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Near real time detection of hazardous airborne substances

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ABSTRACT

A fast near real-time monitoring system for hazardous airborne substances, such as chemical warfare agents (CWA) is presented and limits of detection (LOD) for five CW simulants are determined. A tandem thermal desorber (TTD) continuously collects and pre-concentrates air. The pre-concentrated samples are then separated in a fast gas chromatographic (GC) run of 6.9 min. and detected by a time-of-flight mass spectrometer (TOFMS). The GC–TOFMS signals are evaluated using chemometric methods for deconvolution and target identification.

The high toxicity of nerve agents requires extremely low detection limits; for some as low as 100 ng/m³ (10 ppt). The combination of TTD, TOFMS and chemometric data evaluation methods enables the system to fulfill this requirement. Calibration measurements for five different CWA simulants show lower limits of detection in the range of 10 ng/m³–60 ng/m³ (1–11 ppt). In addition, the ability to detect trace concentrations of real CWA is demonstrated with a measurement of 30 pg Sarin on column. Several other real CWA measurements are shown, like sulfur mustard in diesel, lewisite under humid conditions and VX.

As part of this work the influence of stationary film thickness on peak tailing of organophosphates is investigated for peak shape optimization.

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1. Introduction

Chemical warfare agents (CWA) and explosives pose a terrorist threat and can cause fear and panic among the civilian population. This was demonstrated by the two Sarin attacks With the two Sarin attacks of Aum Shinrikyo in Matsumoto in 1994 and in the Tokyo subway in 1995 [1], it was demonstrated that synthesis of Sarin is relatively easy and that even Sarin at a low purity level can cause a lot of casualties. Most likely the impacts of the Sarin release at Tokyo underground would have been even worse if an effective way of agent release had been applied. Nowadays breakdown of CWA owning regimes in a variety of countries and the obscure whereabouts of the agents is reason enough for considering adequate countermeasures with regards to agent release in context with asymmetric threat scenarios. To counter this heightened terrorist threat it is increasingly necessary to continuously monitor buildings and infrastructures, such as airports and other public locations which are under the greatest risk from this threat.

CWA are lethal even at low concentrations due to their high toxicity. For example the dose required to kill half the members of

a tested population after a specified test duration (LCt_{50}) for VX is only 40 mg min/m³ (rats, whole-body VX vapor exposures) [2] and the vapor pressure is only 0.11 Pa at 25 °C [3]. Table 1 shows the Protective Action Criteria (PAC) values from the U.S. Department of Energy [4]. These values are one of the decision criteria for action forces on how to react in an incident. Therefore the PAC-values are a good reference for the demands on a measurement system. A highly sensitive and rapid measurement technique allowing a short response time is necessary to measure the concentration of CWA in air before hazardous quantities are released. The system presented here, consisting of a tandem thermal desorber (TTD), gas chromatograph (GC) and time-of-flight mass spectrometer (TOFMS) with electron impact ionization, is designed to meet these demands.

The combination of the TTD and the TOFMS results in a very sensitive detection system. In fast GC the substance peaks are often poorly separated. A commercial program for deconvolution was used to separate mass spectra of chromatographically unresolved peaks. Finally, the deconvolved spectra are identified by comparing their patterns to a reference library, like the NIST mass spectral library, using methods of principal component analysis (PCA).

A variety of detection systems for the measurement of airborne CWAs [7,8,9] already exist. Portable devices, using different detector technologies, e.g. ion mobility spectrometry (IMS)

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Table 1
PAC-values^a and vapor pressure p_v of CWAs.

Substance	CAS	TEEL-0 (mg/m ³)	PAC-1 (mg/m ³)	PAC-2 (mg/m ³)	PAC-3 (mg/m ³)	p_v (Pa)
Sarin	107-44-8	7.5e-4	0.00275	0.0344	0.126	197 ^{b,d}
Soman	96-64-0	2.0e-4	0.00134	0.0164	0.127	53 ^{c,d}
Tabun	77-81-6	7.5e-4	0.00278	0.0351	0.258	9.3 ^{c,d}
VX	50782-69-9	6.0e-5	1.75e-4	0.00295	0.00995	0.11 ^{c,e}
S-Lost (HD)	505-60-2	0.02	0.065	0.13	2.08	8.7 ^{b,d}

^a Protective Action Criteria (PAC) values from U.S. Department of Energy (DOE) [4], PAC-1 to PAC-3 correspond, in the case of the 5 CWAs, to 60-minute Acute Exposure Guideline Levels (AEL) values. TEEL-0 is the threshold concentration below which the health of most people would not be affected in case of exposure. PAC-1 is the concentration above which it is predicted that the general population could experience notable discomfort, irritation, or certain asymptomatic, non-sensory, but no irreversible effects. PAC-2 is the concentration above which it is predicted that the general population could experience irreversible or other serious, long-lasting, adverse health effects. PAC-3 is the concentration above which it is predicted that the general population could experience life-threatening adverse health effects or death. For a more detailed definition see [5].

