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Use of aliphatic thiols for on-site derivatization and gas chromatographic identification of Adamsite

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Abstract: The report describes the development of methods for rapid and simple identification of Adamsite in mobile laboratory conditions using a field gas chromatograph coupled with mass spectrometer. Adamsite is a chemical warfare agent with unique properties that cannot be analysed without conversion to a volatile derivative. Derivatization procedures with 5 aliphatic thiols (ethanethiol, 1-propanethiol, 2-propanethiol, 1-butanethiol and 1-hexanethiol) were developed and compared. The retention characteristics of the derivatization products, peak characteristics and the formation of unwanted artifacts in the chromatograms were monitored. The influence of the reaction media and the time dependence of the reaction were also objects of interest. Other investigated parameters were the optimal reaction temperature and the volume of the derivatization agent. Mass spectra of newly created substances that are not yet included in the chemical weapons related databases were recorded. With optimal reagents (1-butanethiol and 1-hexanethiol), the calibration procedures for analyte determination were subsequently developed, and the methods were verified during the Adamsite identification test in selected environmental and urban matrices.

Keywords: mobile laboratory; chemical weapons; mass spectrometry; dumped organoarsenical.

INTRODUCTION

After the end of World War II, the states disposed large quantities of chemical weapons arsenals by dumping them into seas, oceans and rivers in various places. A lot of exact locations are not known to this day and represent significant ecological problems.¹ Munitions with arsenic chemical warfare agents (CWAs), lewisite, Adamsite, Clark I and Clark II and arsenic oil were also dumped.² Arsenic substances can gradually break down into various degradation

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products, often very toxic.³ Complete spontaneous decomposition of arsenic CWAs in water is expected to take more than 100 years, but for Adamsite it may take even longer.⁴

Adamsite (5-chloro-5,10-dihydrophenarsazine, DM) is an irritating and vomiting CWA, its aerosols irritate the upper respiratory system causing breathing difficulties, pain in the lungs and strong salivation. Despite its practical insolubility in water (0.064 g L^{-1}), its concentration in some dump sites is equal to the acute toxicity values of some aquatic organisms.⁵ Death has been reported with excessive exposure.⁶ The literature reports poor solubility even in organic solvents. The boiling point is unusually high ($410 \text{ }^\circ\text{C}$). Its low volatility predetermines it for use in aerosol form. Due to the very stable structure, the compound is relatively inert. It is able to last in water for many years without significant degradation. It is one of the most effective and at the same time one of the cheapest CWAs.⁷

There are a number of methods for the analysis of DM and other arsenic CWAs using adsorption on green phosphorene nanotubes,⁸ liquid chromatography (LC),^{9,10} handheld Raman spectrometry¹¹ or vapour-sampling direct gas chromatography/mass spectrometry (GC/MS).¹² However, these methods are either unsuitable for use in mobile laboratory tasks or do not reach the parameters for the required level of identification. Military mobile laboratories have specific tasks and must identify contaminants in samples on-site in a relatively short time. The groups follow NATO documentation, namely STANAG 4632¹³ and AEP-66.¹⁴ According to these documents, the mobile laboratory should be able to identify chemical substances at the so-called confirmed level. Preferably, chromatography with mass spectrometry is required to meet this criterion. Due to the time-consuming nature of the procedure (6 h for the process of acceptance of the crude sample to the presentation of the analysis protocol and issuance of recommendations), the supporting technique is GC/MS and the procedures must be reasonably rapid. Field devices are often used, which are rugged for transport, but do not reach the parameters of benchtop devices. The amount and volume of other equipment is also limited, especially by the dimensions of the laboratory, which is mostly located in a deployable container.

Some arsenic CWAs have been analysed in the past by GC without derivatization. However, this is not possible with DM due to its very low vapour pressure and other disadvantages (low linearity of the method at low concentrations due to adsorption in the injection port).¹⁵ Derivatization by pyrolytic ethylation or bromination was proposed.¹⁶ The substitution of chlorine atoms bound to arsenic in CWA by alkanethiols has been also reported.¹⁷ The thiolation of arsenic CWAs is used in antidote therapy.¹⁸ Another method for diphenylarsenic compounds was based on derivatization using *n*-propanethiol at ambient temperature or $60 \text{ }^\circ\text{C}$ and 20 min.¹⁹ Muir *et al.*²⁰ used 1-butanethiol and 3,4-disulf-

anyltoluene, but analysed air samples after thermal desorption, which cannot be applied to DM. Using the Clark I substance as an example, ethanethiol and 1-propanethiol were compared. The latter was a more suitable agent.²¹ Tornes *et al.*²² tested water samples containing DM. They derivatized with 1-propanethiol, 1,3-propanedithiol and 3,4-disulfanyltoluene in dichloromethane. The best results were obtained with 1-propanethiol. Other authors also lean towards the same agent.²³

The aim of the research was the development and the optimization of a simple procedure for the identification of DM by GC/MS, which will be applicable in the conditions of a mobile laboratory.

