Analytical Methods

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Derivatization and rapid GC-MS screening of chlorides relevant to the Chemical Weapons Convention in organic liquid samples

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A simple derivatization technique was developed for the analysis of seven Schedule 3 chemicals and one Schedule 2 chemical listed in the Chemical Weapons Convention (CWC). Phosgene, phosphorus oxychloride, phosphorus trichloride, phosphorus pentachloride, thionyl chloride, sulfur monochloride and sulfur dichloride (Schedule 3) as well as arsenic trichloride (Schedule 2) were derivatized using 1-propanol in 40% pyridine solution for analysis with gas chromatography-mass spectrometry (GC-MS). Derivatization temperature and concentration of the derivatization solution were optimized for maximum derivatization recovery. The stabilities of the target analytes and their derivatives in different solvents were studied. The derivatization yield showed a linear response within the analyte concentration range of 0.1–2 mM (10–200 μg ml^{-1}) with correlation coefficients >0.99 (r^2), except for AsCl$_3$ which did not show a linear response after derivatization. Good reproducibility with relative standard deviations (RSDs) from 3 to 13% was achieved. The derivatization recovery was 66% for phosgene and 67–80% for the P-containing chemicals phosphorus oxychloride, phosphorus trichloride and phosphorus pentachloride. Recommendations to use the method for screening the presence of these chemicals in organic liquid samples are given. The method is used when CWC-related samples are screened at VERIFIN.

Introduction

The Chemical Weapons Convention (CWC)[1] entered into force in 1997, but chemical warfare agents (CWAs) are still topical. The threat to the use of these agents has regularly proved to be a source of news in this decade. The Organization for the Prohibition of Chemical Weapons (OPCW)[2] implements the CWC for the prohibition of the development, production, stockpiling, and use of chemical weapons and on their destruction. During the last few years, the OPCW has needed to conduct inspections and samples were collected because of alleged uses of CWA.[3–8] To this end, the OPCW has a network of designated laboratories and conducts proficiency tests (PTs) on a regular basis. These designated laboratories perform chemical verification analysis on the samples taken from the inspected sites and report if CWAs or CWC-related chemicals are identified.

CWAs or toxic chemicals and their precursors are grouped into lists known as Schedule 1, 2, and 3 of the CWC, based on their risks to the convention and their degree of dual use, those in Schedule 1 having the greatest risk.[9] Sample preparation procedures and analytical techniques used widely by the designated laboratories of the OPCW have been published as the Recommended Operating Procedures (ROPs), as monographs.[10–13]

The ROPs were not considered complete, and should never be, as new and better procedures will always emerge for sampling and analysis. Continuous efforts are required to keep these ROPs up-to-date. The increased pace of scientific and technological development further emphasizes this need. Additionally, there are gaps in the coverage of current procedures.[14]

Identification of chemicals by designated laboratories has to be unambiguous requiring separation and analysis by gas, liquid or ion chromatography coupled to spectrometric techniques or by nuclear magnetic resonance spectroscopy. However, some scheduled chemicals require derivatization due to their reactivity and/or inappropriate volatility for direct analysis with gas chromatographic techniques.

In Schedule 3, the three phosphorus containing inorganic chlorides phosphorus oxychloride (POCl$_3$), phosphorus trichloride (PCl$_3$), and phosphorus pentachloride (PCl$_5$) are listed. Little has been published on the analysis of these chemicals: POCl$_3$ and PCl$_3$ were analyzed by GC-MS as well as by direct injection MS,[15] as early as 1990. In addition, the Schedule 3

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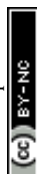
chemical sulfur dichloride (SCl_2) was analyzed. In 2015 the derivatization of SCl_2, as well as of sulfur monochloride (S_2Cl_2) using the electrophilic addition reaction with 3-hexyne was published.[16] The reaction products were analyzed by GC-MS. For some reasons, the third sulfur chloride of the Schedule 3, thionyl chloride ($SOCl_2$), was not analyzed.

Schedule 3 also contains the gaseous carbonyl dichloride ($COCl_2$, phosgene), which is less corrosive than the mentioned phosphorus and sulfur containing chlorides. Phosgene can be analyzed directly in organic samples or extracts by GC-MS, taking into account that it elutes earlier than most of the organic solvents. Either headspace or split analysis should be used when this chemical is suspected in those types of samples.[17] Phosgene can be formed by thermal decomposition of some plastics and chlorinated hydrocarbons. Phosgene also has many different industrial applications. For these reasons on-site methods using sensors and probes to detect phosgene in air have continuously been developed.[18–24] Due to the instability of phosgene in air it has been collected in impingers and sorbent tubes containing a reagent to derivatize phosgene to a stable chemical.[25] Chemical reactions of phosgene are similar to those of acid chlorides and it reacts easily with alcohols.[26] Derivatization methods using mono- and bidentate nucleophiles have been reviewed.[27,28] Phosgene was analyzed in air after derivatization with 2-aminothiophenol, 3,4-dimercaptotoluene (DMT), and 2-hydroxymethylpiperidine. The thermally stable derivatives were trapped with triethylamine onto Tenax® TA resin before thermal desorption (TD) GC-MS analysis.[28] Later Juillet et al.[29] validated sampling and analysis of phosgene using in situ derivatization with DMT on Tenax® GR tubes followed by analysis using TD–GC-MS with low limits of detection. This method is also presented in the latest ROP of air samples.[30]

