Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
*J. Serb. Chem. Soc.* *87* (2) 233–245 (2022)
*JSCS–5518*
*Original scientific paper*
Published 18 September 2021

# Development of a method for the derivatization of ethanolamines and its application to sand samples

TOMAS ROZSYPAL*

*Nuclear, Biological and Chemical Defense Institute, University of Defense, Vita Nejedleho 691, 68203 Vyskov, Czech Republic*

(Received 12 March, revised 12 May, accepted 13 June 2021)

*Abstract*: Nitrogen mustards are dangerous and available blistering chemical warfare agents. In the presented study, six derivatization methods are compared for the analysis of degradation products of the most important blistering nitrogen mustards (ethyl diethanolamine, methyl diethanolamine and triethanolamine) by gas chromatography coupled with mass spectrometry. Five silylation methods (using BSTFA and BSA) and one trifluoroacetylation method (using TFAA) were tested. The derivatization reactions were performed in acetonitrile. As the method with optimal results, trifluoroacetylation by TFAA was selected. Analytes reacted with the corresponding reagent rapidly, quantitatively, with stable kinetics and at room temperature. Calibration curves for quantitative analysis of ethanolamines after TFAA derivatization were created. The corresponding detection limits varied between $9\times10^{-3}$ and $7\times10^{-5}$ mmol·dm$^{-3}$ for the tested analytes. The developed method was applied for the analysis of ethanolamines after extraction from sand using acetonitrile. Limits of detection were 11.4 to 12.3 μg of the analyte in 1 g of sand. The use of the developed method in military deployable laboratories designated for the rapid identification of chemical warfare agents and corresponding degradation products is encouraged.

*Keywords*: nitrogen mustard; gas chromatography; mass spectrometry; chemical warfare agents; deployable laboratory.

## INTRODUCTION

Nitrogen mustards bis(2-chloroethyl)amine (HN-1), bis(2-chloroethyl)methylamine (HN-2), and tris(2-chloroethyl)amine (HN-3) are harmful blistering chemical warfare agents (CWA) scheduled in the 1A Chemical Weapons Convention Schedule.[1] These are chemicals with similar effects to sulfur mustard are persistent toxic chemicals, only slightly soluble in water and with slow hydrolysis rates.[2] Nitrogen mustards are specific by their potent alkylating effects[3] and

* E-mail: tomas.rozsypal@unob.cz
https://doi.org/10.2298/JSC210312047R

they interact with a number of biomolecules and a characteristic manifestation of poisoning is severe blister formation.[4] These are controlled substances, however, the synthetic pathways are quite simple, precursors are available, and nitrogen mustards therefore still pose an actual threat. The hydrolysis degradation products are ethyl diethanolamine (EDEA), methyl diethanolamine (MDEA) and triethanolamine (TEA).

For identification of CWA military deployable laboratories have often been employed. These laboratories search not only for intact CWA but also for degradation products to exclude false negatives. Liquid chromatography (LC) coupled with mass spectrometry (MS) or nuclear magnetic resonance (NMR) techniques were successfully used for the identification of nitrogen mustards and corresponding degradation products in different matrices, such as water and decontamination mixtures,[5] organic samples,[6] wipes and solid samples,[7] urine and serum.[8,9] These methods ensure the identification of analytes at very low concentrations (ng $ml^{-1}$). However, military deployable laboratories mostly do not possess a NMR detector, nor a LC/MS system because of their high purchase price and vibration sensitivity during military transport.

For nitrogen mustard identification, gas chromatography (GC) coupled with a number of detectors is often used.[10] Hydrolysis products could be derivatized with trimethylsilyl (TMS) or *tert*-butyldimethylsilyl (TBDMS) reagents, such as trimethylsilyl iodide (TMSI) + trimethylsilyl chloride (TMCS),[11] *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) + TMCS[12] or *N*-*tert*-butyldimethylsilyl--*N*-methyltrifluoroacetamide (MTBSTFA).[13] A rapid method using trifluoroacetylation by *N*-trifluoroacetylbenzimidazole and *N*-trifluoroacetylimidazole (TFAI) was developed.[14] However, no quantitative data were demonstrated. Methods for sample-applied derivatization of partially hydrolyzed nitrogen mustards were created using silylation,[15] trifluoroacetylation using TFAI and heptafluorobutyrylation.[16] In the last case, better results were obtained in comparison to silylation. Formation of fluorinated derivatives is recommended also for GC coupled with Fourier transform infrared spectrometry (FTIR) analysis because of the high absorptivity of these derivatives in their IR spectrum.[17] Directly for military deployable laboratories, derivatization of ethanolamines by BSTFA in acetonitrile at 60° for 30 min is recommended.[18]

Various matrices contaminated by ethanolamines have been analyzed. A GC/FPD-NPD (flame photometric detection and nitrogen phosphorus detection) method was developed for the determination of nitrogen mustards and ethanolamines in water, soil, organic solvents and PVC.[19] Nerve agent degradation products in soil are derivatized using methylation by trimethyloxonium tetrafluoroborate.[20] Arsenic CWAs in sand samples are identified after thermal desorption.[21] Popiel and Sankowska[22] recommended solid phase microextraction (SPME) as a universal extraction technique for CWA degradation products in

different sample matrices. A simple method for extraction, derivatization, and GC/MS analysis of ethanolamines in sand samples was not presented.