EXPERIMENTAL

Chemicals

5-chloro-5,10-dihydrofenarsazine (DM) 95 % was produced by Military Repair Facility Zemianske Kostolany (Slovakia). Tributyl phosphate 99 % (Sigma Aldrich) was used as the internal standard. As reaction media, acetonitrile (MECN) gradient grade (Sigma Aldrich), dichloromethane (DCM), hexane (HEX) (both reagent grade ACS, Scharlau, Germany), ethyl acetate (ETAC) for HPLC and acetone (ACON) rectapur (both VWR Chemicals, USA) were used. As thiol reagents, ethanethiol 97 %, 1-propanethiol 99 %, 2-propanethiol 97 %, 1-butanethiol 99 % and 1-hexanethiol 99 % (all Sigma Aldrich) were used. The column was calibrated by the alkanes solution C7-C30 1000 $\mu\text{g mL}^{-1}$ in hexane (all Sigma Aldrich, Germany).

Equipment

GC/MS was conducted using mobile GC/MS system EM 640 (electron ionization, 70 eV, quadrupole mass filter, m/z 50–550). The injection was splitless, HP-5MS column (25 $\text{m} \times 0.32 \text{ mm} \times 1.0 \mu\text{m}$) was used. Carrier gas was nitrogen (30 ml/min flowrate).

For the acquisition and evaluation of the data, software packages m.a.c.s. LabStar and Bruker DataAnalysis (all Bruker, Germany) were used. After analysis, the data were exported and interpreted in the automated mass spectral deconvolution and identification system (Tobias Kind, Germany). GC program was: start at 40 °C (1 min hold) – 10 °C min^{-1} gradient until 280 °C (10 min hold). Total time was 35 min.

GC with flame ionization detector (GC/FID) Trace 1310 (Thermo Scientific, USA) was used to verify the retention characteristics. The column was TG-5MS, 30 $\text{m} \times 0.32 \text{ mm} \times 0.50 \mu\text{m}$ (Thermo Scientific, USA). The temperature program was set identically as for GC/MS analytical method described in previous paragraph. The injection port was set at 250 °C, the injection proceeded in split mode (1:20 ratio). A constant flow rate of 1.5 mL min^{-1} of carrier gas (He) was applied to the column. The detector temperature was 280 °C. FID gases were set at flow rate of 350 mL min^{-1} (air) and 40 mL min^{-1} (H_2). All gases were of 5.0 purity. Furthermore, make-up gas (N_2) was introduced into the system in a volume of mL min^{-1} . Chromeleon 7 software (Thermo Scientific, USA) was used for data acquisition and interpretation.

Manual injections were performed in the volume of 2 μL . Microlitre syringes (Hamilton, USA) were used for injection. TriPlus RSH autosampler (Thermo Scientific, USA) was used for GC/FID automatic injections. Ultrasonic bath Sonorex Digitec (Bandelin, Germany) was used to homogenize solutions and for extractions. Multi Reax automatic shaker (Heidolph, Germany) was also used for extractions. For temperature control during reactions, HD-4 thermostat (Julabo, Germany) was used.

As environmental and urban matrices were used distilled water, sea sand pure (Lachema, Czech Republic), Arenosol Epietric soil (Czech University of Life Sciences Prague, Czech Republic), 4 mm Planibel Clearlite soda-lime-silica glass (AGC Glass Europe, Belgium), road concrete curb MONO (BEST, Czech Republic) and spruce deck Standard (Rettenmeier, Slovakia).

Derivatization procedure

Table I lists some parameters of the tested thiols, especially with regard to possible reaction temperatures and storage conditions. It is evident that, especially in the case of ethanethiol, it is necessary to follow certain requirements. Pentanethiol was evaluated as an unsuitable reagent for field conditions due to the necessity of its storage under inert gas. Therefore, the reagent was excluded from the experiments.

