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SAMPLE PREPARATION AND IDENTIFICATION TECHNIQUES FOR CHEMICAL WARFARE AGENTS

A GENERAL SURVEY FOR THE REVISED NATO AC/225 (PANEL/VII) AEP-10 EDITION 4 HANDBOOK, VOLUME 1, CHAPTER 3

by

J.R. Hancock

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ABSTRACT

Sample preparation and identification techniques for chemical warfare agents were surveyed as part of Canada's contribution to a joint NATO project to update the NATO AEP-10 Handbook. Sample preparation techniques such as solid phase extraction, supercritical fluid extraction and derivatization were reviewed with respect to their applicability to chemical warfare agents. Identification techniques including; gas chromatography, mass spectrometry and nuclear magnetic resonance spectroscopy were examined in light of the need to confirm the identification of a chemical warfare agent in the presence of simple to complex background matrices.

RÉSUMÉ

On a examiné des techniques de préparation d'échantillons et de caractérisation des agents de guerre chimique, dans le cadre de la participation du Canada à un projet conjoint de l'OTAN visant à mettre à jour le manuel AEP-10 de l'OTAN. On a examiné des techniques de préparation d'échantillons, comme l'extraction en phase solide, l'extraction en phase supercritique et la formation de dérivés, pour voir dans quelle mesure elles s'appliquaient aux agents chimiques. On a aussi examiné des techniques de caractérisation, dont la chromatographie en phase gazeuse, la spectrométrie de masse et la spectroscopie de résonance magnétique nucléaire en tenant compte de la nécessité de caractériser des agents chimiques en présence de matrices simples et complexes.

ACKNOWLEDGEMENT

The author would like to acknowledge Dr. John McAndless whose contributions to the 3rd edition of the AEP-10 Handbook provided the groundwork for this report.

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1.0 INTRODUCTION

1.1. The alleged use of chemical warfare agents on the battlefield requires the ability to collect, transport, prepare and analyze samples in order that the agent can be identified. Once the agent has been identified, proper protective measures can then be adopted. On-site tentative identification of a chemical warfare agent using in-service detection equipment is possible, however positive confirmation will require the use of instrumentation found in specialized national laboratories. This is especially true for the case of first use of chemical agents or when conflicting results are obtained with field detectors (as may happen with the use of a novel chemical agent).

1.2 The NATO AEP-10 Handbook describes recommended procedures and techniques for the field sampling, packaging, transportation and identification of chemical warfare agents. The Handbook provides general guidance to personnel responsible for carrying out sampling and identification activities in support of NATO command and intelligence requirements.

1.3 Edition 3 of the Handbook was prepared in 1988 by the Group of Experts on Sampling and Identification of Chemical Agents, AC/225 (Panel VII/SICA). Advances in instrumentation and methods of analysis have made it possible to analyze increasingly complex samples and prompted the current Group of Experts to revise the Handbook to reflect current techniques and methods in chemical warfare agent sampling and analysis.

1.4 National representatives to SICA were tasked with preparing individual chapters for the three volumes which comprise the AEP-10 Handbook. Table I lists the various sections of Volume 1 of the Handbook as well as the pilot and supporting nations.

1.5 Volume 2 of the Handbook is being compiled by the Netherlands and contains technical references to the topics discussed in Volume 1. Volume 3 contains spectrometric and chromatographic data on known chemical warfare agents, precursors and decomposition products.

1.6 The revised version of the AEP-10 Handbook is to be published in 1994 with subsequent distribution to NATO countries. This report surveys information on sample preparation and identification techniques that will form the basis of Chapter 3 of Volume 1 of the revised Handbook.

Table I. Chapters of AEP-10 Volume 1 and Pilot and Supporting Nations			
Chapter	Description	Pilot Nation	Supporting Nation
1	Introduction: SICA Concept and Philosophy	Chairman	
2	Sampling of Suspected Contamination, Handling and Transport of Samples	United States	
3	Sample Preparation and Identification	Canada	Norway
4	Data Storage and Retrieval	Netherlands	
5	Mobile Identification Systems	France	Germany
6	Reporting	SHAPE	
7	Training Methods	Denmark	

2.0 Chapter 3.0: Sample Preparation and Identification

2.1 INTRODUCTION

2.1.1 Volume 1, Chapter 2 of this Handbook described the procedures and equipment necessary for the proper sampling of environmental, man-made and biological matrices suspected of being contaminated with chemical warfare agents. The procedures for shipping these samples to the laboratory have been described in the previous chapter. All samples arriving at the laboratory must be assumed to contain toxic material and appropriate precautions taken in handling such samples. Analysis of these samples must be carried out at a properly equipped laboratory experienced in the identification and confirmation of chemical warfare agents.