Arsenic trichloride ($AsCl_3$) is listed in Schedule 2. Due to its reactivity, it hydrolyzes rapidly in air, in water, or in water containing solvents. Wils[15] analyzed directly the chemical with GC-MS without derivatization. Schoene et al.[31] derivatized $AsCl_3$ to thioarsenite with thioglycolic acid methyl ester prior to analysis with GC-MS and GC coupled with an atomic emission detector. In the ROP book 2011, the derivatization of $AsCl_3$ in organic samples by trimethylsilylation was already discussed and derivatization with 1-butanethiol in presence of trimethylamine using an optimized method was proposed.[12,13] Some years ago 1-buthyl-, 1-ethyl- and 1-propylthiol and some small dithiols were used for the derivatization of $AsCl_3$ and lewisite 1 and 2. The chemicals and derivatization reagent were spiked in a water sample and the formed derivate analyzed using hollow fiber liquid phase micro extraction and GC-MS analysis.[32]

Thionyl chloride ($SOCl_2$) reacts with alcohols to form chlorosulfite esters. The fate of these esters depends on the reaction conditions; especially on the stoichiometry, solvent, and amine base (e.g. pyridine is one of the most commonly used). If the appropriate ratios of alcohol and pyridine relative to $SOCl_2$ are used, dialkyl sulfites are formed.[33,34]

Niederhauser was the first to propose derivatization of scheduled chlorides with 1-propanol. The method was developed and tested in 2003 for $COCl_2$, $POCl_3$, PCl_3, $SOCl_2$, S_2Cl_2, and SCl_2 in the Spiez Laboratory.[35] In this study, the method was validated and further investigated in order to develop a more generic derivatization method by VERIFIN in collaboration with the Spiez Laboratory. $POCl_3$, PCl_3, PCl_5, $COCl_2$, $SOCl_2$, S_2Cl_2, SCl_2 and $AsCl_3$ were derivatized with 1-propanol in pyridine for GC-MS analysis (Fig. 1 and Table 1). Derivatization conditions were optimized and the stabilities of the target analytes and the derivatives were investigated. Additionally, the derivatization recovery was determined for chlorides for which the commercially available derivatives dipropylcarbonate (DPC) and tripropylphosphate (TPP) were available as reference standards. Based on the optimization, a recommended sample preparation method was proposed for the derivatization of these chlorides in organic samples and extracts to identify them in OPCW proficiency tests and real samples.

Experimental

Chemicals and reagents

$POCl_3$ of 99% purity (Riedel-de-Haën, Seelze, Germany), PCl_3, PCl_5, and $SOCl_2$ of 99% purity (Merck, Darmstadt, Germany), $COCl_2$ and SCl_2 of 99% purity (Fluka, Buchs, Switzerland), both S_2Cl_2 of 98% and $AsCl_3$ of 99% of purity (Aldrich, St Louis, USA) were used as analytes. Tripropylphosphate (TPP) and dipropylcarbonate (DPC) were of 99% purity and purchased from Aldrich. 1 mM and 2 mM stock solutions of the analytes were prepared in n-hexane (99%, Merck). Toluene (99.5%, Merck), acetonitrile (99.5%, BDH, Poole, England) and dichloromethane (99.5%, Merck) were also tested as solvent for stock solutions. All solvents were dried with molecular sieve of 3 Å pore size (Technical, Ø 1.6 mm, BDH) before use to avoid hydrolysis of the target chemicals. A mixture of 1-propanol containing 10% and 40% (v/v) of pyridine was used as a derivatization reagent. 1-Propanol (>99%) and pyridine (99%) were purchased from Riedel-de-Haën. n-Octane (99%, Fluka) and n-dodecane (99%, ACROS Organics, Geel, Belgium) were used and tested as co-injection solvent to increase the solvent effect for better chromatographic resolution in GC-MS analyses. A solution of tributylphosphate (TBP) 1 mg ml^{-1} in dichloromethane was used as internal standard (IS) for quantitation and added to each sample before analysis. Analyte concentrations from 0.1 to 2.0 mmol l^{-1} were studied. Three parallel samples and method blank samples were prepared and analyzed.

Derivatization procedure

Initially $COCl_2$, $POCl_3$, PCl_3, $SOCl_2$, S_2Cl_2, and SCl_2 were diluted in dichloromethane and derivatized. 100 µl of 1-propanol solution containing 10% of pyridine was added to 100 µl of the analyte solution (100 or 10 µg ml^{-1}). The vial was closed, shaked, and heated at 60 °C for 10 min before GC-MS analysis. For the same analytes as well as for PCl_5 and $AsCl_3$, derivatization of the analytes in n-hexane solution at the same conditions was also tested.