TABLE I. Characteristics of thiol compounds used for Adamsite derivatization

Thiol	Abbreviation	CAS	Boiling point, °C	Storage conditions	Odor
Ethanethiol	EtSH	75-08-1	35	2 to 8 °C	Skunk
1-Propanethiol	1-ProSH	107-03-9	67–68	Cool, ventilated place	Cabbage
2-Propanethiol	2-ProSH	75-33-2	52	Ventilated place	Skunk
1-Butanethiol	BuSH	109-79-5	97–99	Cool, ventilated place	Skunk
1-Hexanethiol	HeSH	111-31-9	151	Ventilated place	Asphalt

The literature does not offer many solvents that dissolve the tested analyte well. As media for reactions between DM and thiols, 4 polar aprotic solvents were used, which were verified to dissolve DM in the used concentration – MECN (dielectric constant 37.5), ACON (20.3), DCM (8.9), ETAC (6.0).

As first thiol, BuSH was chosen, which is used in mobile laboratories for the identification of lewisites. Several aspects that influence the derivatization of DM by BuSH have been investigated. Different solvents, the effect of temperature on the course of the reaction and the time dependence of the reaction were tested. A solution of DM in the appropriate solvent (MECN, DCM, ETAC, ACON) with a concentration of 2 mg mL⁻¹ was prepared. This solution was spiked with an internal standard (tributyl phosphate, 200 nL mL⁻¹). This substance was present in the solution due to mobile GC/MS and hand injections error propagation reduction. 50 µL of BuSH was added to this 1 ml solution. Subsequently, sonication was performed for sample homogenization (2 min). Furthermore, the reaction was monitored at different temperatures – 25 and 60 °C (MECN), 25 and 35 °C (DCM), 25 and 50 °C (ETAC), 25 °C (ACON). The kinetics of the reaction was monitored in the range of 15–180 min. The maximum reaction time of 180 min was chosen for the application reasons. Mobile laboratories are intended for rapid identification of substances in samples. A longer derivatization time would thus be difficult to implement in practice. Chromatograms were always compared to a blank created under identical conditions without the presence of analyte.

In the case of 1-ProSH and HeSH, the same procedure was followed as for BuSH and the same solvents were measured. In the case of 2-ProSH, the reaction in MECN at 60 °C was not observed. In the case of EtSH, due to its high volatility, the reactions were only monitored under mild conditions (25 and 35 °C).

Reaction temperature and reagent volume

Since DCM and ACON are low-boiling solvents, the effect of temperature on the course of the reaction was monitored in MECN and ETAC using BuSH as the derivatizing reagent.

DM solutions were prepared in the appropriate solvent (with spiked internal standard) at concentration of 2 mg mL^{-1} . Then, $50 \mu\text{L}$ of BuSH was added to a volume of 1 mL of solution. The reaction took place at different temperatures ($25\text{--}70 \text{ }^\circ\text{C}$) and was terminated in each case after 60 min .

The optimal volume of thiol was verified in a similar way. DM solutions were prepared in DCM as described above. BuSH or HeSH in a volume of $10\text{--}100 \mu\text{L}$ was added to the solutions. The reaction took place at $35 \text{ }^\circ\text{C}$ and was terminated after 60 min .

Calibration curves

Using thiols with longer alkane chains (BuSH, HeSH), the calibration dependences of the response of the DM derivatized signal on the analyte concentration were developed. DM concentrations were chosen to be 0.2 ; 1.0 and 2.0 mg mL^{-1} in DCM spiked with internal standard. Due to the low reproducibility of the results of the mobile GC/MS system when the device is turned off and on, the calibration curve was always recreated at the beginning of the measurement day to check its stability.

Adamsite identification in environmental and urban matrices

Water, sand, soil, glass, concrete and pre-treated wood were used as sample matrices for recovery tests. The water in a volume of 100 mL was contaminated with the analyte to a final concentration of 2 mg mL^{-1} . Five ml were then sampled and subsequently extracted with 5 mL of DCM (spiked with internal standard) for 10 min by vortexing (1000 rpm). The theoretical maximum yield should thus have been 2 mg mL^{-1} in the tested solution (upper point of the calibration curve). The other matrices were contaminated with 20 mg of DM in a weight of 5 g . Each sample was placed in a sampling vial and 10 mL of DCM with internal standard was added. The extraction took place by ultrasonication for 10 min . The matrices were also contaminated with DM in DCM solution. The resulting mass of contaminant per sample was kept the same as in previous case. The samples were allowed to free evaporate the solvent for 30 min before extraction. Each sample was created and analysed 3 times.

