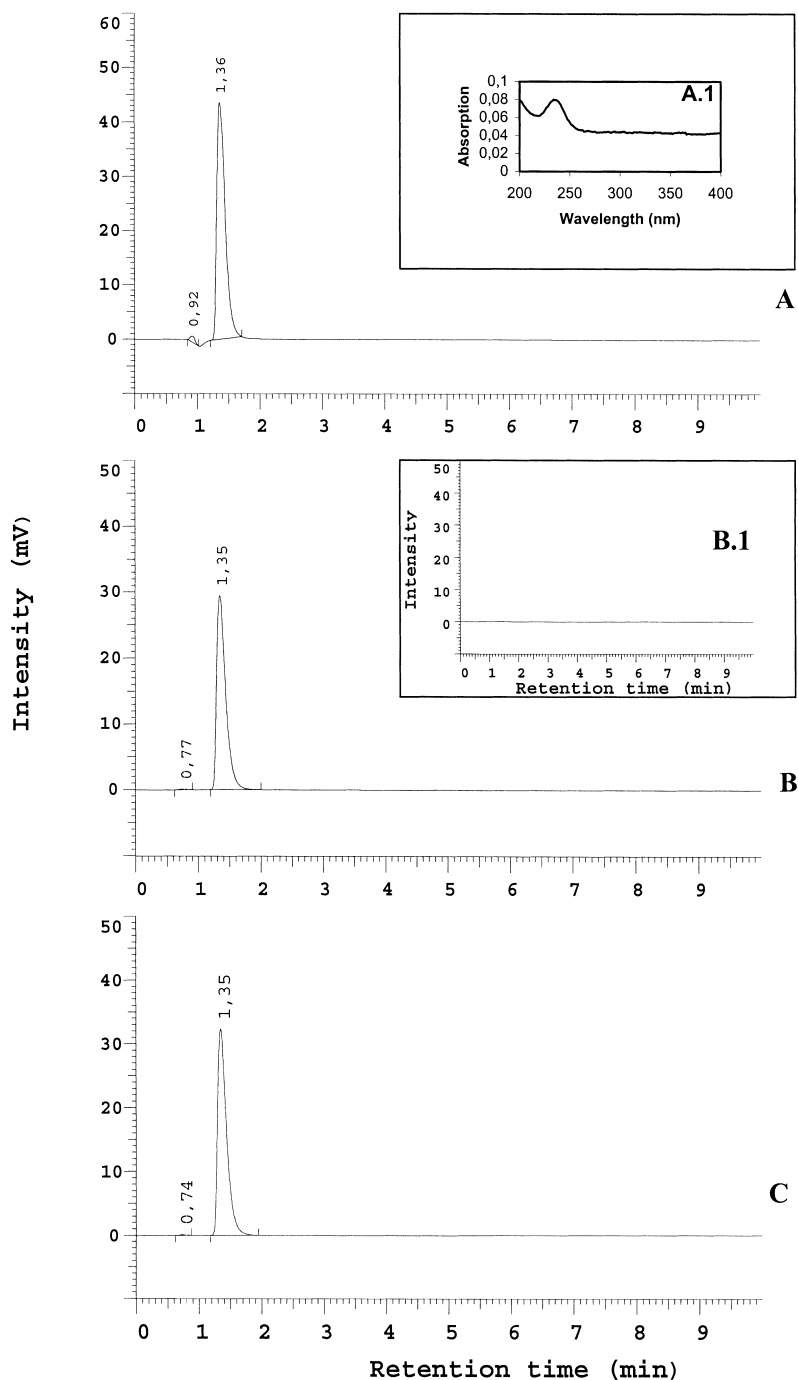


Fig. 1. LC separation of thiourea from a standard solution and an industrial tin bath containing 10% methanesulfonic acid, 10% polyethylene glycol (PEG-400), 5 g/l tin and 2 g/l copper. The peak at 1.35–1.37 min corresponds to thiourea. (A) Standard solution (3.17 mg/l thiourea), (B) freshly prepared tin bath (2.33 mg/l thiourea), (C) used tin bath (2.53 mg/l thiourea). The insert (A.1) shows the absorption spectrum of thiourea in the range of 200–400 nm. The insert (B.1) shows a LC separation of the tin bath without any thiourea. LC conditions: LiChrospher 100 RP-18 column (125×4.6 mm, 5 μ m), UV detection at 236 nm, eluent: doubly distilled water, flow-rate: 1 ml/min, temperature: 35°C.

the detection of thiourea is possible at low concentrations in a short time. For this purpose, we proved the applicability of an LC method for determination of thiourea in different samples.