^b at 20 °C.

^c at 25 °C.

^d [6].

^e [3].

[10,11], flame photometric detectors (FPD) [12], optical spectroscopy [13] and micro sensor arrays [14] are particularly widespread. Often these detectors are combined with a chromatographic separation step to reduce false positives, like the MINICAMS Series 3001 system from OI Analytical or the Viking 573 system from Bruker Daltonics [9]. In addition there are GC-MS systems [15–19]. Systems based on mass spectrometric detectors have some advantage over the other detector systems. The main advantage is the ability to identify substances by their mass spectra and good response factors to almost every airborne compound when using electron ionization (EI).

2. Experimental

2.1. Chemicals

Dimethyl methylphosphonate (DMMP, 756-79-6, 97%, Sigma-Aldrich), Diethyl methylphosphonate (DEMP, 683-08-9, 97%, Sigma-Aldrich) and Triethyl phosphate (TEP, 78-40-0, 99.8+%, Sigma-Aldrich) were used as simulants for Sarin, Soman and Tabun. Methyl salicylate (MS, 119-36-8, 99%, Sigma-Aldrich) is a simulant for mustard gas and the pesticide [(Dimethoxyphosphinothioyl)thio]butanedioic acid diethyl ester, also known as Malathion (Mal, 121-75-5, analytical standard, Sigma-Aldrich), is used as a simulant for VX, because of its low volatility and related structure. The simulants were diluted in Methanol (67-56-1, 99.8+%, Sigma-Aldrich). Methanol was chosen because of its low breakthrough volume on Tenax TA of 0.36 l/g at 20 °C [20]. Hence it is possible to selectively purge the Methanol off the trap before desorption.

2.2. Measurement system

The measurement system consists of three parts, the tandem thermal desorption unit (TTD), the separation unit (GC) and the detection unit (TOFMS).

A tandem thermal desorber (TTD) TT24-7 (Markes International Ltd.) is used for the pre-concentration of the volatile substances. The main parts of the TT24-7 are two Peltier-cooled traps, filled with Tenax TA. The two traps operate in an alternating way. One trap was packed with Tenax and quartz wool on both sides. The other trap

was also packed with Tenax TA and quartz wool at one side, but at the side where the sample is introduced and desorbed the quartz wool had been replaced with two SilcoNert2000 coated meshes. While air is sampled onto one trap at 20 °C (configurable) with a high flow rate of 500 ml/min for 5 min (sample volume 2.5 L), the other trap is desorbed at 300 °C with a low flow of helium, identical to the column flow of the GC in splitless operation, typically 3 ml/min for 3 min. Most substances are desorbed within a short time after the trap was fired and according to the manufacturer, the desorption volume amounts to approximately 200 µl, resulting in a relative concentration enhancement factor of approximately 10,000. Sample air is pumped into the system using a pump and mass flow controller (MFC) downstream of the trap. Before the desorption starts, the trap gets purged with 100 ml/min helium for 1 min to remove air and humidity. It is also possible to desorb offline sample tubes onto the cold trap to verify the calibration.

The TTD is connected to a GC 7890 A (Agilent Technologies) via a heated transfer line (200 °C) enclosing a 1.5 m × 0.25 mm phenyl-sil deactivated fused silica column (CS Chromatographie Service GmbH). The samples are separated on a 15 m × 0.25 mm FS-Supreme-5 ms column (5% phenylpolysilphenylsiloxane, CS Chromatographie Service GmbH). Different film thicknesses, from 0.10 µm to 1 µm have been tested and a final calibration is done using a column with 1 µm film thickness. The helium carrier gas flow has been set to constant at 3 ml/min. The temperature program started with 40 °C, held for 0.5 min and ramped with 50 °C/min to 280 °C and held there for 1.6 min.

The GC is connected to a BenchTOF-dx mass spectrometer (ALMSCO International) via a second transfer line (220 °C). The GC column feeds directly into the ion source (250 °C) of the TOFMS, where the samples are ionized using electron ionization at 70 eV. The ion source of this time-of-flight mass spectrometer is also used as an extraction chamber (in contrast to orthogonal acceleration instruments) maximizing the ion transmission rate and consequently generating full spectral data at conventional SIM sensitivity levels. High acceleration voltages produce classical, library-searchable spectra without skew or bias, an important pre-condition for deconvolution. The internal scanning rate of the TOF is 10,000 Hz. Sets of 2,000 scans are added to a so-called scanset (resulting in a scanset rate of 5 Hz) which is stored to disc. The mass range was set to 40–500 amu.