RESULTS AND DISCUSSION

The reaction of 5-chloro-5,10-dihydrophenarsazine (and other arsenic compounds with an As–Cl bond) with thiols is a nucleophilic substitution that proceeds according to the scheme shown in Fig. 1. The chlorine atom is replaced by an R–S– group and the chlorine atom is cleaved off and forms hydrochloric acid. It is advisable (in some cases necessary) to store thiols in the cold to reduce volatility – these are very malodorous substances. Thus, storage in a refrigerated desiccator is recommended.

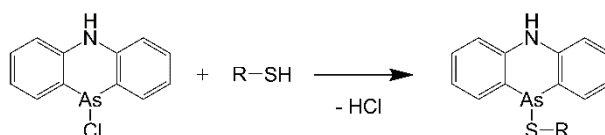


Fig. 1. Thiolation of Adamsite.

Derivatization by ethanthiol

Ethanthiol is a relatively unsuitable reagent due to its very high volatility and strong resistant odour, which can be detected even in trace concentrations.

The following substances were recorded when the reaction was performed in DCM: At retention time (*RT*) 7.94 min (retention index, *RI*, 929) diethyl disulphide was identified. Other signals corresponded to the internal standard tributyl phosphate (*RT* 18.27 min, *RI* 1659) and a double peak of derivatized DM – 5-ethylthio-5,10-dihydrophenarsazine (*RT* 25.78 min, *RI* 2457 and *RT* 26.65 min, *RI* 2545). In addition, the identified DM was characterized by a low signal-to-noise (*S/N*) ratio. In ACON, the peak of diethyl disulphide was very intense, in addition, 2 more EtSH related products were recorded at *RT* 5.37 min (*RI* 787) and *RT* 11.44 min (*RI* 1139). Increasing the reaction time rose the intensity of these artifacts in the chromatogram. Inappropriate results were also noted in ETAC. In the case of all solvents, the signal of the derivatized analyte increased with the extension of the monitored reaction time, and the maximum was not reached after 180 min. Table II lists the most represented fragments of mass spectra of DM derivatives using different thiols.

TABLE II. Retention indexes (*RI*) and the most abundant fragment ions of thiolated Adamsite using different thiols (the first most abundant fragment ion was used for quantification).

Parameter	EtSH	1-ProSH	2-ProSH	BuSH	HeSH
<i>RI</i>	2457, 2545	2613	2563	2706	2985
Relative abundance of fragment ions, %	166 (99.9) 63 (64.2) 113 (57.0) 167 (57.0) 241 (49.9)	242 (99.9) 167 (31.5) 166 (25.8) 140 (15.5) 243 (12.3)	242 (99.9) 241 (74.7) 59 (62.3) 76 (61.3) 63 (51.5)	242 (99.9) 56 (36.3) 167 (32.7) 166 (28.4) 55 (28.3)	64 (99.9) 50 (94.0) 55 (82.3) 87 (58.7) 241 (47.0)
Molecular ion	303	317	317	331	359

Derivatization by 1-propanethiol

In DCM, in addition to the internal standard, peaks were found at 11.15 min (*RI* 1117), which corresponded to dipropyl disulphide, and at 27.50 min (*RI* 2613), which corresponded to 1-ProSH derivative of DM, 5-propylthio-5,10-dihydrophenarsazine. After 60 min of reaction, the chromatographic background before the DM derivative started to rise, so that the identification was complicated. In the case of 1-ProSH, however, MECN was an unsuitable solvent. Before the DM derivative peak, the background began to increase significantly, a large broad peak was formed, which made quantification difficult. In addition to the previously mentioned substances, a peak of 1,3-bis(propylthio)propane (*RT* 30.86 min; *RI* 1915) was noted in the chromatograms. In the case of reactions in ETAC, the chromatogram was not clear, in the *RT* interval 22–27 min a significant increase in the background was recorded, and at 13.51 min (*RI* 1278) there was a 1-ProSH related product. The reagent is preferred by a number of authors^{19,21–23} for the derivatization of organoarsenic toxic substances. However, apparently it is not possible to use 1-ProSH for the field GC/MS identification of DM.