Thiourea was detected in industrial waste water containing high concentrations of different heavy metals (e.g., Sn and Cu) and organic compounds (e.g., methanesulfonic acid, polyethylene glycol). Calibration of the RPLC system was performed with a standard solution of thiourea.

A calibration curve was obtained by plotting the integrated peak areas against increasing thiourea concentrations (0–304.5 mg/l). Linearity for the calibration curve was obtained in the range of 2 µg/l to 304.5 mg/l [correlation coefficient (r^2)=0.999; number of data points=9; triplicates].

As revealed by its absorption spectrum, $(\text{NH}_2)_2\text{CS}$ (thiourea) has a characteristic absorption maximum at 236 nm (Fig. 1A.1). Using this wavelength for the detection of thiourea (3.17 mg/l) in a standard

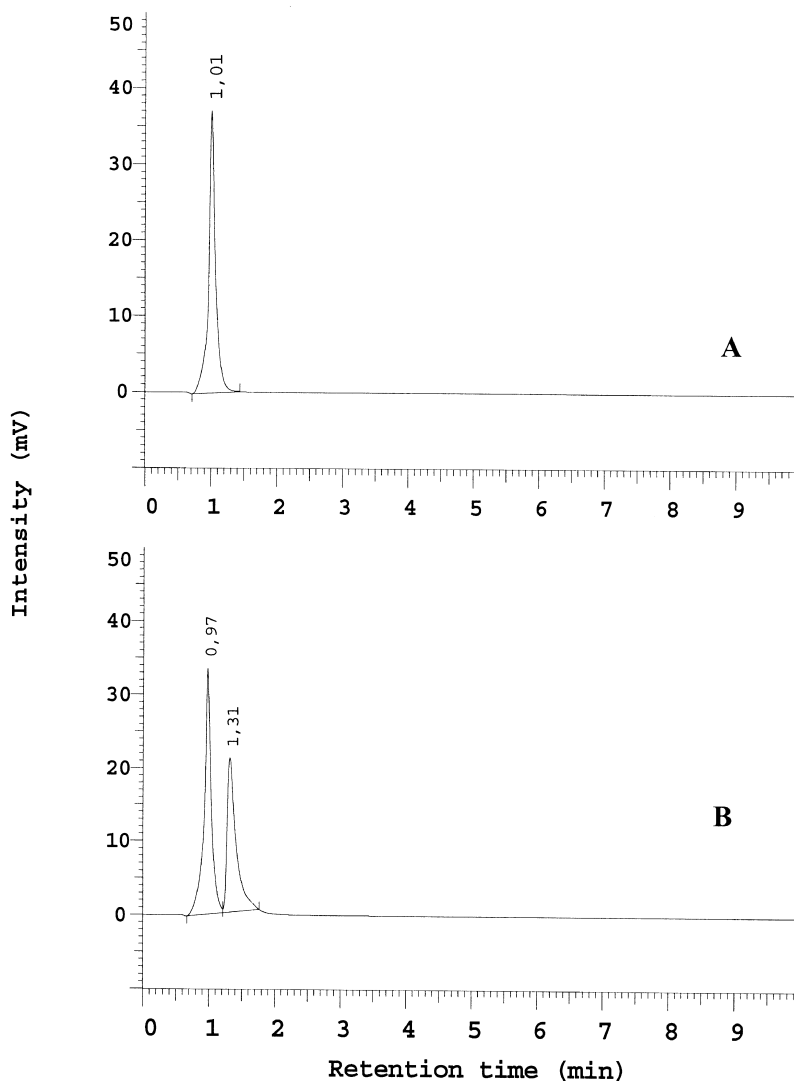


Fig. 2. LC separation of thiourea and chlorobenzene. The peaks at 0.97 and 1.31 correspond to chlorobenzene and thiourea, respectively. (A) Water sample containing only chlorobenzene (1 mg/l), (B) mixture of thiourea (1.58 mg/l) and chlorobenzene (0.93 mg/l). LC conditions as in Fig. 1.