Finally, 10 µl of the IS solution (TBP, 1 mg ml^{-1}), 50 µl of n-octane, 50 µl of 1-propanol solution containing 40% pyridine and 50 µl of the analyte solution were added into a 300 µl glass vial insert in an autoinjector vial (Agilent Technologies, USA). The vial
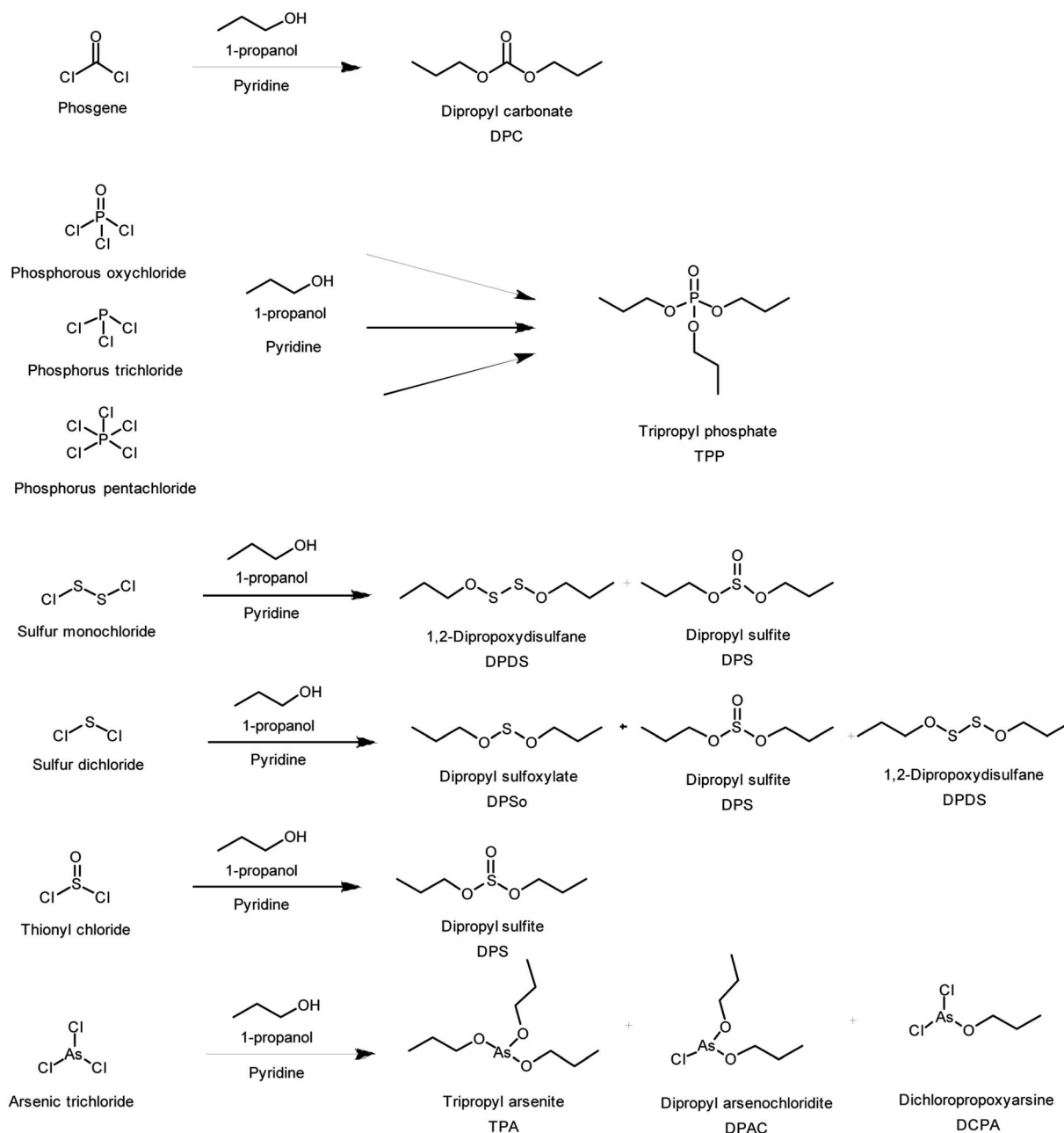
Fig. 1 Structures of studied chlorides and their reaction with 1-propanol in pyridine solution.

was immediately closed and vortexed for three seconds to ensure a proper mixing of the solution. The reaction was carried out at ambient temperature (22 °C) for 15 min before GC-MS analysis. Derivatization at −18 °C and 60 °C was also tested. For AsCl$_3$, the best method was to increase the volume of 1-propanol solution to 100 μl and carry out the derivatization at 60 °C for 15 min.

Instrumentation and analysis

A HP MSD 5972 (Hewlett Packard, USA) mass selective detector coupled to a HP 5890 Series II GC (Hewlett Packard, USA) was used for analysis. The GC was equipped with an auto injector HP 6890 supplied by the same manufacturer. A DB-5 ms column (30 m length, 0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies, USA) was used and the oven was programmed from the initial temperature 40 °C (1 min) to the final temperature of 280 °C at the rate of 10 °C min^{-1}. The final temperature was kept for 15 min. Helium (Aga, Finland) was used as carrier gas with a flow rate of 1 ml min^{-1}. The injector temperature was 250 °C and the injections of 1 μl were carried out in splitless mode with one minute splitless time. The MS was operated in electron ionization (EI) mode at 70 eV ionization energy. Samples were analyzed in full scan mode with a scan range of 40–550 m/z and scan speed of 1.5 scans per sec.