In the current praxis of military deployable chemical laboratories, rugged methods are used that do not suffer from long distance transport of the container. The identification method of choice is GC/MS. The aim of this paper is the development of a simple, quick, reliable, and universal method for the identification of nitrogen mustards ethanolamines EDEA, MDEA and TEA in sand samples using GC/MS, a method usable in military deployable laboratories.

## EXPERIMENTAL

### *Chemicals and equipment*

*N*-ethyldiethanolamine 98 % (EDEA), *N*-methyldiethanolamine 99 % (MDEA) and triethanolamine 99 % (TEA) were used as standards of ethanolamines. As the internal standard, tributyl phosphate 99 % was used. As derivatization reagents, *N*,*O*-bis(trimethylsilyl)trifluoroacetamide 99 % (BSTFA), *N*,*O*-bis(trimethylsilyl)acetamide 98.5 % (BSA), trifluoroacetic anhydride 99 % (TFAA) and trimethylchlorosilane 99 % (TMCS) were used. Acetonitrile gradient grade was used as the extraction solvent (all Sigma Aldrich, Schnelldorf, Germany). Sodium carbonate anhydrous *p.a.* and annealed copper sulfate (both Penta, Prague, Czech Republic) were also used. As the sample matrix, sea sand pure (Lachema, Brno, Czech Republic) was used.

Gas chromatography with mass spectrometry was conducted using the mobile GC/MS system Griffin 465 (FLIR, Wilsonville, USA, electron ionization, ion trap, *m*/*z* 40–425, split injection, standard DB-5MS column (15 m×0.18 mm×0.18 μm). For data acquisition and interpretation, software packages, Griffin System software (FLIR, Wilsonville, OR, USA) and AMDIS 2.72 were used. The chromatographic method was 13.65 min long. The start temperature was 40 °C, held for 1 min. Then a gradient of 30 °C $min^{-1}$ was applied, and the final temperature was 300 °C, which was held for 4 min. The split was set to 1:4 ratio.

For injections micro syringes, Hamilton (Chromservis, Prague, Czech Republic) were used. Extractions were conducted using a Multi Reax shaker (Heidolph, Schwabach, Germany). For temperature control during the derivatization reactions, HD-4 thermostat (Julabo, Seelbach, Germany) was used. Samples were extracted into Supelco 7 mL clear glass vials with screw caps with a solid top and PTFE liner (Sigma Aldrich, Schnelldorf, Germany). For sonication, an ultrasonic bath Sonorex (Bandelin, Germany) was used. X-ray fluorescence (XRF) analysis of the sand matrix was conducted with an ElvaX Mobile (Elvatech, Kyiv, Ukraine). Characterization of the sand grain size distribution was conducted using an AS 200 vibratory sieve shaker (Retsch, Haan, Germany).

### *Sand characterization*

The sand was washed with distilled water, dried and stored in a desiccator prior to analysis. The elemental composition was determined by XRF spectrometry. For this purpose, 5 g of the matrix was added to a XRF vial and it was analyzed in the spectrometer chamber for 1 min using a method developed for soils (35 kV voltage).

Grain distribution of the sand was determined by adding 5 g of the sand into the vibratory sieve shaker and the shaking method proceeded for 2 min. Then the individual sizes of sand grains (from individual sieves) were weighed.

*Derivatization of ethanolamines*

Six derivatization methods were tested. Silylation by BSTFA at 30 °C, silylation by BSTFA at 60 °C, silylation by BSTFA + 1 % TMCS, silylation by BSA, silylation by BSA + + TMCS (5:1) and trifluoroacetylation by TFAA.

A 0.5 mmol $dm^{-3}$ solutions of the corresponding ethanolamine (EDEA, MDEA or TEA) in acetonitrile with internal standard ($1.83\times10^{-4}$ mmol $dm^{-3}$) were created. Then, 1 mL of the solution was added into a vial and the derivatization reagent (or solution) was added in a volume specified in Table I for each derivatization procedure. The vial content was sonicated for 1 min, and then the vial was placed into the thermostat set to the temperature specified for each derivatization procedure in Table I. Then, aliquots of the reaction mixture were taken over time and analyzed by GC/MS to determine the time dependence of the derivatives formation. In a similar way, blank samples (TBP in solvent with derivatization reagent) were always analyzed (with all derivatization methods).