2.1.2 It is unlikely that battlefield samples arriving at the laboratory would be in a form suitable for direct instrumental analysis. Possible exceptions to this may be:

(a) air samples which have been collected on solid adsorbent sampling tubes, in gas sampling bags or stainless steel cylinders,

(b) water samples which are sufficiently clean and concentrated to permit direct analysis by an appropriate technique and

(c) liquid agents removed directly from chemical munitions.

Sample preparation (including extraction, concentration and derivatization) may be necessary prior to instrumental analysis, especially where unequivocal identification is required.

2.2 SAMPLE STORAGE AND CUSTODY

2.2.1 The results of the analysis of samples suspected of being contaminated with chemical warfare agents may be used for military (battlefield), political (allegations of use) or verification (CWC) purposes. It is therefore mandatory that the handling and analysis of the samples be carried out in a legally defensible manner.

2.2.2 When the samples arrive at the laboratory, the integrity of the sealed sample and packaging should be obvious to visual inspection. In cases where samples are collected from the battlefield, comments on the integrity of the package or sample would be noted and the analysis carried out. In political or verification cases where there are questions regarding either the integrity of the package or the sample, no analysis would be performed and the sample should be returned to the originator.

2.2.3 Once the package has been opened, the scientist assigns the sample a sample number, dates and initials the sample to show that it is now in his custody. Proper and uniform procedures for the labelling and tagging of samples must be followed.

2.2.4 The sample is then stored in a locked cabinet (e.g. fumehood, refrigerator) which is under the sole control of the scientist. If the sample is transferred to another scientist, a transfer form is completed which details the transfer. The second scientist now initials and dates the sample thus showing when it was placed into his custody. The detailed history of the sample(s) should be available to guide the analysts toward the most appropriate analytical method. When not in use the sample is returned to the locked cabinet.

2.3 SAMPLE PREPARATION METHODS

2.3.1 GENERAL CONSIDERATIONS

2.3.1.1 Samples, with the possible exceptions noted in section 2.1.2, will be subjected to a variety of preparation methods prior to analysis. Depending on the type of sample and

identification technique used, sample preparation can accomplish some or all of the following objectives:

(1) removal of impurities or matrix materials which interfere with the detection and quantitation of the analytes of interest,

(2) concentration of analyte, thus improving the chances of unequivocal detection and identification,

(3) derivatization of analytes to allow the application of more sensitive detection techniques or to render the analyte more amenable to separation techniques and

(4) removal of sample components that can damage sensitive instrument hardware such as GC columns, HPLC pumps and columns, mass spectrometer sources, etc., prior to introduction of the analyte into the instrument.

2.3.2 LIQUID/LIQUID EXTRACTION (LLE)

2.3.2.1 Liquid/liquid extractions are primarily used for extracting analytes from an aqueous matrix into a water immiscible organic solvent. Extraction efficiency is a function of the distribution ratio of the analyte between the two phases and the ratio of the volumes of aqueous to organic solvent.

2.3.2.2 In practice a known volume of the aqueous sample is combined with a smaller volume of organic solvent (ratios of 10:1 are common) and the two phases vigorous mixed, allowed to separate and the organic layer removed. Depending on the extraction efficiency, additional extractions with fresh solvent may be required. Finally the organic layers are combined, concentrated and analyzed.

2.3.2.3 Liquid/liquid extractions can be used to preconcentrate an analyte, with concentration factors of about ten fold being typical. LLE can be used to cleanup a sample by removing the analyte of interest from a "dirty" matrix. There are numerous water immiscible organic solvents, however in practice only a few such as hexane and dichloromethane are routinely used for the LLE of chemical warfare agents. Emulsion formation especially when using chlorinated solvents is a common problem. Although a solvent may extract an analyte with high efficiency from an aqueous sample, it is likely that the solvent co-extracted a range of other undesired compounds as well.