Derivatization by 2-propanethiol

2-ProSH is the more volatile isomer of 1-ProSH. A peak identifying the oxidized reagent, bis(1-methylethyl)disulfide (*RT* 9.74 min, *RI* 1033) was noted in MECN. Furthermore, there were other artifacts in the chromatogram that would make identification in field conditions difficult. Derivatized DM, 5-(1-methyl)ethylthio-5,10-dihydrophenarsazine, was noted at *RT* 26.84 min (*RI* 2563). However, it was associated with a peak at *RT* 25.83 min (*RI* 2462) that was again related to DM. Moreover, from *RT* 23 min an increase in noise was evident and the results were unsuitable for identification. This phenomenon was then enormous in the environment of ETAC. DCM could be determined as the best reaction medium, no remaining characteristic of previous solvents were found in the extract. Again, the derivatized DM was noted in the double peak, but this could probably be a shortcoming of 2-ProSH itself. As the temperature increased from 25 to 35 °C, the chromatographic background became more intense. The disulphide of the original thiol was not found in DCM.

Derivatization by 1-butanethiol

During the reaction in MECN at a temperature of 60 °C, 4 peaks were recorded in the chromatogram – 14.12 min (*RI* 1320) corresponded to dibutyl disulphide, which was formed by the oxidation of BuSH. Peak intensity increased with temperature, as well as with reaction time. The peak at *RT* 18.27 min (*RI* 1659) corresponded to tributyl phosphate (internal standard), the peak at 23.48 min (*RI* 2179) was identified as tributyl arsenotrithiolite, which is a BuSH derivative of arsenic trichloride, probably a decomposition product of DM. The BuSH derivative of DM, 5-butylthio-5,10-dihydrophenarsazine, was recorded at 28.81 min (*RI* 2706).

Tributyl arsenotrithiolite was not found upon changing the solvent, nor upon derivatization in MECN at 25 °C. In the case of the latter conditions, further in DCM at 25 and 35 °C, only 3 peaks corresponding to the analyte, internal standard and disulphide were recorded. In ETAC (at 25 and 50 °C) the mixture of recorded substances was extended by 2 BuSH related products (*RT* 10.80 min, *RI* 1094 and *RT* 16.05 min, *RI* 1475). Fig. 2 illustrates the mass spectra of the BuSH derivative of DM alongside all other newly identified derivatization products using additional thiols.

Derivatization by 1-hexanethiol

Due to its highest mass, HeSH had high retention and was recorded in the chromatograms (in MECN *RT* 8.32 min, *RI* 949). Due to its high concentration in the solution, the acquisition of mass spectra in subsequent measurements was started 10 min after injection. Dihexyl disulphide, a HeSH oxidation product, was also found in MECN at 18.96 min (*RI* 1730). The 5-hexylthio-5,10-dihydrophen-

arsazine was found at RT 32.19 (RI 2985), which is a relatively high value for field analysis. Significant peak broadening was associated with this high retention of substance in the column. In addition, an increased chromatographic background was noted in the region of RT 26–28 min. When the temperature increased from 25 to 50 °C, additional artifacts arose (a significant peak at RT 23.41 min, RI 2194, which came from HeSH related product) and the noise was significant from the 15th min. The broad HeSH peak of the DM derivative was encountered in all tested solvents. The best results in terms of number of artifacts and noise level were recorded using DCM (25 and 35 °C) and ME CN at 25 °C. Several other interfering peaks were found in ACON, at 12.73 min (RI 1225), 14.83 min (RI 1379), 21.02 min (RI 1933), 22.09 min (RI 2045) and 22.99 min (RI 2146). In all cases, these were HeSH related products.

Fig. 2 illustrates the chromatograms obtained after thiolation of DM in DCM at 35 °C using different thiols. The reaction time was 60 min.