TABLE I. Parameters of the derivatization procedures tested for the derivatization of ethanolamines

| Derivatization procedure | BSTFA at 30 °C | BSTFA at 60 °C | BSTFA + TMCS | BSA | BSA + TMCS | TFAA |
|---|---|---|---|---|---|---|
| Volume of the reagent added, μL | 20 | 20 | 20 | 20 | 20 | 30 |
| Derivatization temperature, °C | 30 | 60 | 30 | 30 | 30 | 30 |

*Test of the effect of solvent on derivatization by TFAA*

A 0.5 mmol $dm^{-3}$ solution of MDEA in hexane with internal standard ($1.83\times10^{-4}$ mmol $dm^{-3}$) was created. Then, 1 mL of the solution was added into a vial and 30 μL of TFAA were added. The vial content was sonicated for 1 min, and then the vial was placed into a thermostat at 30 °C for 30 min. After the specified reaction time, the sample was analyzed by GC/ /MS. Then, ethyl acetate was tested as the reaction solvent in the same manner.

*Calibration curves formation*

For each ethanolamine (EDEA, MDEA and TEA), calibration solutions were prepared with a concentration of 0.05, 0.25 and 0.50 mmol $dm^{-3}$ in acetonitrile with TBP internal standard ($1.83\times10^{-4}$ mmol $dm^{-3}$). To each of these solutions, 30 μL of TFAA was added sequentially, and each mixture was derivatized at 30 °C for 30 min. After the specified reaction time, each sample was analyzed by GC/MS. Each calibration dependence was determined five times and each time, it was verified that the instrument was turned on. From the obtained responses, calibration dependences for individual ethanolamines were created to compare the extraction yields from sand samples in the following steps.

*Extraction of kind regards ethanolamines from sand*

For each ethanolamine (EDEA, MDEA and TEA), calibration solutions were prepared with concentration of 0.5, 2.5 and 5.0 mmol $dm^{-3}$ in acetonitrile with TBPas the internal standard ($1.83\times10^{-4}$ mmol $dm^{-3}$). These concentrations were chosen so that the resulting maximum concentrations after extraction from the sand corresponded to the calibration concentrations from the previous paragraph. Then, 1 g of sand was dosed into 7 mL vials for each sample. Then, 300 μL of the ethanolamine solutions described above were then added into the individual sand samples. Thus, 3 samples of analyte in sand with increasing concentration for each ethanolamine were created. The solvent was allowed to freely evaporate from the samples to the dry state of the sand (90 min). Then, 3 mL of acetonitrile with internal standard

($1.83\times10^{-4}$ mmol $dm^{-3}$) were added to each sample. The samples were extracted for 5 min on a shaker at 1600 rpm. The sample was then centrifuged and 1 mL of the liquid was collected in a vial. To the solution was added 30 μL of TFAA and the mixture was derivatized at 30 °C for 30 min. After the specified reaction time, the sample was analyzed by GC/MS. Each sample was generated and analyzed five times.

## RESULTS AND DISCUSSION

### *Sand characterization*

The elemental composition (weight-to-weight) of the sand was determined by XRF spectrometry: light elements (up to Na) 98.8 %, Ca 0.27 %, Ti 0.25 %, Rh 0.22 %, Ag 0.20 %, Cd 0.11 %, Fe 0.05 %, Ni 0.03 %, Zr 0.02 %. The results of the determination of the grain size distribution of the matrix are given in Table II.

TABLE II. Matrix characterization by determination of the grain size distribution

| Grain size, μm | Contribution, % | Grain size, μm | Contribution, % |
|---|---|---|---|
| 500 | 0.70 | 150 | 24.10 |
| 400 | 2.48 | 100 | 3.94 |
| 300 | 15.60 | 50 | 0.40 |
| 200 | 52.72 | – | – |

### *Derivatization of ethanolamines by BSTFA at 30 °C*

In the derivatization of ethanolamines by BSTFA, trimethylsilylated ethers were formed *via* nucleophilic substitution of the hydroxy groups. The substitution proceeded fairly readily, only fully silylated derivatives were recorded on the chromatograms. In the GC/MS method, it was necessary to shift the MS data acquisition to retention time (*RT*) by 2.57 min due to the late elution of BSTFA, which interfered in the chromatogram.

In the case of EDEA, an artifact co-eluted with the derivatized analyte, which caused an increase in the intensity of the background signal and a deterioration in the resolution of the analyte peak. The peak was low and wide and ranged from *RT* 5.10 to 5.25 min. A similar phenomenon has been reported with MDEA. A small broad peak formed in the *RT* range of 4.85–4.95 min. In the case of TEA, the chromatogram was not disrupted by artifacts, however, silylated TEA was characterized by an *RT* very close to the TBP used as the internal standard. The chromatograms obtained by silylation of ethanolamines are shown in the Fig. 1. The retention indices of the individual silylated derivatives and the EI--MS data of the most abundant fragment ions are given in the Table III.

The graph (Fig. 2) records the kinetics of the formation of the silylated derivatives, *i.e.*, the concentration of the final products as a function of the reaction time with BSTFA. It is evident that the final products were formed relatively quickly and after 30 min, the yields did not increase much, so even at ambient temperature the desired products were formed relatively rapidly.