2.3.3 SOLID PHASE EXTRACTION (SPE)

2.3.3.1 Solid phase extraction is a physical extraction method in which an analyte, usually in aqueous solution, is passed through a solid adsorbent bed. Under proper conditions the analyte interacts with the adsorbent and is selectively extracted from the aqueous solution. SPE is often used as an alternative to liquid/liquid extractions of aqueous samples.

2.3.3.2 Solid phase adsorbents are typically modified silica which are packed into cartridges ready for use. The adsorbent is solvated with an appropriate organic solvent and then washed (typically water for aqueous samples) prior to the application of the sample. The sample is applied to the cartridge, then using either vacuum or positive pressure the sample is passed through the cartridge. The analyte is desorbed from the cartridge using a solvent capable of interrupting the analyte/adsorbent interaction.

2.3.3.3 This form of extraction can be used to preconcentrate an analyte with concentration factors of 10-100, or to cleanup a sample by removing the analyte of interest from a "dirty" matrix. Typical solvents used in SPE include: hexane, dichloromethane, isopropanol and acetone. Emulsion formation is not a problem as is the case in liquid/liquid extraction. There are documented cases of the irreversible adsorption/decomposition of chemical warfare agents on solid adsorbents, therefore detailed studies need to be carried out with the analyte of interest prior to the use of solid adsorbents. As with liquid/liquid extraction, the extraction process is not totally specific. It should be expected that a range of other compounds from the sample will be retained and subsequently desorbed from the adsorbent.

2.3.4 LIQUID/SOLID EXTRACTION (LSE)

2.3.4.1 Liquid/solid extractions is a physical extraction method used for extracting analytes from solid matrices such as soil, adsorbents or swabs. Organic solvents are typically used as the extracting solvent, although in a number of cases water has been used successfully. Due to the volumes of solvents employed, this form of extraction is typically used for sample cleanup rather than concentration. Concentration of the extracts in volatile organic solvents is discussed in section 2.3.10.

2.3.4.2 Extraction is carried out by placing a sample of the solid material into a vessel containing an appropriate solvent. For short extraction times (up to 2 hours), the use of ultrasonification can enhance the extraction of organics from solids. For longer times, a soxhlet type extractor is often used. In both cases a suitable solvent must be chosen that will extract the analyte of interest from the matrix, but leave behind the bulk of the undesired matrix components. It is possible to carry out sequential extractions with various solvents in order to selective remove analytes from the matrix. If the analyte is absorbed on a non-environmental surface such as a clothing sample or aerosol filter, care must be taken in choosing a solvent which will not react with or dissolve the surface upon which the

sample is absorbed.

2.3.4.3 Chloroform, a solvent that has been used in LSE, is usually stabilised with a small amount of ethanol. This additive may react with organophosphorus agents in the presence of a solid matrix (e.g. soil, molecular sieves) resulting in artifact formation. The use of ethanol-stabilized solvents for LLE is not recommended. Methylene chloride (dichloromethane) is recommended as a substitute for chloroform in these cases.

2.3.5 SUPERCRITICAL FLUID EXTRACTION (SFE)

2.3.5.1 Supercritical fluid extraction is a physical extraction method in which analytes are extracted from either solid or liquid matrices by a fluid maintained at supercritical conditions. Typically the matrix is a solid such as soil and the method may be used to cleanup the sample or preconcentrate the analyte of interest.

2.3.5.2 A supercritical fluid is a fluid that has been raised above its critical temperature and pressure. Under such conditions it has viscosity similar to a gas and the solvating power of a liquid. In most applications carbon dioxide is used as the supercritical fluid.

2.3.5.3 This technique has been used for some time in industrial environments, but is relatively new in the analytical laboratory. Indeed to date the application of this technique to the preparation of samples suspected of being contaminated with chemical warfare agents is extremely limited. SFE offers the potential of high concentration factors where the analyte is extracted from the matrix and deposited onto a media followed by elimination of the supercritical fluid.

2.3.5.4 In the laboratory, a sample is loaded into an extraction thimble and installed in the extractor. A supercritical fluid is then either allowed to flow though the thimble (dynamic extraction) or fills the thimble for a preset time (static extraction). The density of the supercritical fluid and the temperature under which the extraction is carried out will influence the extraction efficiency. The supercritical fluid carrying the analyte is then depressurized and vented to atmosphere and the extracted analyte recovered.