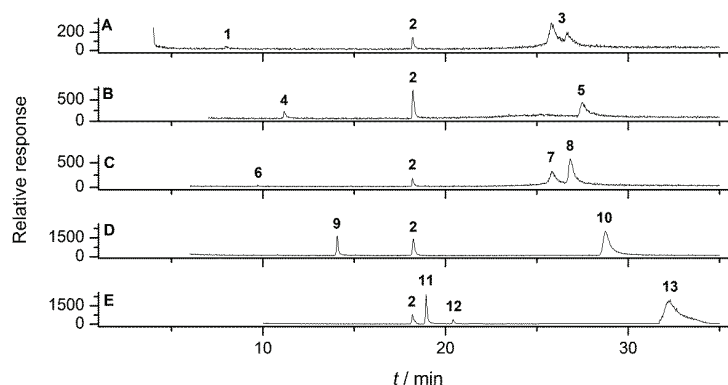


Fig. 2. Chromatograms after direct injection of the reaction mixtures: Adamsite + EtSH (A), 1-ProSH (B), 2-ProSH (C), BuSH (D) and HeSH (E). The reactions were performed in dichloromethane. Peaks correspond to: diethyl disulfide (1), tributyl phosphate internal standard (2), 5-ethylthio-5,10-dihydrophenarsazine double peak (3), dipropyl disulfide (4), 5-propylthio-5,10-dihydrophenarsazine (5), bis(1-methylethyl)disulfide (6), 5-(1-methyl)ethylthio-5,10-dihydrophenarsazine related product (7), 5-(1-methyl)ethylthio-5,10-dihydrophenarsazine (8), dibutyl disulfide (9), 5-butylthio-5,10-dihydrophenarsazine (10), dihexyl disulfide (11), HeSH related product (12), 5-hexylthio-5,10-dihydrophenarsazine (13).

Fig. 3 illustrates the comparison of the best methods for each thiol in the kinetic curves. S/N ratios and peak area ratios of derivatized DM and internal standard were taken into account during the selection. In terms of signal intensity, the hexanethio- derivatives of the investigated substance dominate significantly. It should also be mentioned that when short thiols are used, the reaction must be prolonged to maximize the yield, while for longer thiols (BuSH, HeSH) 60 min of reaction is sufficient and prolonging the reaction no longer leads to an increase in the concentration of the reaction products. The DCM environment,

when using shorter thiols (EtSH, 1-ProSH, 2-ProSH), caused product decomposition after 60 min.

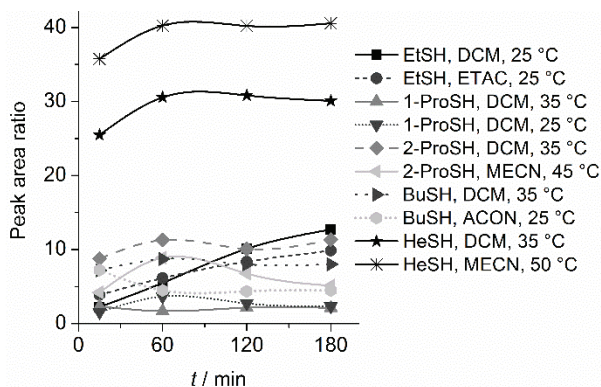


Fig. 3. Kinetics of reactions of Adamsite with derivatizing agents in different media.

Optimal reaction temperature

Fig. 4 illustrates monitoring the effect of the reaction temperature on the intensity of the resulting signal of the derivatized analyte. The results are displayed as a percentage change when the ratio of the peak areas of DM/internal standard at room temperature equals 100 %. Increasing the temperature to 35 °C resulted in a ratio increase of 5 % (ETAC) and 14 % (MECN). A further temperature increase of 10 °C only led to an increase in the ratio of 3 % (ETAC) and 2 % (MECN). The intensity difference between 25 and 65 °C is 9 % (ETAC) and 17 % (MECN). The optimal temperature for thiolation of DM is 35 °C and the reaction takes place smoothly even at room temperature.

Reagent volume

The testing of the optimal volume of the derivatization reagent was carried out in the range of 10 to 100 μL (1 to 10 % of the total volume of the reaction mixture), which are reasonable values to avoid unnecessarily large consumption.

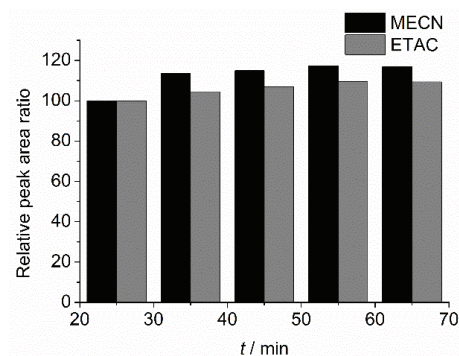


Fig 4. Effect of reaction temperature on the signal intensity of derivatized Adamsite in acetonitrile (MECN) and ethyl acetate (ETAC).