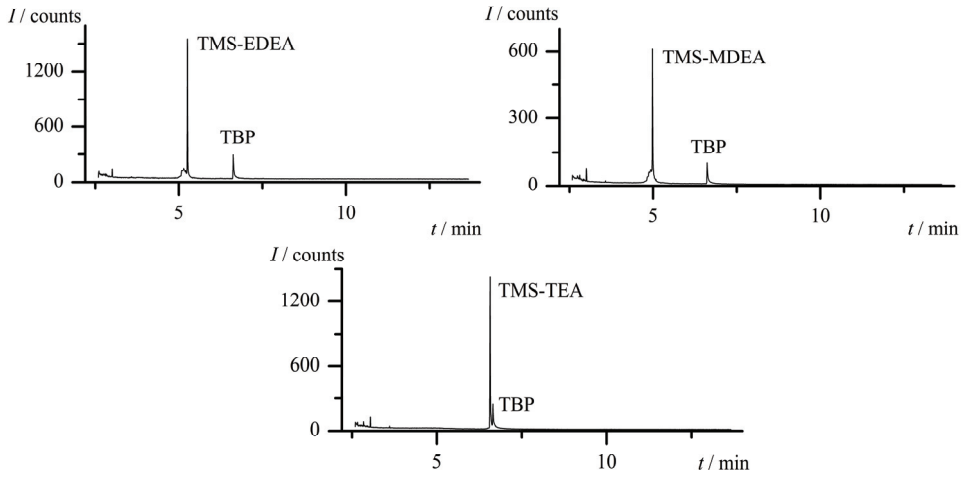


Fig. 1. Chromatograms of TMS derivatives of ethanolamines spiked with the internal standard tributyl phosphate (TSB).

TABLE III. Retention times (*RT*) and corresponding retention indexes (*RI*) of trimethylsilylated analytes – EDEA, MDEA and TEA and internal standard tributyl phosphate, and the most abundant fragment ions (the first most abundant ion was used for quantification)

| Parameter | EDEA | MDEA | TEA | TBP |
|---|---|---|---|---|
| *RT*–min | 5.26 | 4.98 | 6.57 | 6.64 |
| *RI* | 1348 | 1298 | 1629 | 1647 |
| Relative abundance of fragment ions, % | 174 (100.0) | 160 (100.0) | 263 (100.0) | 99 |
| | 73 (45.0) | 73 (51.1) | 73 (52.0) | |
| | 117 (10.6) | 161 (6.8) | 264 (11.5) | |

*Derivatization of ethanolamines by BSTFA at 60 °C*

When derivatizing ethanolamines at higher temperatures, similar results were obtained as in the previous case. With silylated EDEA and MDEA, the same artifacts eluted with *RT* values close to the analytes. In the case of MDEA, this interfering peak was wider than in the case of derivatization at 30 °C. Fig. 2 A and B shows the resulting silylated ethanolamine products as a function of the reaction time. Compared to the course of the reaction at a lower temperature, the results were characterized by higher deviations and were thus more difficult to quantify. As at 30 °C, the maximum values were reached after a reaction time of 30 minutes and thus, the increase in temperature did not have a significant effect on the acceleration of the derivatization.

*Derivatization of ethanolamines by BSA*

BSA, like BSTFA, derivatives alkoxy groups by trimethylsilylation. The silylated derivatives formed relatively quickly and the maximum yield was reached after only 30 min. In addition, higher peak signals were observed for TEA, indi-