2.3. Generation of Samples

A direct liquid injection calibration gas generator (CGG) (HovaCAL 3435SP-VOC, IAS GmbH [21]) is used for calibration, which produces low concentrations of volatile components in a carrier gas, e.g. air. Two syringes are working in a push-pull operation. One syringe dispenses solution to the vaporizer, while the second syringe gets drawn and filled with solution. Valves enable a continuous process. In an evaporator the solution evaporates and is mixed with purified compressed air (air-treatment system BA-C, M&C TechGroup Germany GmbH). In two optional dilution stages consisting of heated capillaries with constant pressure drop the gas can be diluted down to 1/50,000 of the initial concentration after the vaporizer. The solution used is a dilution of a gravimetrically prepared stock solution containing the five simulants dissolved in methanol (Table 2).

With the CGG a sample gas stream containing the five simulants is generated and diluted in the first stage down to concentrations in the range of 5000 ng/m³ and in the second stage down to concentrations in the range of 0.5–250 ng/m³. This gas stream is led onto the cold traps of the TTD.

The calibration with the CGG is verified by measurements with desorption tubes, which are loaded with a calibrated solution of the five simulants. The sample is injected with a microliter-syringe via

Table 2
Diluted solution of the five simulants in methanol.

Simulant	Concentration C [µg/ml]
DMMP	3.1 ± 0.1
DEMP	2.2 ± 0.1
TEP	2.1 ± 0.1
MS	2.4 ± 0.1
Mal	2.3 ± 0.1

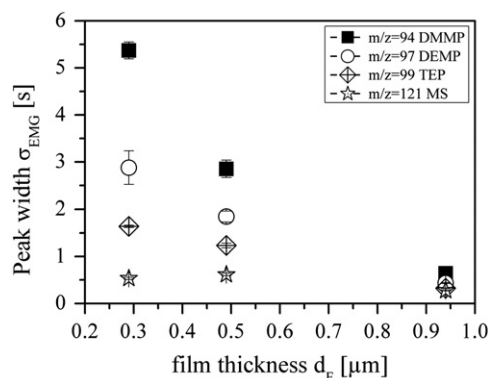


Fig. 1. Peak width σ_{EMG} as a function of film thickness d_F , strong correlation for the organophosphonates DMMP, DEMP and TEP, weak correlation for methyl salicylate (MS).

a helium flushed cold injector (the Calibration Solution Loading Rig from Markes International Ltd.) onto glass desorption (Markes International Ltd.) tubes filled with 50 mg Tenax TA.

2.4. Data evaluation

The correlation between peak shape and film thickness of the stationary phase is calculated using a quantifier ion. Different quantifier ions are specified for each simulant and an exponentially modified Gaussian function (EMG) [22] is fitted to the data. The quadratic sum of σ (the width of the Gaussian term) and τ (the exponential modification factor) expressed as σ^2_{EMG} is used as a measure for the peak width (Fig. 1).

The calibration measurements are analyzed using a newly developed chemometric deconvolution software, which is now commercially available as TargetView (Almsco International). In a first step a low-pass-filter algorithm is applied to the chromatograms in order to subtract a slowly moving dynamic background. In a second step the background compensated chromatograms are deconvolved and the deconvolved spectra matched against database spectra using a PCA algorithm. For hits found by the PCA algorithm matching coefficients are calculated using the INCOS algorithm [23]. The hits are then reported with their retention time, matching coefficient and area counts for quantitative analysis.

The LOD is determined according to [24,25] by the 95%-prediction band of the calibration line calculated with the weighted least-square method and two one-side hypothesis tests for false positives ($\alpha=0.05$) and false negatives ($\beta=0.05$). For the weighting a combination of weighting by y -error err_i and weighting by matching coefficient mc_i is used:

$$W_i = (wy_i + wmc_i) / \sum (wy_i + wmc_i),$$

with

$$wy_i = (1/err_i^2) / \sum (1/err_i^2)$$

and

$$wmc_i = mc_i / \sum mc_i.$$

Therefore hits with a lower matching coefficient are penalized. This is the case mostly for very low concentrations around and below the LOD.

3. Results and discussion

3.1. Peak tailing of organophosphates

Organophosphates, much like amines, have a converse behavior on the stationary phase compared to many other substances. A thinner film leads to broader peaks with strong tailing [9]. This broadening effect leads to a deterioration of the detection limit relative to thicker film columns. This is caused by the relative strong hydrogen bonds between silanol-groups on the SiO_2 surface of the column with the P=O and P-O-R groups of the organophosphates. Studies about the interaction between DMMP and Silica showed that this molecule adsorbs through hydrogen bonds between the two methoxy groups and SiOH [26,27] and by the P=O group with two silanol groups [28]. The bonding is not as strong as for amines but stronger than for methoxysilanes [27]. The bonding of Sarin on silanol groups of silica was also simulated in this study [28]. Apart from the most stable H-bond by the P=O group adsorption through the propoxy group and the Fluor atom is also possible. The calculated adsorption energies for DMMP (−20 kcal/mol) and Sarin (−19.9 kcal/mol) are almost the same [28]. It can be concluded that optimization of the film thickness with respect to sharp peaks of DMMP should lead to optimized results for Sarin, and other organophosphate CWA, as well.