The effects of the different experimental parameters on the derivatization yield were evaluated by comparing the peak areas

Table 1 Derivatized chlorides, their chemical formula, CAS number and schedule as well as the names of the reaction products with CAS numbers and molecular weights (Fig. 1 shows the reaction schemes and products of each chloride)

Analyte (schedule name, IUPAC name)	Chemical formula	CAS number	Schedule	Derivative	CAS number	MW
Phosgene, carbonyl trichloride	$COCl_2$	75-44-5	3.A.01	Dipropyl carbonate, DPC	623-96-1	146
Phosphorus oxychloride, phosphoryl trichloride	$POCl_3$	10025-87-3	3.B.05	Tripropyl phosphate, TPP	513-08-6	224
Phosphorus trichloride, trichlorophosphane	PCl_3	7719-12-2	3.B.06	Dipropyl sulfoxylate, DPSo	3359-70-4	150
Phosphorus pentachloride, pentachlorophosphane	PCl_5	10026-13-8	3.B.07	Dipropyl sulfite, DPS	623-98-3	166
Sulfur monochloride, hypochlorous dithioperoxyanhydride	S_2Cl_2	10025-67-9	3.B.12	1,2-Dipropoxydisulfane, DPDS	3359-05-5	182
Sulfur dichloride, hypochlorous thioanhydride	SCl_2	10545-99-0	3.B.13	Tripropyl arsenite, TPA	15606-91-4	252
Thionyl chloride, sulfurous dichloride	$SOCl_2$	7719-09-7	3.B.14	Dipropyl arsenochloridite, DPAC	50880-08-5	229
Arsenic trichloride, trichloroarsane	$AsCl_3$	7784-34-1	2.B.07	Dichloropropoxyarsine, DCPA	3141-09-1	205

of the derivatives with the peak area of the IS in the corresponding total ion chromatograms (TIC).

Results and discussion

Amount of derivatisation reagent and composition of the solution

In the first experiments 1-propanol containing 10% of pyridine was tested to derivatize $COCl_2$, $POCl_3$, PCl_3, $SOCl_2$, S_2Cl_2, and SCl_2. Dichloromethane was used as the solvent for the analytes. Fig. 1 shows the reaction schemes and products identified and their names, CAS numbers and molecular weights are listed in Table 1. $COCl_2$, $SOCl_2$ and $POCl_3$ reacted with 1-propanol forming the corresponding dipropyl or tripropyl derivatives DPC, DPS or TPP. PCl_3 oxidized and formed TPP, the same derivate as for $POCl_3$. Similarly, S_2Cl_2 and SCl_2 derivatized to the corresponding dipropyl derivatives, DPDS and DPSo, and their oxidized form DPS, the same derivative as for $SOCl_2$. In addition, DPDS was formed as a side product from SCl_2.

When the above-mentioned analytes as well as PCl_5 and $AsCl_3$ were dissolved in *n*-hexane instead of in dichloromethane, the derivatization was not successful for some of the analytes. Only $COCl_2$, $POCl_3$, and PCl_3 showed the expected reactions reacted as listed in Table 1. For this reason, before next experiments all solvents and solvent mixtures were dried on a molecular sieve and stored in vials and sample bottles containing molecular sieve.

Derivatization experiments with $POCl_3$ during the test phase had shown, that increasing the amount of pyridine, the reaction time as well as the reaction temperature did not have an effect on the yield of TPP.[36] However, the volume of 1-propanol turned out to be critical. A large excess of 1-propanol containing 40% of pyridine was needed to derivatize 50 µl of 1 mM of the target chemical. This amount was also enough for the derivatization of $COCl_2$, $POCl_3$, PCl_3, PCl_5, $SOCl_2$, SCl_2 and S_2Cl_2, since a large excess of 1-propanol in pyridine compared to the amount of the target analyte was required. The same reaction products as shown in Fig. 1 were identified. PCl_5 oxidized similarly as PCl_3 forming TPP, the same derivate as for $POCl_3$. When different

concentrations of the analytes were tested, the responses were linear from 0.1 up to 2 mM indicating complete derivatization in the concentration range.

$AsCl_3$ reacted with 1-propanol containing 40% of pyridine forming TPA but some amount of di- and mono propyl derivatives were also formed. The concentration of $AsCl_3$ affected the ratio of the three derivatives TPA, DPAC, DCPA when 50 µl of 1-propanol containing 40% pyridine was used. At low $AsCl_3$ concentrations (0.1–0.3 mM) TPA and DPAC were formed. When the concentration was 1 mM or higher, in addition to TPA and DPAC, DCPA was formed. The presence of DPAC and DCPA indicated that the derivatization was not complete. For this reason, the volume of 1-propanol solution was increased stepwise to 200 µl. The amounts of TPA and DPAC were increased in the reaction mixture but DCPA was still observed. DCPA was always formed when the $AsCl_3$ concentration was 1 mM or higher. It could be shown that $AsCl_3$ did not derivatize only to TPA. Finally, 100 µl of 1-propanol containing 40% pyridine for $AsCl_3$ derivatization was a good compromise to produce TPA as the main reaction product without diluting the sample too much.

The total ion chromatograms (TICs) of the derivatized samples and EI mass spectra of the main derivatization products are shown in Fig. 2 and 3. Table 2 shows retention times of the main derivatives and the most intense ions of their mass spectra.

The intensities of the molecular ions (M^+) and other specific ions were typically very low in the mass spectra of the examined sulfur-containing derivatives. In addition, the non-specific base ion m/z 43 is also prominently present in the mass spectra of hydrocarbons. Therefore, screening for low concentrations of the target derivatives in complex matrices containing hydrocarbon background using extracted ion chromatograms from low intensity ions will be problematic. The sensitivity and selectivity of the GC-MS analyses could be enhanced with GC-MS/MS experiments in selected reaction monitoring mode (SRM).

