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Short communication

SHORT COMMUNICATION

Preventing decomposition of 2-mercaptobenzothiazole during gas chromatography analysis using programmable temperature vaporization injection

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Abstract: 2-mercaptobenzothiazole (MBT) is a chemical compound which is widely used in various processes in chemical industry, and it was also detected in environmental samples. Most of the researchers employed liquid chromatography (LC) or gas chromatography (GC) for determination of MBT. When GC was used, derivatization was necessary in order to prevent decomposition of MBT inside of the hot GC inlet. In this study, a new approach for preventing decomposition of MBT using programmable temperature vaporization (PTV) was presented. The sample was injected in a cold inlet (40 °C) and the temperature was raised gradually until the analyte was evaporated. Contrary to hot splitless injection, no decomposition of MBT was observed using PTV. Compared to derivatization, PTV requires no chemicals and the duration of analysis is reduced.

Keywords: solvent vent mode; inlet; GC; MBT; PTV.

INTRODUCTION

2-Mercaptobenzothiazole (MBT) is an aromatic heterocyclic chemical compound consisted of 1,3-thiazole ring fused to benzene ring and substituted with mercapto functional group at methine position in thiazole ring.[1] MBT may exist as thione and thiol tautomers (Fig. 1),[2] and crystallographic analysis showed that thione form is predominant.[3] pK and K_{ow} of MBT are 7.2, and 2.41, respectively.[4,5]

Some applications of MBT are as copper corrosion inhibitor,[6] vulcanization accelerator in rubber production,[7] in organic synthesis including deoxygenation of epoxides and in the preparation of alkynes.[8] Some derivatives of MBT have antimicrobial and antifungal activities.[9] MBT has been extensively employed in

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chemical industry before it was tried as a flotation collector;[10] it has been used for flotation of copper, lead and zinc minerals.[11–14]

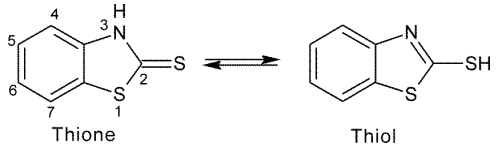

Fig. 1. Thione and thiol tautomer of MBT.[2]

MBT and related benzothiaziole derivates have been found in many environmental matrices. These compounds are released with treated municipal wastewater and have a considerable lifetime in surface waters.[15] Benzothiazoles enter the environment from a number of sources such as the leaching of rubber products, fine particles of automobile tires, and antifreeze.[16] Sorption and desorption processes of benzothiazoles onto sandy aquifer material is very important for the understanding of behaviour of these compounds in the environment.[17]

Table I lists chromatographic methods applied for analysis of MBT, including matrix types, extraction techniques and limits of detection (*LOD*). Gas chromatography (GC) and liquid chromatography (LC) are both widely used for determination of MBT. Sample preparation methods include solid phase extraction (SPE), solid phase microextraction (SPME), liquid–liquid extraction (LLE), dispersive liquid–liquid microextraction (DLLME) and direct injection. Prior to LC determination, no derivatization of MBT is necessary. Some researchers derivatized MBT to thioethers prior to GC analysis,[18–20] while others carried out analysis without derivatization.[21,22] Main reason for derivatization of MBT, prior to GC analysis, is the reactivity of the thiol group inside of a gas chromatograph.[19] Other methods have also been reported for analys of MBT, including voltammetry and spectrophotometry.[23,24] Most of the researchers determined MBT simultaneously with other related chemical compounds.

In our study, instead of derivatization, the programmed temperature vaporization (PTV) was used for the prevention of decomposition of MBT during GC determination. PTV was initially presented in 1979 by Vogt *et al.*[31,32] The three most important modes of PTV operation are cold split injection, cold splitless injection, and solvent elimination injection (also called solvent split injection or solvent vent mode).[33–35] Among these, the solvent elimination injection has been the most widely used PTV technique and it was also used in our study. In this mode, sample is introduced at temperature below the solvent boiling point and the solvent is eliminated via split exit while the higher-boiling analytes are retained in the liner. After the solvent elimination, PTV is rapidly heated and the retained analytes are transferred to the analytical column. When splitless transfer is completed, the split exit is reopened to remove the residual solvent vapour and low-volatile matrix compounds from the inlet.[34] The advantages of PTV injection

over other techniques consist in decreased analyte discrimination during the injection step, better recoveries of thermodegradable compounds, less pronounced adverse effects of non-volatiles present in the sample on the injection process and the possibility to introduce large volumes of samples (up to hundreds μL) into GC system.[36]