It can be assumed that DEMP and TEP also form H-bonds with the two/three ethoxy-groups and/or the P=O group. This interaction takes effect across the entire stationary phase. Molecules which are solved in the stationary phase are closer to the inner surface of the fused silica capillary and therefore they can interact with remained silanol groups. The thinner the stationary phase film is, the smaller is the distance for the molecules to the silanol groups and the interaction is stronger.

It is a common treatment to deactivate the silanol groups with alkyl siloxanes. The used columns were treated this way by the manufacture with a phenyl siloxane coating. But beside this measure not all silanol groups could be capped because of sterically hinderance.

Three columns with a nominal film thickness of 0.25 µm, 0.50 µm and 1.00 µm were used to find the optimal film thickness for subsequent measurements. A sample mixture of DMMP ($c_{DMMP}=1.00 \mu\text{g}/\text{m}^3$), DEMP ($c_{DEMP}=0.92 \mu\text{g}/\text{m}^3$), TEP ($c_{TEP}=1.25 \mu\text{g}/\text{m}^3$) and methyl salicylate ($c_{MS}=1.55 \mu\text{g}/\text{m}^3$) was produced with the CGG and 2.5 l were sampled onto the TT24-7, which corresponds to amounts between 2.3 ng and 3.88 ng on the cold trap.

Fig. 1 shows σ_{EMG} of the four simulants versus the film thickness. The three organophosphates show a strong correlation between the peak width and the film thickness. MS, as a substance without phosphor, shows a very weak correlation. The influence of the film thickness of the stationary phase follows the order DMMP > DEMP > TEP, which leads to the assumption that the bonding forces of these three organophosphates on silanol groups follows the same order. Apart from the narrower signals with thicker films an increase in signal height and a shifting of the retention times to higher values is observed.

A column with a film thickness of nominal 1 µm (0.94 µm) was used in the subsequent calibration measurements to estimate the limit of detection.

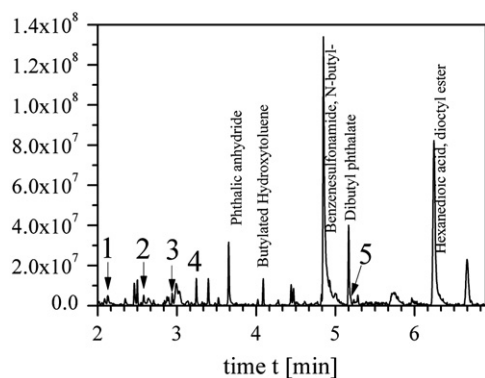


Fig. 2. Chromatogram from a calibration measurement with 1—DMMP 150 ng/m³–2.125 min, 2—DEMP 107 ng/m³–2.580 min, 3—TEP 102 ng/m³–2.935 min, 4—Methyl salicylate 116 ng/m³–3.247 min, 5—Malathion 111 ng/m³–5.187 min.

Table 3

Results of the linear regression and LOD determination according to the method shown in Fig. 3.

Simulant	R ²	LOD [ng/m ³]	LOD _{ppt} ^a [ppt]	m _{LOD} ^b [pg]
DMMP	0.91	57	11.1	142.5
DEMP	0.96	42	6.6	105.0
TEP	0.98	16	2.1	40.0
MS	0.99	7.3	1.2	18.3
Mal	0.97	58	4.2	145

^a The limit of detection expressed in parts per trillion, $LOD_{ppt} = LOD \cdot V_m / M$, with V_m being the molar volume of air and M the molar mass of the simulant;

^b The sampled mass of the simulant, $m_D = t_s \cdot J_s \cdot LOD$, with t_s sample time and J_s sample flow.

3.2. Calibration and LOD

Concentrations from 0.5 ng/m³ to 5000 ng/m³ of Malathion in air were generated by the CGG and measured with the TTD-GC-TOF for at least 20 repetitions, i.e. 10 measurements for each of the two cold traps were done at each concentration step. In this work, only the results for the traps with SilcoNert2000 coated meshes are presented as they proved to be superior to the traps with quartz wool on both sides. Fig. 2 shows a chromatogram with the five simulants.