The results (Fig. 5) are displayed as the relative peak area ratio between the derivatized analyte and the internal standard, where the value of the ratio for a thiol volume of 50 μL was marked as 100 %. Under these conditions, increasing the reagent volume from 10 to 50 μL resulted in the rise of the relative ratio value from 35 to 100 % (BuSH) and from 29 to 100 % (HeSH). A two-fold increase in the volume of the reagent to 100 μL then only led to the rise of the monitored value by 19 % (BuSH) and 27 % (HeSH), respectively. Increasing the volume thus no longer leads to a linear increase in the signal. In addition, it is demonstrated that the derivatization by HeSH is more sensitive to increasing the volume of the reagent.

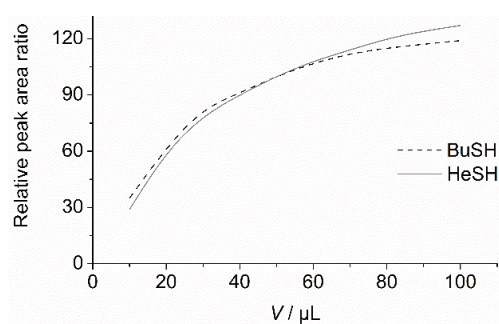


Fig 5. Effect of the volume of the derivatization reagent (BuSH and HeSH) on the signal intensity of the derivatized analyte.

Application of the methods in the identification of Adamsite in matrices

Table III documents the parameters of the calibration curves using BuSH and HeSH as derivatization reagents, the reaction was carried out in DCM at 35 $^{\circ}\text{C}$ (35 $^{\circ}\text{C}$ for EtSH) and was terminated after 60 min. The reproducibility of the measurements was increased using the internal standard. Switching the mobile GC/MS system off and on again led to error propagation, and therefore three-point calibration curves were always created at the beginning of the measurement day, reducing the *RSD* of repeat measurements from 35 to 15 %. The detection limit of the methods was determined according to the calibration curve for the *S/N* ratio of the derivatized analyte equal to 3. Relatively high limits of detection are associated with the low reactivity of the substance and its high molecular weight and the parameters of the mobile GC/MS system. The linearity of the methods was verified in the range of 0.2–4.0 mg mL^{-1} . The parameter is documented in Fig. 6 that illustrates the linearity of the curve was created three times on different measurement days. It demonstrates that linearity was maintained even though curve shifts occurred.

TABLE III. Calibration curves parameters

Thiol	Coefficient of determination	<i>RSD</i> / %	Detection limit, mg mL^{-1}
BuSH	0.993	16	0.10 \pm 0.02
HeSH	0.994	14	0.05 \pm 0.01

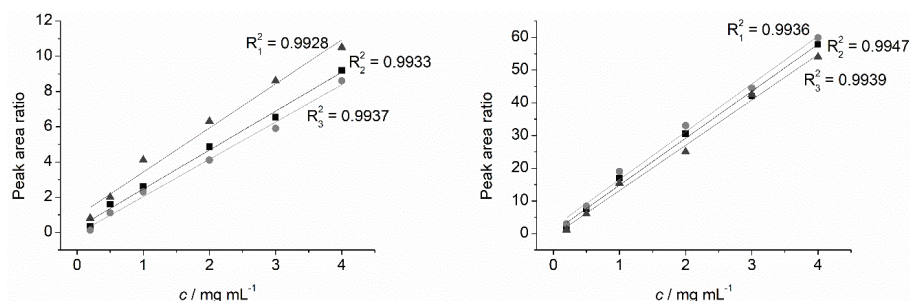


Fig. 6. Linearity of derivatization reaction of Adamsite by BuSH (left) and HeSH (right).

Table IV demonstrates the use of the above methods for DM identification in environmental and urban matrices. The results demonstrate that neat DM can be extracted from samples more efficiently than in the case of a matrix contamination by DM solution. It is more evident with porous matrices. This is due to the greater penetration of the contaminant into the depth of the matrix when using a liquid solution. In the case of water, the organic DM sample was not tested. No significant difference in efficiency value was noted when HeSH was used instead of BuSH as the derivatizing reagent. None of the matrices caused unwanted interference in the area of analyte retention. Both methods were assured to be valid for the 6 sample matrices tested.