2.3.5.5 Although this is a relatively new technique, it is clear that no single trapping method has proven to be suitable for all analytes. Trapping methods include; bubbling through a solvent, depressurizing the fluid into an vial (either empty or containing glass beads) and depressurizing the fluid onto a solid phase extraction cartridge. Although carbon dioxide currently is the most commonly used supercritical fluid, it does not possess a very high solvating power and for this reason modifiers such as methanol are added to the fluid. This technique has had only limited success with very polar compounds, so the extraction of the decomposition products of nerve agents will likely prove a challenge based on the current

state of the art.

2.3.6 PURGE AND TRAP

2.3.6.1 This is a procedure for the extraction and concentration of volatile organics from aqueous samples prior to analysis. An inert gas (e.g. nitrogen) is bubbled through the sample contained in a small glass chamber. The effluent from the chamber is then collected either in a sampling bag, on a porous polymer absorbent or cryogenically focused onto the head of a chromatographic column.

2.3.6.2 Purge and trap can therefore be used as both a sample cleanup and concentration technique. In practice it is useful to be aware that the sample collected for analysis is only a true representation of the analytes in the vapour phase. The varying volatilities of analytes will result in an inaccurate reflection of the composition of the bulk liquid.

2.3.7 HEADSPACE

2.3.7.1 Headspace sampling can be used for the sample cleanup and concentration of analytes from liquid or solid samples. Although there are a number of variations in how headspace sampling, typically the vapour above a sample is collected and analyzed for the presence of volatile compounds.

2.3.7.2 Some of the variations in headspace sampling include whether the sample is heated, whether the headspace is sampled directly or preconcentrated and whether sampling is carried out under dynamic or equilibrium conditions.

2.3.7.3 Concentration factors for these systems are difficult to calculate, but it is clear that when the analyte is trapped onto a solid adsorbent preconcentration will occur. In practice it is useful to be aware that the sample collected for analysis is only a true representation of the analytes in the vapour phase. The varying volatilities of analytes will result in an inaccurate reflection of the composition of the bulk sample.

2.3.8 THERMAL DESORPTION

2.3.8.1 Thermal desorption is not normally considered a sample preparation technique. It is generally regarded as a means of sample introduction into an analytical instrument. However given the range of matrices (solid-gases) that are amenable to thermal desorption, the technique occupies a unique place among sample preparation techniques.

2.3.8.2 Thermal desorption when combined with a chromatographic technique can be used to analyze volatiles collected using the headspace technique described previously. In some cases, portions of a solid sample may be placed in the thermal desorption apparatus itself and desorbed directly.

2.3.8.3 For liquids or extracts in volatile organic solvents, relatively large volumes (e.g. > 100 μL) may be injected on to absorbent tubes followed by removal of the solvent using a gentle stream of inert gas. The preconcentration of analytes arises due to differences in "breakthrough volumes" (adsorption affinities) between the solvent and the analytes.

2.3.8.4 Analysis of these samples is carried out by heating the tube to thermally desorb the organics into a gas chromatograph for subsequent analysis. Proper temperature selection during the thermal desorption step may permit selective desorption of certain materials to the exclusion of others depending, in part, on the relative volatilities and absorbent affinities exhibited by the adsorbed analytes.

2.3.9 DERIVATIZATION

2.3.9.1 Derivatization of analytes may be necessary in order that they are amenable to identification or separation from matrix components. This is especially the case with samples containing the hydrolysis products of chemical warfare agents. The derivatization reaction may be applied:

(1) before extraction, to improve separation from matrix materials or

(2) after extraction, to improve chromatographic separation and/or detection during instrumental analysis.

In some cases, the derivatization may also be employed after chromatographic separation by using a post-column reactor to produce derivatives to which specific instrument detectors are especially sensitive.

2.3.9.2 Some general derivatization methods applicable to chemical warfare agents and decomposition products are described as follows:

(1) Diazoalkylation

This traditional approach produces completely alkylated phosphonates which can be analyzed by gas chromatography. The disadvantage of this method is that reagents such as diazomethane are hazardous and potentially explosive.