The chemometric program TargetView was used to qualitatively and quantitatively evaluate the five simulants in the approximately 600 measurements. Matching coefficients and area counts were averaged for the repeat measurements. The results, together with the coefficient of determination (R²), are shown in Table 3.

Fig. 3 shows typical deconvolved elution profiles of the simulants, together with the four adjacent co-eluting substances.

The limits of detection determined for the three organophosphates DMMP, DEMP and TEP follow the order of the peak width. The limits are considerably smaller than the TEEL-0 values of Sarin, Soman and Tabun (Table 1). The mass spectra start to overload at concentrations of about 1000 ng/m³.

Methyl salicylate is a substance with a very low limit of detection. The mass spectrum consists mainly of a few fragments with high intensities. Therefore the signal of the base peak in the mass spectrum is already overloaded for a relatively low concentration of 300 ng/m³. In the chromatogram there is no co-eluting substance present in the purified air.

In contrast, Malathion is difficult to detect. It has a more complex mass spectrum. The base peak in the spectrum is overloaded from a concentration of 4000 ng/m³ on. This substance also co-elutes with high amounts of a phthalate acid ester, dibutyl phthalate, probably

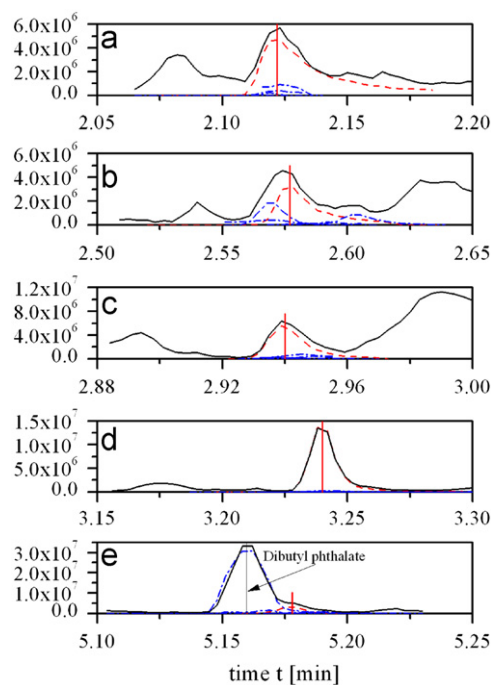


Fig. 3. Deconvolved elution profiles (dashed lines) of the five simulants (a) DMMP 150 ng/m³, (b) DEMP 107 ng/m³, (c) TEP 102 ng/m³, (d) methyl salicylate 116 ng/m³ and (e) Malathion 111 ng/m³, with the four next neighboring elution profiles of co-eluting substances (dash-dotted line) and TIC (line). The retention time of the simulants is marked with the vertical line. In the case of (b) DEMP and (e) Malathion a strong superposition with other co-eluting substances (Dibutyl phthalate) is evident. Whereas (d) Methyl salicylate is totally separated; deconvolved elution profile is identical to the TIC.

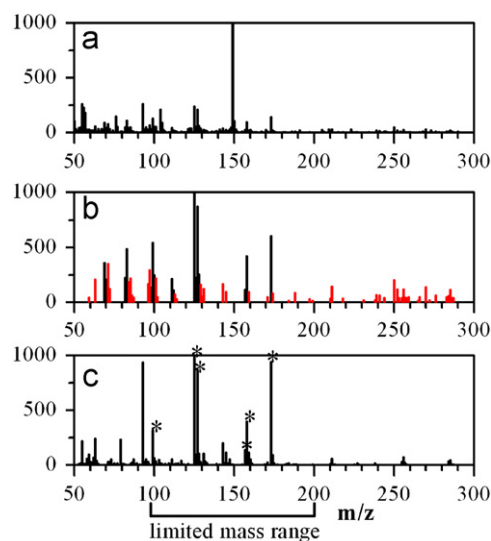


Fig. 4. (a) Full mass spectrum at 5.184 min, superposition of Malathion with Dibutyl phthalate; (b) deconvolved mass spectra of Malathion at 5.185 min, red lines uncertain masses; (c) NIST database mass spectra of Malathion—one of the main masses of Malathion $m/z=93$ is missing in the deconvolved spectra. For calibration of Malathion the mass range was limited to $m/z=98$ to $m/z=200$ and library spectrum was reduced to the masses marked with an asterisk; Malathion concentration 111 ng/m³. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

caused by outgassing from sealings (Figs. 3(e) and 4). One of the main ions of Malathion, $m/z=93$, is also present in the mass spectra of the plasticizer Dibutyl phthalate with a lesser proportion. But the concentration of the plasticizer is several orders of magnitude larger than the concentration of Malathion and therefore a chemometric

separation is difficult, see Fig. 3e). Consequently it was necessary to adjust the database spectra of Malathion and only ion fragments with masses higher 97 amu are used. The estimated LOD is in the range of 60 ng/m³, the TEEL-0 (Table 1) value of VX. This means, the measurement system should be able to detect airborne VX at non-toxic concentration levels Fig. 4.