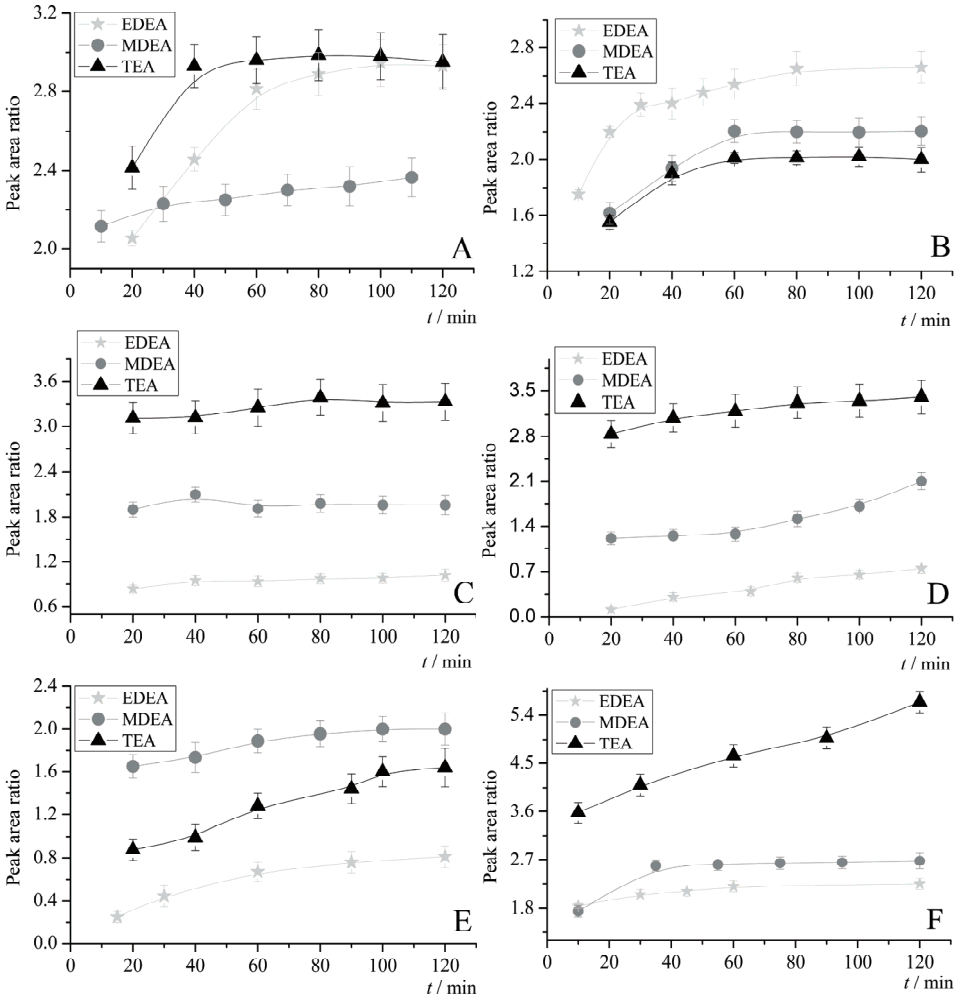


Fig. 2. Kinetics of the formation of trimethylsilyl derivatives after derivatization of ethanolamines by BSTFA at 30 (A) and at 60 °C (B); BSA (C), BSA + TMCS (D), BSTFA + TMCS (E) and the formation of trifluoroacetyl derivatives after derivatization by TFAA (F). The *y*-axis denotes area ratio between analyte and tributyl phosphate peaks.

cating higher yields compared to BSTFA derivatization. The results were characterized by higher deviations compared to BSTFA and were thus less suitable for quantitative purposes. A graphical representation of the formation of the derivatization products as a function of the reaction time is given in Fig. 2C and D.

*Derivatization of ethanolamines by BSA + TMCS*

TMCS-catalyzed BSA derivatization (5:1 BSA + TMCS mixture) showed worse results than BSA alone, probably due to the high TMCS content. Reaction

yields were lower, with slower kinetics, and were also characterized by high deviations, which had a negative impact on quantitative evaluation. The chromatograms were full of peaks that interfered with identification, in the case of EDEA the derivatized analyte co-eluted an artifact with a broad peak base in the region of *RT* 5.00–5.24 min. In the case of MDEA, an artifact also eluted with a broad base in front of the analyte peak in the *RT* 4.70–4.96 min region. In the case of TEA, the derivatized analyte eluted very close to the internal standard. A graphical representation of the formation of derivatization products as a function of the reaction time is depicted in Fig. 2C and D.

*Derivatization of ethanolamines by BSTFA + TMCS*

BSTFA with TMCS (1 %), a mixture used to derivatize poorly derivatizable substances was also tested. Trimethylsilylated ethers of ethanolamines were formed with the same parameters as in the previous cases, together with artifacts similar to those produced by derivatization of ethanolamines only by BSTFA alone. However, the trimethylsilylated products formed with slower kinetics, as can be seen in Fig. 2E and F.

Previous studies dealing with the silylation of ethanolamines[11–13] have shown low detection limits, however, in none of the studies did the authors mention a relatively large number of artifacts in the resulting chromatograms, nor the co-elution of other substances with derivatized ethanolamines. This article also points out the low long-term stability of the resulting TMS derivatives.

*Derivatization of ethanolamines by TFAA*

The reaction of TFAA with ethanolamines resulted in trifluoroacetylation of hydroxy groups. Esters with trifluoroacetylated all possible hydroxy groups were formed readily (Fig. 3). Unlike silylating agents, TFAA did not create a peak of the unreacted reagent in the chromatogram, and MS could be acquired immediately after elution of the solvent. There were also no artifacts recorded on the chromatograms that would interfere with the identification or quantification, happened in previous cases. Chromatograms of the trifluoroacetylated ethanolamines spiked with TBP are depicted in Fig. 4. The retention indices of the derivatized analytes together with the EI-MS data (the most abundant fragment ions) are given in Table IV.

Perfluoroacylation was tested by Chandra *et al.*[16] in the derivatization of half-nitrogen mustards to determine fragmentation pathways. When compared to silylation under similar conditions,[15] perfluoroacylation was preferred as the derivatization technique for half-nitrogen mustards due to more intense molecular ion peaks. In the case of the fully hydrolyzed nitrogen mustards studied by us, this hypothesis was also confirmed. Moreover, trifluoroacetylated products were formed relatively rapidly and with stable kinetics. In the case of EDEA and

MDEA, the products were formed in maximum yield after only 30 minutes and it was not necessary to extend the reaction time.