TABLE IV. Adamsite recovery as BuSH and HeSH derivatives from different matrices after contamination with neat analyte (E_{neat}) and analyte dissolved in dichloromethane (E_{sol}). The results are given as efficiency value when derivatized by BuSH / by HeSH

Sample	$E_{\text{neat}} / \%$	$E_{\text{sol}} / \%$	Sample	$E_{\text{neat}} / \%$	$E_{\text{sol}} / \%$
Water	82 / 85	—	Glass	92/88	90/93
Soil	76 / 75	45 / 51	Concrete	70/74	35/29
Sea sand	80 / 81	62 / 58	Wood	75/70	38/31

Fig. 7 illustrates the applicability of DM derivatization via HeSH after extraction from the most problematic matrix in terms of chromatographic back-

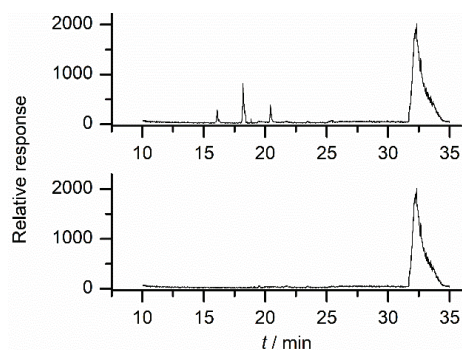


Fig. 7. Comparison of chromatogram after extraction of Adamsite from soil and subsequent derivatization with HeSH (top) and chromatogram of the same measurement after background subtraction (bottom).

ground – soil. The mobile GC/MS did not have the ability to perform automatic background subtraction. However, after data export and external subtraction, it can be seen that only the derivatized analyte peak is visible in the chromatogram after the hiding of background effects. A disadvantage of the used mobile GC/MS system is also the fact that when the experiment is repeated, the mass spectra are not identical in the area of ions with lower abundance. The first 5 fragment ions were always the same (Table II).

CONCLUSION

It has been shown that Adamsite, which in its neat form has very unsuitable analytical properties, can be analysed by gas chromatography. All investigated aliphatic thiols are able to convert the substance into a more volatile derivative by nucleophilic substitution. Due to the large weight of the Adamsite molecule, the derivatives have considerable retention in the standard HP-5 column, and with the growing alkane chain of the reagent, it is necessary to adjust (especially prolong) the chromatographic method. Aromatic thiols would thus be inappropriate reagents for field analysis.

The best results in terms of the signal intensity and the associated characteristics (detection limit, *S/N* ratio) were achieved using HeSH. However, the substance was significantly retained by the column (RI 2985) and the peak was broad.

A high *RI* is associated with the length of the method, which must be at least 35 min. However, the derivative was recorded with a significantly higher resulting signal even after 15 min of derivatization. For other reagents (BuSH comes into consideration), it is recommended to extend the derivatization time to 60 min.

ИЗВОД

УПОТРЕБА АЛИФАТИЧНИХ ТИОЛА ЗА *ON-SITE* ДЕРИВАТИЗАЦИЈУ И ИДЕНТИФИКАЦИЈУ АДАМСИТА ГАСНОМ ХРОМАТОГРАФИЈОМ

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У овом раду је описан развој методе за брзу и једноставну идентификацију Адамсита у мобилној лабораторији, применом гасне хроматографије са масеном спектрометријом. Адамсит је хемијски бојни агенс са јединственим особинама да се не може анализирати без конверзије у испарљив дериват. Развијена је и упоређена дериватизација са пет алифатичних тиола (етантиол, 1-пропантиол, 2-пропантиол, 1-бутантиол и 1-хексантиол). Праћене су ретенционе карактеристике деривата, карактеристике пикова главних једињења и нежељених пикова на хроматограмима. Праћени су такође и утицај реакционог медијума и време реакције. Испитивани су оптимална реакциона температура и запремина реагенса за дериватизацију. Снимљени су масени спектри новоформираних деривата, који се још увек не налазе у базама података хемијских бојних супстанци. Калибрација потребна за одређивање је изведена са оптималним реагенсима (1-

-бутантиол и 1-хексантиол) и метода је верификована тестом идентификације Адамсита у одабраним матрицама из природне и околине и урбане околине.

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