In addition to the calibration measurements three different amounts of the simulants (0.1–0.3 µl) were injected with a 0.5 µl-syringe onto glass tubes. These tubes were desorbed in the tube mode of the TT24-7 and measured with the GC-TOFMS system. Three repetition measurements were done for each concentration. Except for the lowest amount of TEP (high variation of the three repetitions, see Fig. 5) all the measured values lie within or near the prediction bands.

3.3. Long-term validation measurement

In a long-term study (over 110 cycles, i.e. 55 measurements for every cold trap, the first measurement is rejected) the five simulants were measured at low concentrations ($c_{DMMP}=86$ ng/m³, $c_{DEMP}=61$ ng/m³, $c_{TEP}=58$ ng/m³, $c_{MS}=66$ ng/m³, $c_{Mal}=64$ ng/m³) and evaluated with TargetView.

For Methyl salicylate and TEP these concentrations are much higher than the estimated LOD and the substances were identified in 100% and 98.1% of the cases with a medium matching coefficient of 0.89 ± 0.02 and of 0.77 ± 0.03 . DMMP and DEMP are found in 98.1% and 96.3% of the measurements with matching coefficients of 0.81 ± 0.05 and 0.82 ± 0.06 . The concentration for DMMP and DEMP

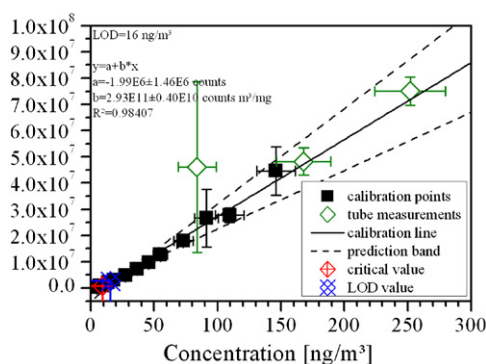


Fig. 5. Calibration data for TEP with calibration line, prediction band, critical limit, LOD and tube measurements for verification of the CCG.

used in the long term study was slightly higher than the LOD values. Based on the definition of the LOD with $\beta=0.05$ (accepted probability for false negatives), in at least 95% of the measured samples the simulants should be found. This is the case for the first four simulants and therefore the real LOD for these simulants should lie between the estimated LOD and the concentration used in the long-time measurements.

Malathion, which was measured at a concentration near the LOD value, has only a hit ratio of 68.5% and a medium matching coefficient of 0.81 ± 0.06 . This poor result, compared to the determined LOD, could be the consequence of a re-conditioning of the cold traps of the TT24-7 between the LOD measurements and the long-term measurements.

3.4. CWA measurement

Measurements with classical chemical warfare agents using the same analytical system were conducted at the Bundeswehr Research Institute for Protective Technologies and NBC Protection, a reference laboratory of the Organization for the Prohibition of Chemical Weapons (OPCW).

The samples are generated in a permeation oven with concentrations in the range of 100 ng/l (100 µg/m³). For the measurement shown in Fig. 6 an air stream with Sarin from a permeation oven was pumped through a Tenax TA filled desorption tube to sample 6 ml of air on the adsorbent. This tube is then desorbed in the TT24-7 with a split ratio of 1:20, resulting in 30 pg on column. The Sarin measurement was evaluated by TargetView and showed a matching coefficient of 0.904. In contrast to the calibration measurement with the simulants, the starting temperature of the GC-oven was set to 60 °C.

In another experiment different CWAs were measured under the influence of different matrices to investigate matrix effects on the measurement system and the deconvolution software. For these measurements a standard column was used, 30 m × 0.25 mm FS-Supreme-5 ms column (5% phenylpolysilphenylsiloxane, CS Chromatographie Service GmbH) with 0.25 µm film thickness, a column flow of 1.5 ml/min and a slower temperature program with two ramps, a first from 60 °C (hold for 1 min) to 160 °C with 10 °C/min and a second from 160 °C to 250 °C with 20 °C/min. The measured substances are Sarin in gasoline, HD in diesel and Lewisite in humid air. Furthermore VX in air was analyzed. Because of the relatively high concentrations the TOFMS was operated in a less sensitive mode. The CWA concentrations (except VX) were generated by a permeation oven system with typical concentrations in the range of 100 ng/l.