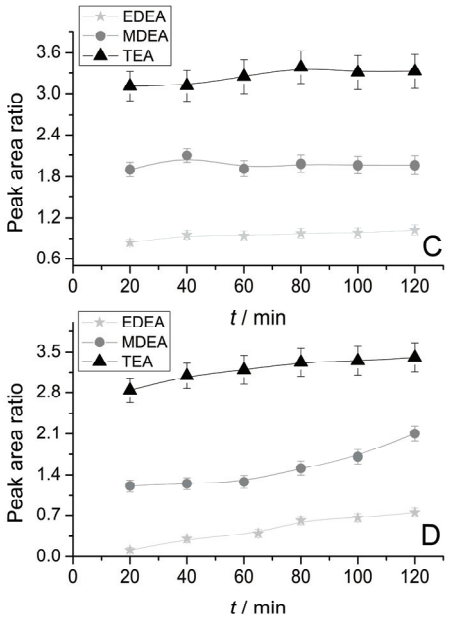


Fig. 3. Trifluoroacetyl derivatives of ethanolamines–bis(2-trifluoroacetoxyethyl)ethanamine (A), bis(2-trifluoroacetoxyethyl)methanamine (B) and tris(trifluoroacetyl)triethanolamine (C).

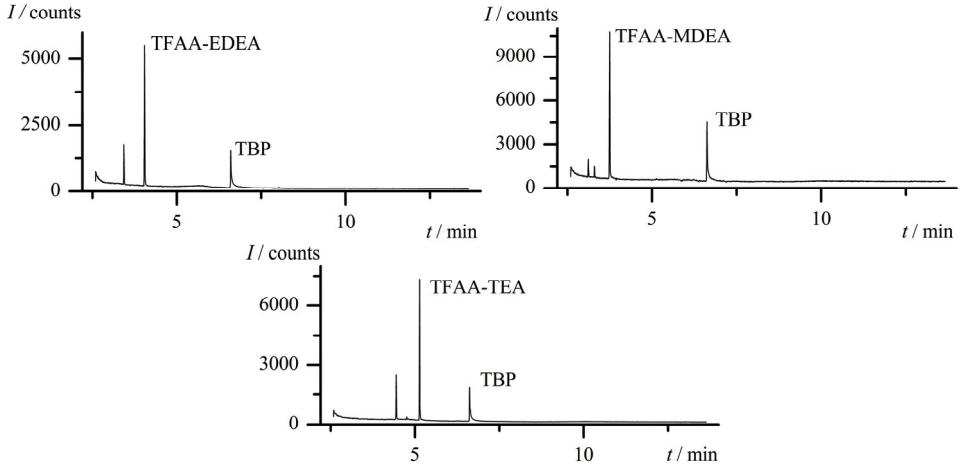


Fig. 4. Chromatograms of trifluoroacetyl derivatives of ethanolamines spiked with the internal standard tributyl phosphate.

In the case of TEA, there was a linear increase in yields throughout the observed reaction (120 min). This fact can be explained by the need to esterify 3 hydroxy groups compared to 2 groups in EDEA and MDEA. TEA derivatives with 1 and 2 substituted hydroxy groups were not recorded in the chromato-

grams, probably due to the high polarity of these substances. There was also no change in the ratios of trifluoroacetylated product and the internal standard when the samples were left and reanalyzed after several hours. Due to the stable kinetics and low deviations, the optimal reaction time of 30 min was chosen for the experiments in the next phase. A graphical representation of the formation of the derivatization products as a function of the reaction time is given in Fig. 4.

TABLE IV. Retention times (*RT*) and retention indexes (*RI*) of trifluoroacetylated analytes – EDEA, MDEA and TEA and internal standard tributyl phosphate, and the most abundant fragment ions (the first most abundant ion was used for quantification)

| Parameter | EDEA | MDEA | TEA | TBP |
|---|---|---|---|---|
| *RT* / min | 4.07 | 3.75 | 5.15 | 6.64 |
| *RI* | 1135 | 1083 | 1326 | 1647 |
| Relative abundance of fragment ions, % | 141 (100.0) | 141 (100.0) | 141 (100.0) | 99 |
| | 198 (89.2) | 184 (81.4) | 311 (33.9) | |
| | 69 (28.5) | 69 (37.0) | 69 (32.3) | |

In comparison to the results given by Pardasani *et al.*,[14] acetonitrile was found suitable and there is no need to use *n*-heptane, which is not commonly used in a mobile laboratory. TFAA is also a cheaper variant for trifluoroacetylation. The results were quantitative after 30 min reaction and it took place at room temperature, unlike some of the methods presented by the cited authors.

*Calibration curves*

Trifluoroacetylation by TFAA was chosen as the optimal method for the derivatization of nitrogen mustard ethanolamines due to stable kinetics, low deviations, fast reaction time and the absence of interfering or other peaks in the chromatogram. The chromatograms did not even contain peaks of the reagent alone.

Calibration curves were generated as dependences of the size ratio of the chromatographic peak areas of the respective derivatized analyte and TBP on the analyte concentration. The analyte concentrations were chosen so that the theoretical maximum yields fell within the calibrated ranges during the subsequent formation of contaminated sand samples. Each calibration curve was measured five times and gross errors were ruled out using the Q-test. The parameters of the linear regression equation for the respective dependencies are listed in Table V.

The results were mainly characterized by high values of the correlation coefficient for EDEA and TEA. The table also shows the values of the average standard deviation of individual points in the calibration dependences.