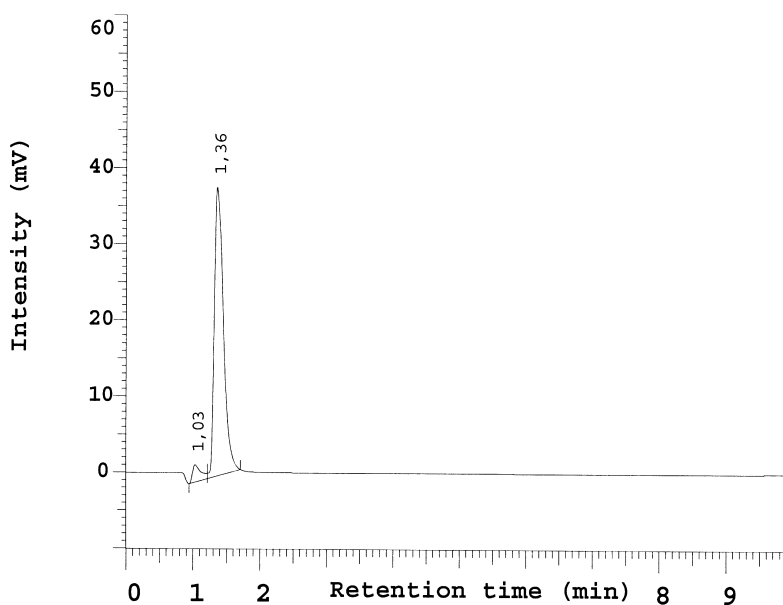


Fig. 3. LC separation of thiourea from sea water containing marine sediment. The peak at 1.36 min corresponds to 2.79 mg/l thiourea. LC conditions as in Fig. 1.

solution (Fig. 1A) or in industrial process (Fig. 1B) and waste water (Fig. 1C) samples (2.37 or 2.53 mg/l, respectively) by the LC method described, retention times of $1.35 \text{ min} \pm 5\%$ were obtained. Disturbance of thiourea separation and detection by heavy metals (data not shown) or other compounds (Fig. 1B.1) was not observed. Addition of heavy metals as copper or tin had no influence on the retention of thiourea, neither when metal ions were added (copper and tin 0–50 mg/l each) to the thiourea standard used nor to waste water samples (data not shown). The recovery for the thiourea injected was $100 \pm 5\%$ (data not shown).

Peaks with a retention time of 0.74–0.77 min correspond to organic components in the waste water and those with 0.92 min as well as 1.03 min to unknown contaminations in the commercial thiourea, used to prepare the standard solution (Fig. 1).

The addition of chlorobenzene to the samples and standard solution of thiourea did not interfere with separation and detection of thiourea (Fig. 2). The early elution of chlorobenzene ($0.97 \text{ min} \pm 5\%$) and the distinct separation from the thiourea peak reveals that the short retention time of the polar thiourea is not the effect of a major stumbling block.

Detection of thiourea was not disturbed in sea water and pore water samples from marine sediments (Fig. 3), showing the practicality of the presented method also for natural samples.

4. Conclusions

The detection of thiourea in highly contaminated industrial waters and natural samples is possible at very low concentrations by using only doubly distilled water as eluent on a C_{18} phase. Usage of (i) doubly distilled water as isocratic eluent, (ii) the small sample volume of 10 μl and (iii) the short retention time of only 1.35 min is of great advantage for industrial purposes and for high sample throughput. Therefore, construction of an automatic thiourea detection system with non-toxic eluents and without expensive equipment seems to be possible and especially recommendable.

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