Derivatization temperature

Besides derivatizing at ambient temperature, derivatization at −18 °C and 60 °C were also tested. Generally, there was no
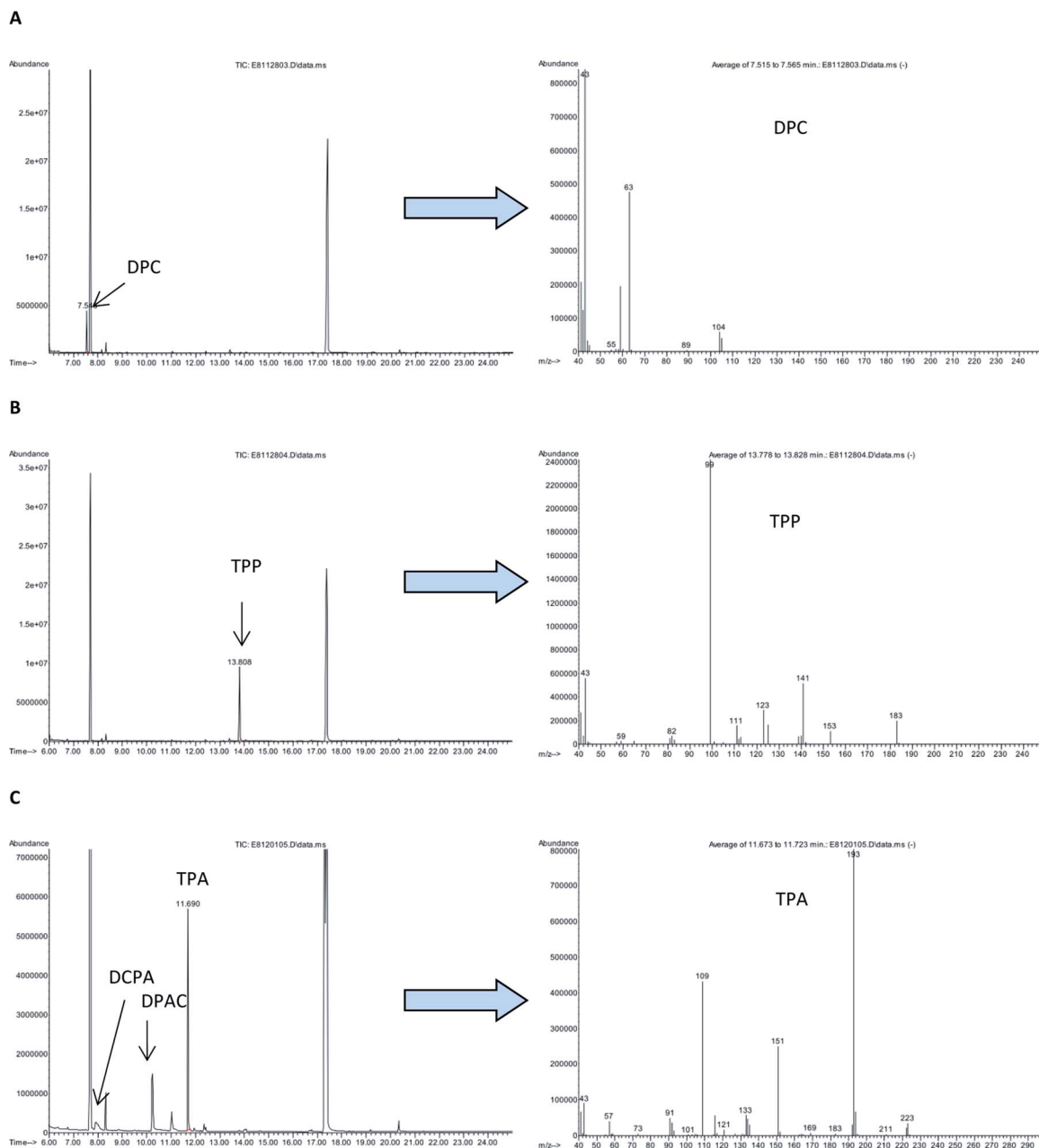
Fig. 2 Total ion chromatograms (left) and EI mass spectra (right) of the derivatives (A) DPC (derivative of $COCl_2$, t_R 7.543 min), (B) TPP (derivative of $POCl_3$, t_R 13.808 min), and (C) TPA (derivative of $AsCl_3$, t_R 11.69 min).

substantial difference between the derivatives and their amounts of different chlorides despite of the different reaction temperatures. The only exception was $AsCl_3$: as the relative response of its derivative TPA increased notably when the derivatization was carried out at 60 °C.

Peak splitting

Due to the sample composition (50% hexane, 20% pyridine, 30% 1-propanol) solvent effect (solvent focussing) did not work and peaks eluting after 10 min were splitting.[37] At first split injection was tested to avoid peak splitting. Split ratios 1 : 10 and 1 : 20, which should be suitable for the used column

diameter,[38] did not work. Splitting 1 : 3 lead to an acceptable peak shape but the sensitivity decreased clearly. Addition of a nonpolar solvent was tested. 50 µl of n-octane or n-dodecane was added to the derivatization mixture. With both hydrocarbons, the peak shapes of the derivatives were improved and the sensitivity was not significantly affected. The wide peak of C_{10} eluted at retention time 7.5–13.2 min interfering the detection of the derivatives, however.