An experiment was also conducted to exchange the derivatization solvent, acetonitrile for hexane and ethyl acetate. In this case, about 10 % of the derivatization efficiency value compared to acetonitrile (in the case of hexane) and 50 % of the efficiency value in the case of ethyl acetate were achieved.

TABLE V. Analytical parameters of the calibration curves for the determination of nitrogen mustard ethanolamines (EDEA, MDEA and TEA); *x*-axis – analyte concentration, mmol $dm^{-3}$; *y*-axis – absolute value of the ratio of the peaks of the derivatized analyte and TBP

| Compound | $k^a$ / $dm^3$ $mmol^{-1}$ | $q^a$ | $s_{y/x}{}^b$ | $R^{2c}$ | $SD^d$ / % |
|---|---|---|---|---|---|
| EDEA | 4.2833 | –0.0848 | 0.016 | 0.9999 | 2 |
| MDEA | 5.5462 | –0.2691 | 0.265 | 0.9780 | 4 |
| TEA | 8.3431 | –0.1299 | 0.001 | 1.000 | 1 |

[a]Parameters of the regression equation according to $y = kc + q$; [b]standard deviation of $y$ for each value of $x$; [c]value of the reliability of linear regression; [d]relative standard deviation of the calibration points

*Limit of detection and quantification*

Signal to noise (*S*/*N*) ratios were recorded for all peaks of trifluoroacetylated analytes (EDEA, MDEA and TEA) and the corresponding TBP peaks, from which calibration curves were constructed. Then, the analyte concentrations at *S*/*N* 3 (limit of detection) and 10 (limit of quantification) were estimated. The values obtained are given in the Table VI. Control samples for verification were also created for the determined concentration values.

TABLE VI. Limits of detection and quantification of the developed methods for quantitative analysis of nitrogen mustard ethanolamines (EDEA, MDEA and TEA) after trifluoroacetylation, limits of detection of the methods applied to sand samples

| Compound | *LOD* µmol $dm^{-3}$ | *LOQ* µmol $dm^{-3}$ | *LOD* in sand µmol $dm^{-3}$ | *LOD* in sand µg $g^{-1}$ |
|---|---|---|---|---|
| EDEA | 0.08 | 0.50 | 30 | 11.4 |
| MDEA | 9.00 | 11.00 | 30 | 11.4 |
| TEA | 0.07 | 0.30 | 30 | 12.3 |

*Extraction of ethanolamines from sand*

Ethanolamines were extracted from the sand with acetonitrile due to the suitability of this solvent for derivatization as well as the considerable polarity compared to other organic solvents. In addition to the limits of detection and quantification of the calibration methods, Table VI also lists the detection limits of the respective developed methods for the extraction of ethanolamines from sand. The limits of detection are comparable for all ethanolamines. Due to the high extraction efficiency, this technique is more suitable for field conditions than thermal desorption[21] or SPME.[22]

## CONCLUSIONS

It was found that silylation, which is a commonly recommended technique for the field identification of alcohols related to the Chemical Weapons Convention, is not the most suitable derivatization technique for ethanolamines. However, TFAA reacted with ethanolamines at room temperature and within 30 minutes and the results were quantitative and accurate. The identified trifluoro-

acetylated derivatives were not disturbed by the presence of other substances in the chromatogram, the derivatizing reagent itself did not generate a signal in the chromatogram, which in comparison with silylating agents allows the acquisition of MS immediately after elution of the solvent (acetonitrile) and thus possible additional analytes with low *RT* values can be identified in the mixture. In addition, the trifluoroacetylated derivatives were stable in the solvent and did not decompose gradually. The method was applied to sand samples of ethanolamines, where the limits of detection in tens of μg $g^{-1}$ were reached.

The high efficiency, robustness and low price of this liquid–liquid extraction procedure make it more suitable compared to thermal desorption or SPME and it is recommended for application in the field analysis of chemical warfare agents.

## ИЗВОД

## РАЗВОЈ МЕТОДЕ ЗА ДЕРИВАТИЗАЦИЈУ ЕТАНОЛАМИНА И ЊЕНУ ПРИМЕНУ НА УЗОРКЕ ПЕСКА

TOMAS ROZSYPAL

*Nuclear, Biological and Chemical Defense Institute, University of Defense, Vita Nejedleho 691, 68203 Vyskov, Czech Republic*

Азотни иперити су опасни и доступни хемијски бојни отрови из групе пликаваца. У овом раду је упоређено шест метода дериватизације за анализу производа деградације најважнијих азотних иперита пликаваца (етил-диетаноламин, метил-диетаноламин и три-диетаноламин) применом гасне хроматографије спрегнуте са масеном спектрометријом. Тестирано је пет метода силиловања (коришћењем BSTFA и BSA) и једна метода трифлуороацетиловања (кришћењем TFAA). Реакције дериватизације изведене су у ацетонитрилу. Метода која даје оптималан резултат је метода трифлуороацетиловања. Аналити су са одговарајућим реагенсом реаговали брзо, квантитативно, са стабилном кинетиком и на собној температури. Конструисане су калибрационе криве за квантитативну анализу етаноламина после дериватизације помоћу TFAA. Детекциони лимити за тестиране аналите су варирали између $9\times10^{-3}$ и $7\times10^{-5}$ mmol·$dm^{-3}$. Развијена метода је примењена за анализу етаноламина после екстракције из песка помоћу ацетонитрила. Лимити детекције су били у опсегу 11,4–12,3 μg/g песка. Охрабрујућа је могућност примене развијене методе у мобилним војним теренским лабораторијама, за брзу идентификацију бојних отрова и одговарајућих производа деградације.