(2) Trimethylsilylation

Trimethylsilylation of phosphorous acids produces derivatives which are readily hydrolyzed in the presence of water. This can be reduced by using N-methyl-N-(t-butyldimethylsilyl) trifluoroacetamide reagent (MTBSTFA) which produces more stable t-butyldimethylsilyl alkyl methylphosphonates which are readily amenable to analysis by gas chromatography and GC/MS. The derivatization reaction is simple, rapid and produces compounds which are stable, easily chromatographed and detected.

(3) Pentafluorobenzylation

The advantages of pentafluorobenzylation include enhanced sensitivity for electron-capture GC, for ultraviolet detectors in HPLC and for negative-ion chemical ionization mass spectrometry. The derivatization reaction is relatively slow and requires the use of sodium hydride and 18-crown-6 ether at 45°C for several hours to ensure complete conversion.

(4) Methylation

The decomposition products of nerve agents have been methylated with trimethylphenylammonium hydroxide and the derivatives analyzed by gas chromatography. The advantage of this method is that trimethylphenylammonium hydroxide may be used as an eluting solvent after trapping the decomposition products on an ion exchanger.

(5) Thioesterification

The analysis of lewisite by gas chromatography is difficult even with deactivated fused silica capillary columns. Lewisite either thermally decomposes or is adsorbed on the chromatographic column. Lewisite can be rapidly derivatized using thiols such as 2,3-dimercaptotoluene or 1,2 ethanediol to form a stable derivative that can be analyzed by gas chromatography. The disadvantage of this method is that both lewisite and its major decomposition product lewisite oxide form the same derivative, making it impossible to determine whether the original sample contained the chemical warfare agent lewisite, the decomposition product or both.

2.3.9.3 In general derivatization should be avoided unless absolutely necessary, as it requires additional steps in the sampling and identification procedure. This increases the chances of sample contamination and artifact formation. The compounds identified using this technique are derivatives not the "parent" chemical agents. Detection of the derivatives provides confirmatory evidence, but confirmed identification requires identification of the intact chemical warfare agent.

2.3.10 SOLVENT EVAPORATION/CONCENTRATION

2.3.10.1 Many of the sample preparation techniques described above produce sample extracts in organic solvents requiring further concentration prior to instrumental analysis. Concentration by solvent evaporation can be achieved through the use of a Kuderna-Danish evaporator or by solvent blowdown using a gentle stream of nitrogen. The key considerations for concentration by solvent reduction are summarized below:

(1) highly volatile agents (e.g. GB) may be lost;

(2) samples containing volatile components should not be evaporated to complete dryness since analyte loss through volatilisation, irreversible surface absorption or heat-induced thermal decomposition may occur;

(3) trace constituents in the solvent may also become relatively concentrated and interfere with the analysis. In addition they may react with the analytes in the presence of glass surfaces or water which has not been removed. This problem may be minimized by using high purity solvents.

2.4 SAMPLE PREPARATION PROBLEM AREAS

2.4.1 Analysis of chemical warfare agents may involve many steps some or all of which may introduce errors. Precision and accuracy in such analyses depends on identifying the random and systematic errors and then eliminating or correcting for them.

2.4.2 During solvent extraction, solvents, reagents, glassware and other sample preparation hardware may yield discrete artifacts or elevated "background" causing misinterpretation of the analytical results. These materials must be demonstrated to be free from interferences under the given conditions by running method blanks. Interferences co-extracted from the sample will vary considerably depending on where the sample was collected. Unique samples may require additional clean-up beyond the general solvent extraction techniques available. An example of this type of problem is the solvent extraction of an aerosol filter element in a military NBC canister used to collect suspected chemical agent contaminants. Such filter elements can contain many extractable compounds, resins, etc. which preclude simple gas chromatographic analyses without further clean-up of the extracted sample.

2.4.3 For purge and trap types of extraction, impurities in the purge gas and organic compounds outgassing from the plastic fittings and lines often account for the majority of interferences. Blank samples must be run according to the selected procedure to demonstrate that the sample preparation system (and analytical system) is free from

interferences. The use of non-Teflon plastic tubing, thread sealants or flow controllers with rubber components should be avoided.