Linearity, limit of detection, and precision

Linear regression was performed on the total peak area of ion chromatograms for each derivative. r^2 values were >0.99
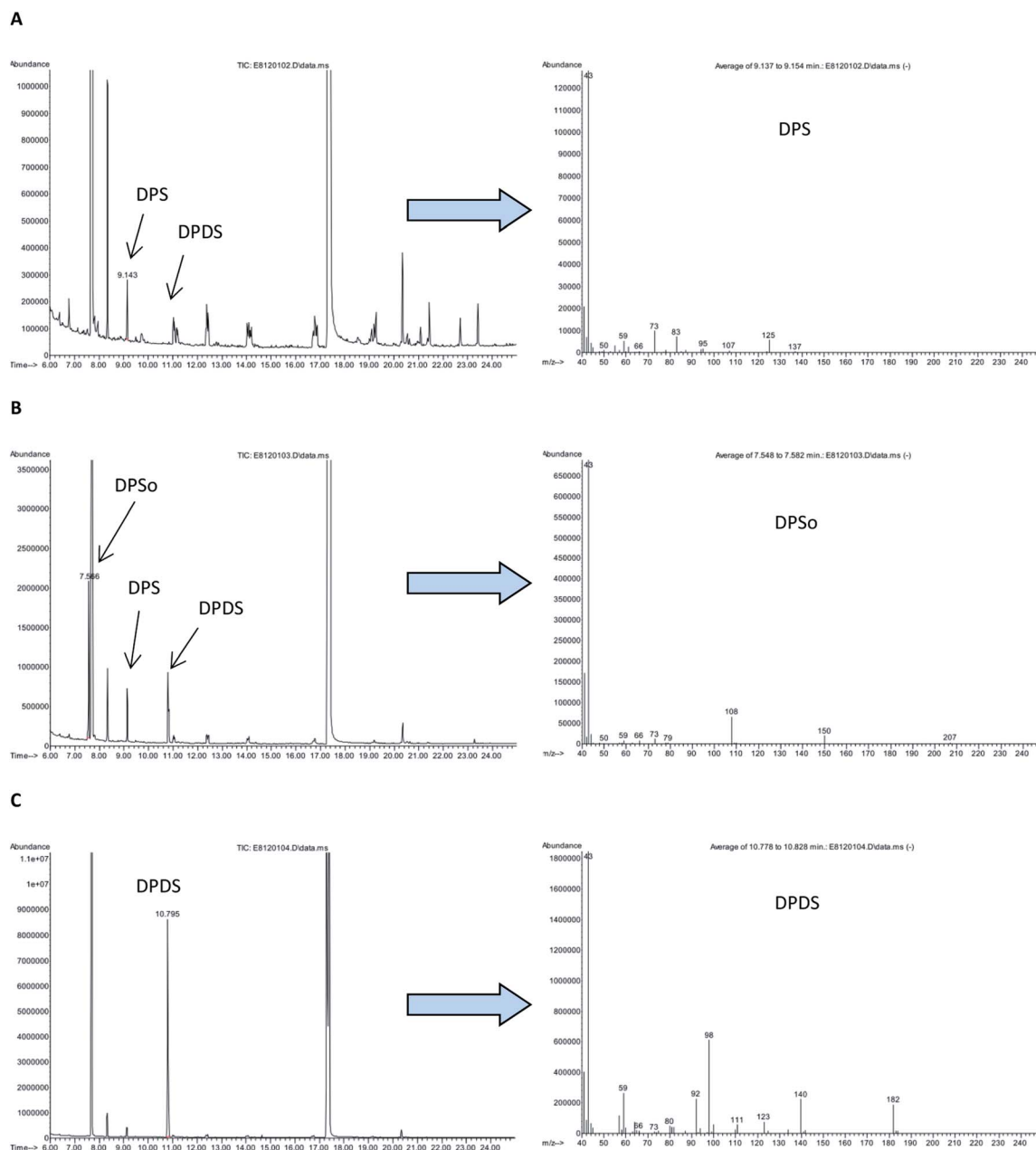
Fig. 3 Total ion chromatograms (left) and EI mass spectra (right) of the derivatives (A) DPS (derivative of $SOCl_2$, t_R 9.143 min), (B) DPSo (derivative of SCl_2, t_R 7.566 min), and (C) DPDS (derivative of S_2Cl_2, t_R 10.795 min).

confirming linearity of the calibration range. In general, the calibration curves of the derivatives were linear in a concentration range from near the limit of detection (LOD) 0.1 mM to

2.0 mM except for the derivative TPA of $AsCl_3$, where the linear range was limited. The LODs were calculated for a signal-to-noise ratio of 3 and were shown to be approx. 0.01 mM for

Table 2 Derivatives, their absolute retention times t_R and corresponding mass spectra (8 most intense ions and their relative abundance)

Derivative	t_R (min)	Mass spectrum
Dipropyl carbonate, DPC	7.5	41 (25), 42 (15), **43 (100)**, 44 (4), 59 (23), 63 (56), 104 (7), 105 (5)
Tripropyl phosphate, TPP	13.8	41 (11), 43 (23), **99 (100)**, 111 (6), 123 (12), 125 (7), 141 (21), 183 (8)
Dipropyl sulfoxylate, DPSo	7.6	41 (25), 42 (2), **43 (100)**, 44 (3), 66 (1), 73 (2), 108 (10), 150 (3)
Dipropyl sulfite, DPS	9.1	41 (16), 42 (5), **43 (100)**, 44 (4), 59 (4), 73 (8), 83 (6), 125 (4)
1,2-Dipropoxydisulfane, DPDS	10.8	41 (22), **43 (100)**, 57 (6), 59 (14), 92 (12), 98 (33), 140 (12), 182 (10)
Tripropyl arsenite, TPA	11.7	41 (7), 43 (9), 109 (49), 116 (6), 133 (7), 151 (30), **193 (100)**, 194 (8)

all examined analytes. This corresponds to 1 μg ml^{-1} for $COCl_2$.