TABLE I. Analytical techniques used for determination of MBT

Matrix	Extraction technique	Analytical technique	LOD for MBT	Reference
Tap water, surface water, urban effluent	SPME; polyacrylate	GC–MS/MS	0.7–1.2 μg l^{-1}	22
River water, urban and industrial wastewater	SPE	LC–MS/MS	6 ng ml^{-1}	25
Wastewater	SPE	GC–MS	–	21
Tap, river and industrial waters, wastewaters	DLLME	LC–Flu–UV	0.3 μg l^{-1}	26
Municipal wastewater	SPE	LC–MS	50–120 ng l^{-1}	27
Tannery wastewater	Direct injection	LC–MS/MS	20 ng l^{-1}	28
Ozonized water	LLE-derivatization	GC–MS	–	20
Urine	LLE-derivatization	GC–MS	0.12 μmol l^{-1}	19
Industrial wastewater	LLE	LC–UV, GC-FID	5 μg l^{-1}	29
River water	Direct injection	LC-ED	0.82 μg l^{-1}	30
Water and sediment	LLE-derivatization	GC-FPD	0.04 ppb	18

This article provides useful information about the operating conditions of GC inlet that may be applied for the determination of MBT without the decomposition of this compound. It also provides information about conditions of GC inlets for determination of MBT developed by other authors, and a comparison of these conditions with those described in this study.

EXPERIMENTAL

Agilent GC/MSD 7890B/5977A was employed for the qualitative determination of MBT. GC unit included G4513A autoinjector, multimode inlet and HP-5MS capillary column ((5 %-phenyl)-methylpolysiloxane packing, 30 m length, 0.25 mm ID, 0.25 μm film). Helium was used as a carrier gas. MSD unit was consisted of a single quadrupole mass analyzer and ion source with electron ionization.

Technical flotation reagent SKIK (Metoha Technology) containing 50 % water solution of sodium-2-mercaptobenzothiazole was used for experiments in this study. 1 ml of the reagent was dissolved in 100 ml of deionized water. Diluted hydrochloric acid was added to the solution to form the white precipitate composed of MBT. Suspension was transferred to separatory funnel and the extraction was carried out using dichloromethane. After vigorous shaking of separatory funnel, the suspended particles from water layer were dissolved in dichloromethane. Organic layer was separated, extract was dried using anhydrous sodium sulfate and diluted 100 times with hexane.

In order to compare performances of PTV and hot splitless injection for the determination of MBT, two runs were performed using same injection volume of extract, temperature

program of oven and mass spectrometer parameters, but with different temperature programs of inlet. In both runs, injected volume of diluted extract was 1 μL, temperature program of oven was: 40 °C for 2 min, then 15 °C/min to 190 °C for 0 min, then 5 °C/min to 280 °C for 15 min; acquisition mode of mass spectrometer was scan; total run time was 45 min.

In the first run, inlet mode was splitless, temperature was 280 °C and purge flow to split vent was set at 2 min. Second run was carried out using solvent vent mode. Temperature program of inlet was: 50 °C for 0.1 min, then 130 °C/min to 280 °C until the end of run. Purge flow to split vent was set at 2 min, same as in the first run.

RESULTS AND DISCUSSION

In the first run, when the hot splitless injection was used, two chemical compounds emerged on the chromatogram: benzothiazole (BT) and MBT. When the second run was performed, using the solvent vent mode, only MBT was identified on chromatogram. It was concluded that BT was the product of partial decomposition of MBT due to high inlet temperature during the first run. Both compounds identified in first run exhibit the sharp peak shape, indicating that the degradation observed took place completely within the injector.[37] Retention times of BT and MBT were 9.024 and 16.559 min respectively. Chromatograms acquired using the hot splitless and solvent vent mode are shown in Fig. 2.

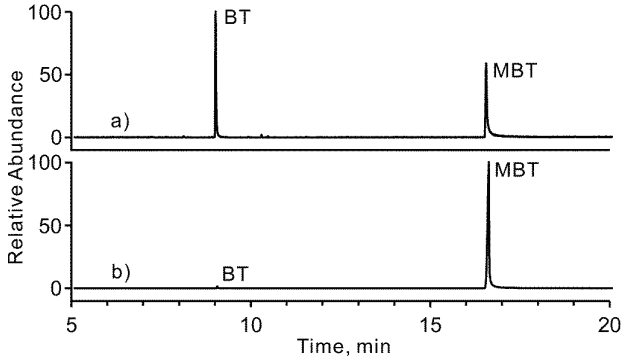

Fig. 2. Chromatogram acquired by injecting sample solution using: a) hot splitless (280 °C) and b) solvent vent mode (40 °C).