2.4.4 Cross-contamination can occur whenever highly-contaminated and trace-contaminated samples are sequentially prepared and analyzed. The purging device, sample syringe, etc. must be rinsed between samples with clean solvent or organic-free water. Preparation and analysis of exceptionally contaminated samples must be followed by a solvent blank. This will indicate carry-over in the analytical equipment. For liquid extractions or solvent extractions of solid samples, clean glassware must be used for each individual sample unless it can be demonstrated by running and analyzing a solvent blank that the extraction system was not contaminated by the sample.

2.5 SAMPLE PREPARATION EXAMPLES

2.5.1 This section describes the application of a number of the sample preparation techniques described above as they appeared in NATO AC/225 (Panel VII/SICA) Notices from 1987 to 1992. These methods apply to the sample preparation of environmental and man made matrices.

2.5.2.1 Solid phase extraction This technique was applied to the sample preparation of environmental and man made samples containing chemical warfare agents. The current method described by Norway in N/201 was based on the adsorption of agents on to Bond-Elut C-18 cartridges followed by elution with acetone or dichlorormethane.

2.5.2.2 The general procedure was as follows; the cartridge was solvated with methanol, washed with distilled water, then the aqueous sample was passed through the cartridge and finally the analytes were eluted from the cartridge with acetone or dichloromethane. The analytes were then analyzed by gas chromatography with a variety of detectors.

2.5.2.3 Recoveries of the agents were satisfactory and ranged from 50 to 100%. The recovery of sarin varied considerable depending on the original sample matrix (snow, water, grass, sand and soil). This may indicate strong sample adsorption onto the matrix or decomposition of sarin in the matrix or on the cartridge.

2.5.2.4 The Netherlands in N/150 reported on problems with storage of VX on C18 Sep-Pak cartridges. Recoveries of VX from freshly spiked cartridges were low (30-50%), however when spiked cartridges were stored for 20 hours no VX was recovered. The Netherlands concluded that the VX had decomposed on the Sep-Pak C18 cartridges. Norway in N/201 reported on recoveries of VX after 7 days storage on Bond Elut C18 cartridges, indicating that in some cases analyte recovery depended on the type and manufacturer of the solid phase extraction tubes.

2.5.3.1 Liquid-solid extraction Reports on the use of this technique focused primarily on the extraction of chemical warfare agents from soil. The Netherlands (N/182), Canada (N/184), the U.K. (N/186) and France (N/194) reported on the sample preparation and analysis of soil samples distributed as part of an international round robin exercise.

2.5.3.2 A few grams of soil were placed in an extraction vessel to which a minimum volume of solvent was added. The solvents used included: hexane, chloroform, dichloromethane, methanol and water. Organic solvents were used to extract the agents from the soil while water was typically used to extract the acids of organophosphorous nerve agents (for subsequent derivatization and GC analysis) or polar organic compounds such as thiodiglycol that are sparingly soluble in organic solvents.

2.5.3.3 Once the extracting solvent had been added to the soil, the sample was ultrasonified for a period ranging from a minute to an hour depending on the solubility of the agent and the potential for co-extraction of unwanted matrix material.

2.5.3.4 The UK in N/219 reported on the sample preparation and analysis of samples from a suspected CW incident in Kurdistan. Dichloromethane was used to extract contaminated soil and the solution dried with sodium sulphate. The extract was then concentrated using a gentle stream of nitrogen. GC-MS analysis revealed the presence of mustard and a number of mustard related compounds.

2.5.4.1 Thermal desorption Belgium in N/96 reported on the use of thermal desorption gas chromatography for the analysis of chemical warfare agents on charcoal found in military respirator canisters. Using gas chromatography-mass spectrometry they identified soman that had been thermally desorbed from the charcoal found in a canister supplied from various NATO countries.

2.5.4.2 The Netherlands reported in N/147 on the difficulties associated with the thermal desorption of VX from the solid adsorbent Tenax using the Chrompack thermal desorption unit. Compared to on-column injection little or no VX was observed under thermal desorption conditions. The following year Canada in N/173 reported on the thermal desorption of VX using their Minitube Air Sampling System thermal desorption unit. Detection limits in the low picograms were obtained using this approach. Initial problems with thermal decomposition of VX were traced to the presence of metal screens used to retain the adsorbent in the minitube. Replacing the screens with silanized glass wool minimized the problem.