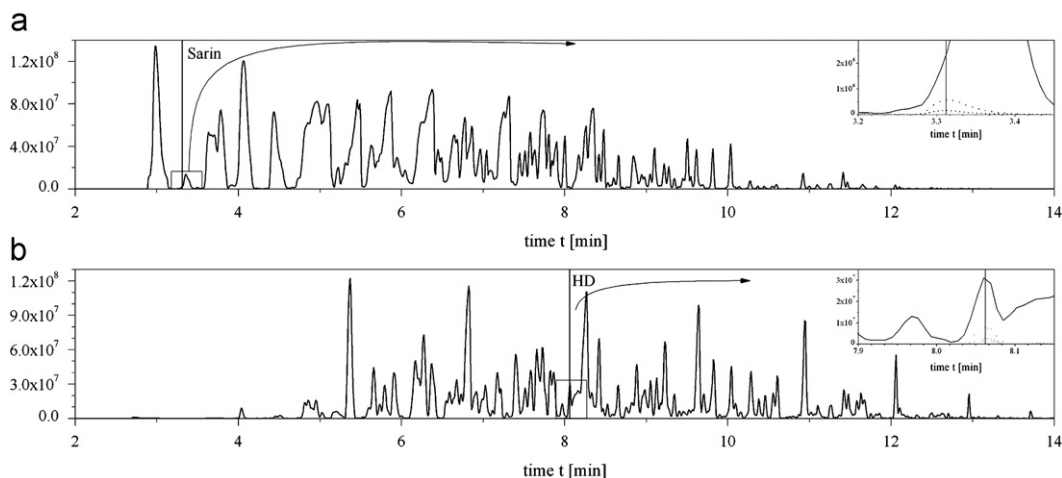


Fig. 6. Background compensated Chromatograms of (a) Sarin in gasoline and (b) mustard gas (HD) in diesel. The CWAs are marked with the red line and on the right side a detail view with the main m/z -traces is shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