The mass spectrum of MBT, acquired by measurement of sample aliquot (Fig. 3), matched the mass spectrum of MBT from database by 96.8 %. This indicates that the chemical compound was identified with high reliability.

Some researchers derivatized MBT prior to GC analysis in order to prevent decomposition, while the others used different analytical technique. Prior to the GC-MS determination of MBT in ozonized samples, Fiehn *et al.*[20] carried out methylation using diazomethane in order to protect thiol group from decomposition. As a result, MBT was identified as *S*-methylated product. Shinohara *et al.*[18] methylated MBT prior to GC-FPD analysis using dimethyl formamide diacetal as methylation reagent, and Manninen *et al.*[19] derivatized samples with

pentafluorobenzyl bromide. Rennie[30] used HPLC for determination of MBT instead of gas chromatography because of degradation problems.

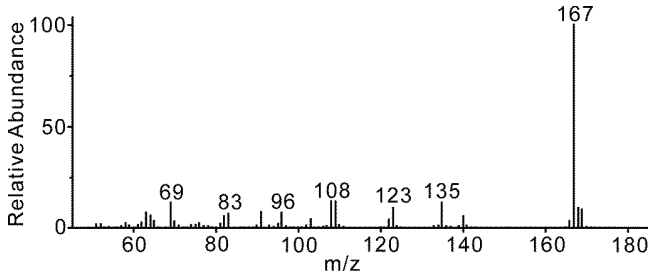

Fig. 3. Mass spectrum acquired by GC–MS analysis of MBT in hexane solution.

Some researchers preferred to determine MBT using GC without derivatization. Domínguez *et al.*[21] carried out GC–MS determination of benzothiazoles using six different ionic liquid stationary phases. In their study, samples were injected in splitless mode at injector temperature of 270 °C. Six different columns were tested for MBT and related compounds. MBT have eluted from only one column, but with very poor response of mass spectrometric detector. Among that, the response for BT was much higher than the responses of other compounds of the same concentration in standard mix solution. This may indicate that MBT was possibly partially degraded to BT using these GC conditions. Naccarato *et al.*[22] also performed analysis of MBT in splitless mode and by setting the injector temperature at 290 °C.

The result of the present work suggests that hot splitless injection should be avoided for the determination of MBT. This suggestion is consistent with the results of researchers mentioned above who derivatized MBT prior to GC analysis. However, in some recent papers MBT was determined together with many other compounds in splitless mode and with high injector temperature. According to results obtained in our study and studies in which derivatization was performed, the response of MBT acquired using hot splitless injection might be lower than actual response due to decomposition.

CONCLUSION

A new approach for preventing the decomposition of MBT was presented in this study. Instead of derivatization, PTV injection was proven to be efficient in preventing the decomposition of MBT during GC determination. This approach requires no chemical reagents for derivatization and shortens the time of analysis. Finally, it may be stated that the derivatization or the application of PTV injection is highly recommended when the analysis of MBT is performed using GC. Hot splitless injection may cause partial decomposition of MBT and it may lead to biased results.

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ИЗВОД

СПРЕЧАВАЊЕ РАЗГРАДЊЕ 2-МЕРКАПТОБЕНЗОТИАЗОЛА ТОКОМ ГАСНО ХРОМАТОГРАФСКЕ АНАЛИЗЕ ПРИМЕНОМ ИНЈЕКТОРА СА МОГУЋНОШЋУ ПОДЕШАВАЊА ТЕМПЕРАТУРЕ ИСПАРАВАЊА

СТЕФАН ЂОРЂИЕВСКИ, ЗОРИЦА СОВРЛИЋ, ТАМАРА УРОШЕВИЋ, ЈЕЛЕНА ПЕТРОВИЋ и ВЕСНА КРСТИЋ

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2-меркаптобензотиазол (MBT) је хемијско једињење које се широко користи у многим гранама индустрије, а такође је детектовано и у узорцима из животне средине. Највећи део истраживача користило је течну (LC) или гасну (GC) хроматографију за одређивање MBT. Када је коришћена GC, дериватизација је била неопходна како би се спречила разградња MBT унутар загрејаног GC инлета. У овом раду представљен је нови приступ за спречавање разградње MBT коришћењем инјектора са могућношћу подешавања температуре испаравања (PTV инјектор). Узорак је инјектован у охлађен инлет (40 °C) и температура је повишавана постепено док аналит није испарио. За разлику од *splitless* инјектовања, применом PTV инјектора није примећена разградња MBT. У поређењу са дериватизацијом, за PTV нису потребне хемикалије и време анализе је краће.

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