Precision was evaluated in terms of repeatability with the relative standard deviation percentage (RSD) of each derivate and TBP peak areas resulting from the analysis of 5 replicates. Repeatabilities were good: RSDs were lower than 7% for all chlorides except 13% for SCl_2 (DPSo) and 10% for $AsCl_3$ (TPA), respectively.

Stability of the chlorides

Due to the high reactivity of the tested chlorides, their stability in stock solutions was examined. Stock solutions of each chloride were prepared in dried *n*-hexane, toluene, acetonitrile and dichloromethane and stored in darkness at −18 °C. The solutions were derivatized and analyzed just after preparation as well as after three and six days. The changes in relative peak areas of the derivatives in GC-MS TIC after storage were compared to those obtained just after the preparation of the solution (relative response of the peak in the starting day = 100%).

Fig. 4A shows that $POCl_3$ was stable in *n*-hexane for six days, as the yield of its derivative was not decreased. All the other chlorides were less stable. The peak areas of PCl_3 and PCl_5 and $COCl_2$ decreased 3%, 15%, and 26% in six days, which shows that PCl_3 and PCl_5 were also relatively stable in *n*-hexane. The peak area of the S_2Cl_2 derivative decreased 12% and SCl_2

degraded significantly during storage resulting in a decrease of 56% of its derivative's peak area. Similarly, after storage of $AsCl_3$ solution for six days and derivatization, only 16% of the derivative TPA could be found. However, the peaks of other derivatives of $AsCl_3$ were significantly increased (DCPA 31%, DPAC 99%), suggesting that hydrolysis of $AsCl_3$ was in progress. After six days of storage, the derivative of $SOCl_2$ was no more detectable.

In general, similar results were obtained for these chlorides in acetonitrile, dichloromethane or toluene solutions. However, TPA was not formed when $AsCl_3$ was dissolved in acetonitrile or dichloromethane solution. It seems obvious that one reason for this might be the higher solubility of water in acetonitrile or dichloromethane than in *n*-hexane.

Stability of the derivatives

The stability of the prepared derivatives using *n*-hexane, acetonitrile, dichloromethane, and toluene were monitored during eight hours. The derivatized samples were analyzed 15 min after preparation as well as after four and eight hours. The changes in relative peak areas were monitored as already described.

Fig. 4B shows that the most stable derivative in *n*-hexane is DPC, the derivative of phosgene ($COCl_2$). No degradation was observed after eight hours. TPP from PCl_5 and DPS from $SOCl_2$ were degraded roughly 5% after four hours and all the other derivatives showed a degradation rate of 3–15% within eight
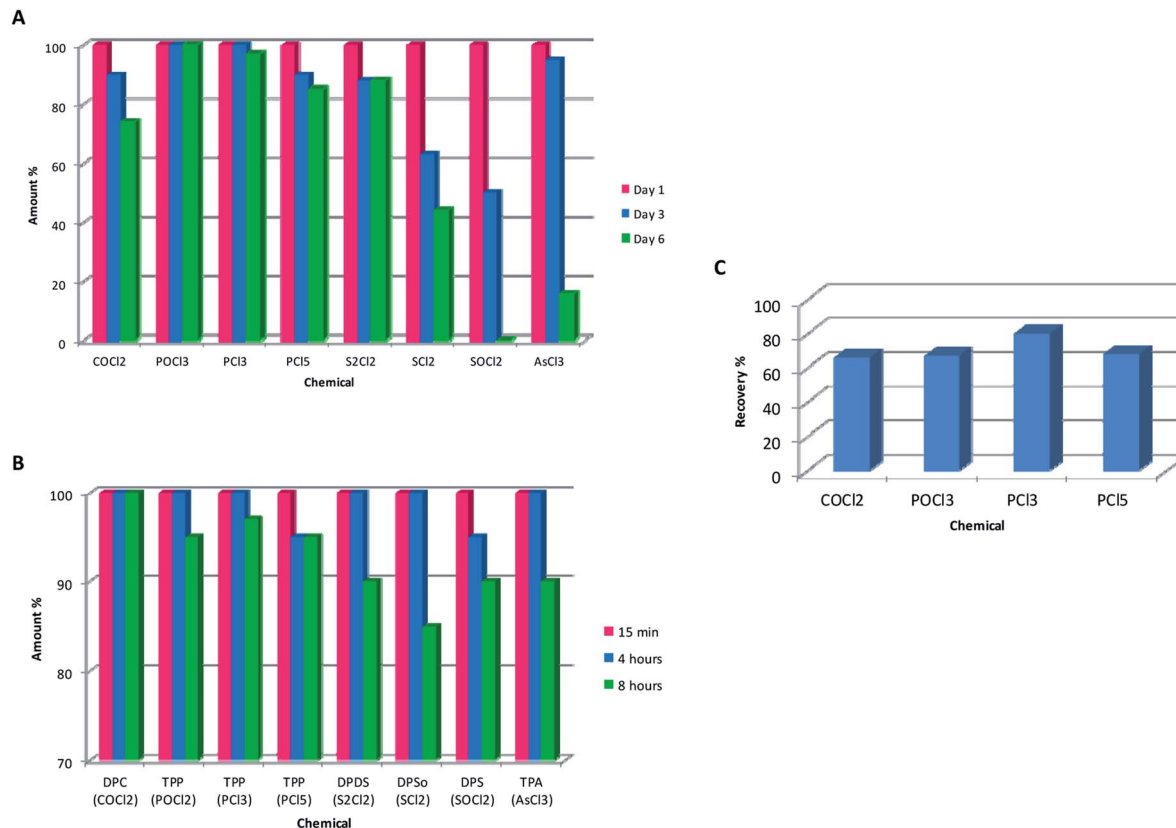