(Примљено 12. марта, ревидирано 12. маја, прихваћено 13. јуна 2021)

## REFERENCES

1. *Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction*, OPCW, Paris 2020 (https://www.opcw.org/sites/default/files/documents/CWC/CWC_en.pdf)
2. T. Rozsypal, *JPC-J. Planar Chromatogr.* **33** (2020) 669 (https://doi.org/10.1007/s00764-020-00072-7)
3. Y.-H. Jan, D. E. Heck, D. L. Laskin, J. D. Laskin, *Toxicol. Lett.* **326** (2020) 78 (https://doi.org/10.1016/j.toxlet.2020.03.008)

4. N. Tewari-Singh, R. Agarwal, *Ann. NY Acad. Sci*. **1374** (2016) 184 (https://doi.org/10.1111/nyas.13099)
5. H.-C. Chua, H.-S. Lee, M.-T. Sng, *J. Chromatogr., A* **1102** (2006) 214 (https://doi.org/10.1016/j.chroma.2005.10.066)
6. A. Mazumder, A. Kumar, A. K. Purohit, D. K. Dubey, *J. Chromatogr., A* **1217** (2010) 2887 (https://doi.org/10.1016/j.chroma.2010.02.071)
7. S. A. Willison, *J. Chromatogr., A* **1270** (2012) 72 (https://doi.org/10.1016/j.chroma.2012.11.013)
8. M. Otsuka, H. Miyaguchi, M. Uchiyama, *J. Chromatogr., A* **1625** (2020) 461306 (https://doi.org/10.1016/j.chroma.2020.461306)
9. M. Otsuka, H. Miyaguchi, M. Uchiyama, *J. Chromatogr., A* **1602** (2019) 199 (https://doi.org/10.1016/j.chroma.2019.05.015)
10. Z. Witkiewicz, M. Mazurek, J. Szulc, *J. Chromatogr., A* **503** (1990) 293 (https://doi.org/10.1016/S0021-9673(01)81514-4)
11. R. M. Black, B. Muir, *J. Chromatogr., A* **1000** (2003) 253 (https://doi.org/10.1016/S0021-9673(03)00183-3)
12. L. Kenar, O. Alp, *J. Chromatogr. Sci.* **49** (2011) 631 (https://doi.org/10.1093/chromsci/49.5.361)
13. I. Ohsawa, Y. Seto, *J. Chromatogr., A* **1122** (2006) 242 (https://doi.org/10.1016/j.chroma.2006.04.076)
14. D. Pardasani, M. Palit, A. K. Gupta, P. K. Kanaujia, D. K. Dubey, *J. Chromatogr., A* **1059** (2004) 157 (https://doi.org/10.1016/j.chroma.2004.10.039)
15. B. Chandra, K. Sinha Roy, M. Shaik, C. Waghmare, M. Palit, *Rapid Commun. Mass Spectrom.* **34** (2020) 1 (https://doi.org/10.1002/rcm.8586)
16. B. Chandra, K. Sinha Roy, M. Shaik, C. Waghmare, M. Palit, *Rapid Commun. Mass Spectrom.* **34** (2020) 1 (https://doi.org/10.1002/rcm.8777)
17. P. Garg, A. Purohit, V. K. Tak, D. K. Dubey, *J. Chromatogr., A* **1216** (2009) 7906 (https://doi.org/10.1016/j.chroma.2009.09.032)
18. C. A. Valdez, R. N. Leif, S. Hok, A. K. Vu, E. P. Salazar, A. Alcaraz, *Sci. Total Environ.* **683** (2019) 175 (https://doi.org/10.1016/j.scitotenv.2019.05.205)
19. R. B. Sousa, P. F. P. M. Alves, S. F. Cavalcante, L. B. Bernardo, C. S. Barros, C. N. Ferreira, A. L. S. Lima, *Rev. Virtual Quím*. **6** (2014) 601 (https://doi.org/10.5935/1984-6835.20140039)
20. P. Vanninen, *Recommended operating procedures for analysis in the verification of chemical disarmament*, University of Helsinki, Helsinki, 2017 (ISBN 978-951-51--3917-7)
21. D. T. D. Qadah, J. H. Aldstadt, *Anal. Lett.* **51** (2018) 1321 (https://doi.org/10.1080/00032719.2017.1379531)
22. S. Popiel, M. Sankowska, *J. Chromatogr., A* **1218** (2011) 8457 (https://doi.org/10.1016/j.chroma.2011.09.066).