2.5.4.3 Both the Netherlands (N/113) and Canada (N/114) reported on the inclusion of solid adsorbent air sampling tubes as part of the equipment included in a field sampling kit for chemical warfare agents. Canada demonstrated the potential for sampling tubes by the collection of vapour above an artillery shell suspected of containing a chemical warfare

agent. The sampling tube was thermally desorbed and analyzed by gas chromatography and was found to contain mustard.

2.5.5.1 Derivatization Underivatized, lewisite can be analyzed at high concentrations by gas chromatography. Below approximately 100 nanograms no peak is observed for lewisite in the chromatogram. The U.K. in N/134 reported on the use of dimercaptotoluene to derivative lewisite into a form amenable to analysis by gas chromatography. Canada and Denmark in a joint report (N/210) reported a detection limit of less than 1 nanogram for the dimercaptotoluene derivative of lewisite. The derivative could be extracted from water with hexane and recovered from soil using dichloromethane. The U.K. recorded the mass spectrum of the derivative, while Canada and Denmark recorded the vapour phase infrared spectra of the dimercaptotoluene reagent and the corresponding lewisite derivative.

2.5.5.2 Canada in N/93 reported on the use of t-butyldimethylsilyl derivatives of alkyl and alkyl methyl phosphonic acids. The acids were dissolved in acetonitrile with 200 μL of MTBSTFA and 200 μL of toluene and heated for 1 hour at 60°C. These derivatives were stable in solution and were analyzed by GC-MS.

2.6 IDENTIFICATION TECHNIQUES

2.6.1 GENERAL CONSIDERATIONS

2.6.1.1 Analysis of samples suspected of containing chemical warfare agents, especially when the agent is present in a complex matrix or when the agent is new or unusual must be carried out at a properly equipped laboratory experienced in the identification and confirmation of chemical warfare agents.

2.6.1.2 Currently, three analytical techniques can provide the structural information which satisfies the criteria for identification of chemical warfare agents given in Section 2.6.2. These techniques are; mass spectrometry, infrared spectroscopy and nuclear magnetic resonance spectroscopy. Confirmed identification of an agent requires agreement from two of the three techniques.

2.6.1.3 On the nanogram level and below, the most useful techniques employ chromatographic separations in conjunction with a variety of detectors. Gas chromatography-mass spectrometry is currently the technique of choice for CW agent separation, detection and identification. When molecular ion information is not observed during electron impact mode (EI) ionization, chemical ionization (CI) using gases such as ammonia and isobutane has proved to be extremely useful. Samples requiring liquid chromatographic separations may employ other MS techniques such as thermospray or electrospray.

2.6.2 CRITERIA FOR IDENTIFICATION

2.6.2.1 Sampling Criteria

a) samples should be taken and transported to an analytical laboratory according to the procedures described in Volume 1, Chapter 2 of this handbook,

b) in cases where it is possible and appropriate, control samples should be taken,

c) samples should be sent to at least two laboratories trained for the analysis of CW agents and

d) reports from medical units or units equipped with detection kits and/or mobile identification systems should indicate the use of CW agents(s).

2.6.2.2 Analytical Criteria

2.6.2.3 The analytical criteria are arranged according to the amount of material available. The first two sets of criteria are considered appropriate for the unequivocal identification of a CW agent used for the first time. The third set of criteria can be applied for the analysis of samples once the first use has been proven and is of particular value for the analysis of biological samples.

2.6.2.4 Large Amounts of Material Available

2.6.2.5 The amount of material is sufficient to perform every chromatographic or spectrometric analysis described in this chapter. The material is relatively pure and does not require chromatographic separation prior to having the spectrum recorded. In cases of multicomponent mixtures requiring chromatographic separations, the criteria in section 2.6.2.6 would be more appropriate.

a) agreement between at least two different recorded spectra (IR, Raman, NMR and MS) and reference spectra,

b) if the molecular ion is not present in the EI mass spectrum, chemical ionization must be carried out to confirm the molecular weight of the compound and

c) GC retention indices or times and/or TLC Rf values may provide additional evidence.

2.6.2.6 Small Amounts of Material Available

2.6.2.7 In this case, the compound will most likely be present in an extract or on an adsorption tube and identification has to be carried out on a submicrogram level using combined methods (e.g. GC-MS).

a) GC retention indices or times must agree,

b) agreement between at least two recorded spectra (IR, Raman, NMR and MS) and reference spectra,

c) if the molecular ion is not present in the EI mass spectrum, chemical ionization must be carried out to confirm the molecular weight of the compound and

d) GC specific detection (NPD or FPD), may provide additional evidence of phosphorous, sulphur or nitrogen content.