Fig. 4 (A) Stability of the investigated chlorides in *n*-hexane. (B) The stability of the derivatives in *n*-hexane (in A and B relative response of the peak in the starting day = 100%). (C) The recovery of the derivatization of $COCl_2$ to DPC, and $POCl_2$, PCl_3, and PCl_5 to TPP.

hours. Similar decomposition rates of the derivatives were observed in acetonitrile, dichloromethane and toluene. Nevertheless, it is recommended to analyze the derivatized samples just after derivatization.

As shown above, dryness of the solvents and reagents was important. It is therefore essential to close the vials immediately after addition of the chemicals with airtight caps particularly when sulfur-containing chlorides are derivatized. Moreover, to minimize hydrolysis of the analytes before derivatization, the sample should be added to the derivatization solution. For successful derivatization of samples, the following order of the derivatization steps is recommended: (1) n-octane (C_8), (2) IS (if used), (3) 1-propanol containing 40% pyridine, (4) sample.

Derivatization recovery

DPC and TPP are commercially available and were used to determine the recoveries of the derivatization of $COCl_2$, $POCl_3$, PCl_3, and PCl_5. The chlorides were derivatized with 1-propanol containing 40% of pyridine and analyzed by GC-MS. The recovery was calculated by comparing the peak areas of the corresponding derivatives with those of standard solutions of DPC and TPP. The results are shown in Fig. 4C. The derivatization recovery of DPC was 66% for $COCl_2$, while the TPP recoveries were 67% for $POCl_3$, 80% for PCl_3, and 68% for PCl_5, respectively.

Validation during testing

This method is in use at VERIFIN and has been tested successfully and reproducibly during several OPCW PTs. We have screened organic liquid samples with a solvent composition that may have contained the chlorides in question, *e.g.* dodecane sample in the 35th PT. When the method is validated during testing (on-the-job validation) the operation of the method is demonstrated by spiking the sample matrix with a known amount of chemicals (*e.g.* PCl_3, $SOCl_2$, and $AsCl_3$). The sample preparation procedure and analysis has been carried out using the same approach as for the real PT sample usually at the same time. Identification of these spiked chlorides had ensured that the chemicals would have been identified in the PT sample, if it had been in the sample. For the present only $AsCl_3$ has been used as a spiking chemical in the 25th PT, however.[39,40]

Conclusions

A simple method was developed using 1-propanol with 40% of pyridine for the derivatization of CWC-related inorganic chlorides of Schedule 2 and 3. The derivatization temperature did not significantly affect derivatization of phosgene, $POCl_3$, PCl_3, PCl_5, $SOCl_2$, S_2Cl_2, and SCl_2. However, the derivatization of $AsCl_3$ was dependent on temperature leading to varying amounts of the different derivatives. When the temperature was increased, TPA yield was increased.

In GC-MS chromatograms, the peaks of 1-propyl derivatives eluted separately from those of solvents and derivatization reagents. These derivatives shew unique mass spectra that can be used for their identification. A satisfactory chromatographic

resolution was achieved by adding n-octane to increase the solvent effect in splitless injection mode. The linear dynamic range of the quantification was in the concentration range of 0.1–2.0 mM (10–200 μg ml^{-1}). The Schedule 2 chemical $AsCl_3$ did not show a linear response after derivatization. The derivatization recovery was 66% for phosgene and 67–80% for the P-containing chemicals $POCl_3$, PCl_3, and PCl_5. The derivatives also seem to degrade over time and the extent of degradation depends on the analyte and the solvent. Therefore it is recommended to analyse the derivatized samples as soon as possible preferably within the same working day.

As shown, the described method suits well for screening of the presence of phosgene, phosphorus oxychloride, phosphorus trichloride, phosphorus pentachloride, thionyl chloride, sulfur monochloride, and sulfur dichloride as well as arsenic trichloride in organic solvent samples and solvent mixtures (*e.g.* organic solvent waste) providing there is no water present in the samples. If the derivative of interest is co-eluting with matrix components of the sample after GC-MS analysis, 1-propanol can be replaced by alternative alcohols for derivatization. This will result in different derivatives, shifted retention times (and different spectra) and the corresponding separation from the matrix components in GC analysis.

The best results are achieved when the chlorides were stored in dichloromethane or n-hexane. However, n-hexane is recommended as solvent, because the solubility of water in hexane is very low compared to the solubility of water in dichloromethane. The presence of water rapidly hydrolysed all target chemicals and the method could no longer be utilized. Therefore, it is recommended to dry the solvents using 3 Å molecular sieves before use. The stock solutions degrade over time and the degradation speed and amount depends on the analyte and the solvent. Therefore, dry fresh stock solutions should be used.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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