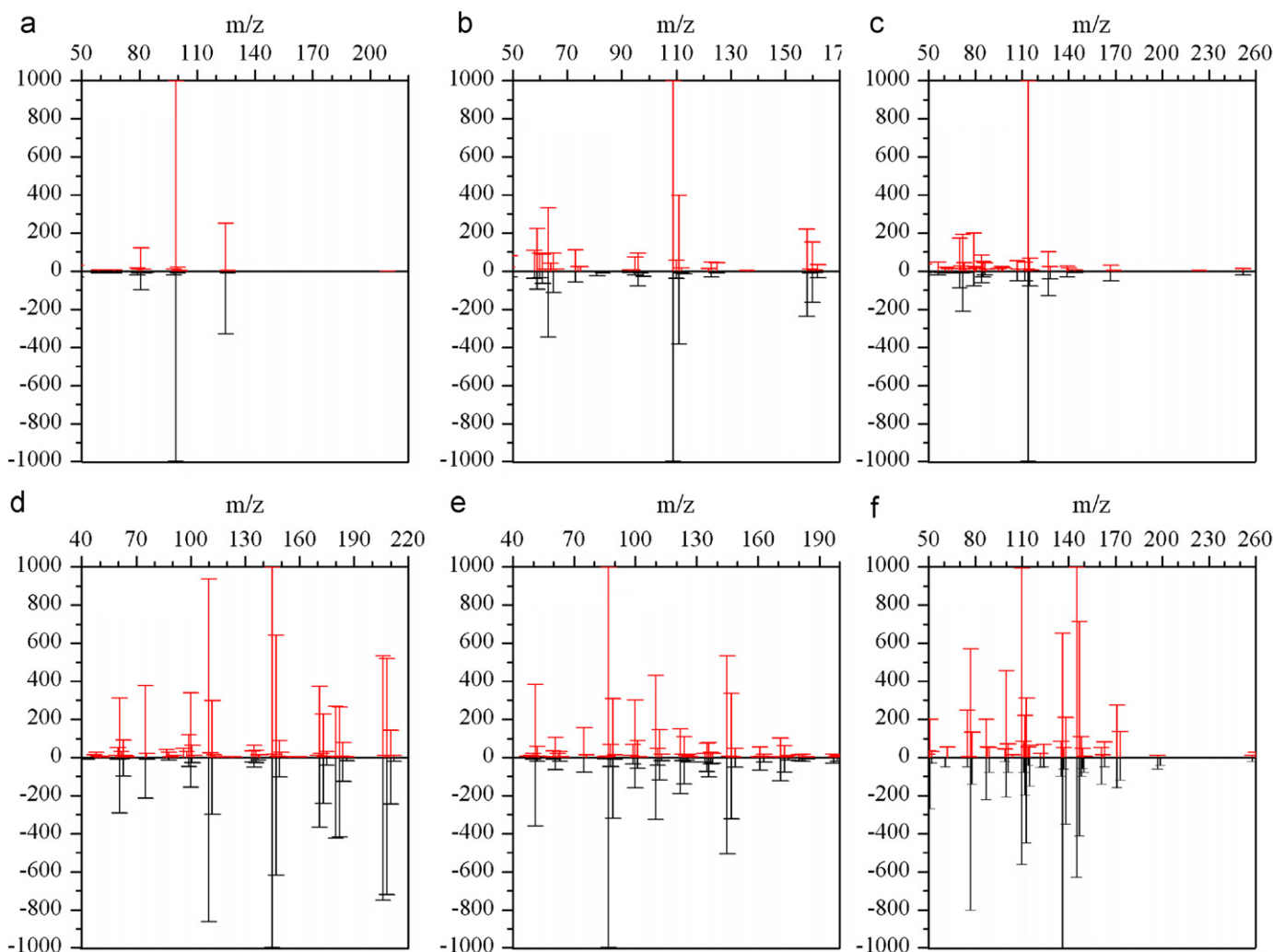


Fig. 7. Mass spectra of (a) 30 pg Sarin, (b) HD in diesel, (c) VX and the three (d)–(f) Lewisite derivatives, upwards (red) is the measured spectra, downwards (black) the NIST reference spectra. The matching coefficient for 30 pg Sarin is, for HD in diesel it is 0.903 and for VX it is 0.872. For Lewisite 1 the matching coefficient is 0.904, for Lewisite 2 0.942 and for Lewisite 3 0.871. The peak area of Lewisite 3 is less than 0.2% of the peak area of Lewisite 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6(a) shows the complex background compensated chromatogram of 15 ng of Sarin in gasoline. It could be identified with a matching coefficient of 0.835. In Fig. 6(b) 30 ng of HD in diesel is shown, with a matching coefficient of 0.903.

A high concentration of Lewisite 1, approximately 2 $\mu\text{g/l}$, was measured under the influence of moisture (relative humidity of 70%). 70l of the gas was sampled on a desorption tube with Tenax TA. Because of the subsequent and fast hydrolysis [29] the sampled amount of Lewisite is not known. In addition to Lewisite 1 two derivatives of Lewisite, Lewisite 2 and 3 were also detected. While the peak area of Lewisite 1 and 2 were nearly the same, Lewisite 3 was found with a relative peak area of only 0.2% of the Lewisite 1 peak area. This is caused by impurity and the reaction of Lewisite 1 with moisture.

Fig. 7 shows the deconvolved mass spectra of 30 pg Sarin, HD in diesel, VX and the three Lewisite derivatives in comparison to the database spectra. The matching coefficient for Lewisite 1: 0.904, for Lewisite 2: 0.942 and for Lewisite 3: 0.871.

The TTD-GC-TOFMS measurements show the ability of this set-up to detect and identify low quantities of classical CWA in complex matrices. Other CWAs successfully detected by this system, but not shown, are Tabun, Soman, Cyclosarin and nitrogen mustards.

4. Conclusion

It was shown, that the TTD-GC-TOFMS system presented here can successfully detect and identify airborne concentrations of CW simulants below 100 ng/m^3 . With the same measurement system it was possible to detect several real CWAs at low airborne concentrations and in complex matrices. The full mass spectra were used for identification and quantification without retention time information. The LOD of CW simulants was estimated to 20–150 pg, which is two to three orders of magnitude lower than LOD for CWAs measured with a GC combined with fullscan quadrupole MS (0.8–2.9 ng) [18].

A fast chromatographic method was developed allowing sufficient separation for the subsequent deconvolution. All substances of interest elute within 5.2 min. The measurement cycle time is determined by the purge time in the TTD before the cold trap is desorbed (1 min), the GC runtime (6.9 min) and the cooling time of the GC (4.2 min). The total runtime for one measurement cycle with the present set-up is therefore 12.1 min.

Further developments will focus on shorter GC columns and higher heating rates. However, the most time consuming step in this setup is the cooling time of the GC. In future the conventional GC-oven will be replaced by a low thermal mass GC. This allows

higher heating rates and, more importantly, faster cooling rates [12,30,31]. This should allow measurement cycles below 5 min for continuous CWA monitoring.

On the other hand, a longer measurement cycle time could be used for a longer sample time and therefore a lower limit of detection should be achievable. The limits of detection for the simulants (Table 3) are determined for a sample volume of 2500 ml. A longer sample time would result in a higher sample volume, if the sample flow is kept constant.

Although the system is mobile it is not portable and therefore more suited for stationary or transportable applications such as monitoring certain key security areas. The use of a universal GC-TOFMS detector enables the measurement of a wide range of hazardous substances. A large number of CWA and their derivatives could be detected as well as certain airborne explosives (DNT, TNT). The application area can be extended to toxic industrial chemicals (TIC) and drugs. A field of application could be monitoring the air of security related rooms or spot-check inspections of cargo containers.

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