2.6.2.8 Very Small Amounts of Material Available

2.6.2.9 Generally in this case the amount of material is so small (picogram level) that a complete mass spectrum cannot be obtained. Consequently multiple ion detection (MID) has to be carried out. Because of the limited information provided by this technique the following criteria are considered to be sufficient for tentative identification, but could not be used to confirm the first use of a CW agent.

a) GC retention indices or times must agree,

b) GC specific detection (NPD, FPD) must be carried out in appropriate situations,

c) GC-MS with multiple ion detection has to be performed on at least three individual ions for the compound. The peaks obtained during GC-MS should have coincident maxima, the same peak width at half height, a signal to noise ratio of at least three. The ratio of the three ions used for MID should fall within 10% of the values of an authentic reference material.

2.6.2.10 General

a) at least two samples should be analyzed leading to comparable results,

b) the results of the identifying laboratories should be in agreement,

c) the analytical procedures applied to blank control samples should not result in positive identification,

identification,

d) in order to check the recovery efficiency of the analytical procedure a blank control should be spiked and analyzed,

e) a rough estimate of the quantity must be carried out and reported along with the identified CW agent(s) and

f) the detection limit of the methods employed should be indicated in case no CW agents were found.

2.6.2.11 Remarks

2.6.2.12 GC retention indices must agree within 5 units when analyzed on the same stationary phase and under standardized conditions. GC retention times must agree within 5 seconds in cases where a direct comparison is made between a compound and a reference. This can only be achieved if the compound and reference are analyzed with the same column under identical conditions.

2.6.2.13 In addition to the specific detection reactions standardized TLC values must agree with reference data within limits which are determined by the standard deviations of the reference data (AEP-10 Handbook, Vol III, Chapter 4).

2.6.2.14 GC-MS with multiple ion detection can only be achieved if the compound is compared with a reference analyzed with the same equipment under the same conditions.

2.6.2.15 Final Considerations

2.6.2.16 The above described criteria are only applicable to known CW agents such as the organophosphorus nerve agents which are not naturally occurring. For compounds such as tricothecene mycotoxins additional criteria has to be fulfilled. Due to the fact that these compounds are found naturally, consideration should be given to the natural concentration levels and the combination of compounds are of importance. For unknown CW agents for which no analytical data is compiled in Vol III of the AEP-10 Handbook other reference data (see Vol I) has to be consulted. However if insufficient data is available preparation of the proposed compound(s) will be necessary. Evidence provided by decomposition products or precursors is less conclusive than evidence of the CW agents themselves. No general rules can be given. For example the identification of pinacolyl alcohol or thiodiglycol will strongly point to the use of soman or thiodiglycol respectively. However consideration must be given to the finding of thiodiglycol as it is widely used in industry whereas pinacolyl alcohol is used for soman production.

2.6.3 GAS CHROMATOGRAPHY

2.6.3.1 Gas chromatography (GC) is a separation technique in which a multicomponent sample, in the gas phase, is resolved into it's various components. The first step in this technique is the introduction of the sample into a chromatographic column where the separation will occur. Liquid samples can be injected into the column using either an on-column injector or a split/splitless injector. Gas samples are injected using: gas sampling valves, headspace injection where vapour is collected above a heated sample or in cases where vapour is adsorbed onto solid adsorbents, thermal desorption devices such as the Perkin Elmer ATD-50, Chrompak TCT or CCAI Minitube ATDU are used.

2.6.3.2 As the sample moves through the column it partitions between the carrier gas and a stationary liquid phase. Each component of the sample spends a different length of time in the liquid phase. The time that it takes a component to travel through the column is related to the time spent in the liquid phase and is known as it's retention time. The retention time for a component on a specific column is a reproducible characteristic. For example, if the retention time for soman under specified conditions is 8 minutes, then any component that does not have retention time of 8 minutes is not soman. However the converse is not true, if a component has a retention time of 8 minutes it is not necessarily soman.

2.6.3.3 In practice, retention time data are difficult to reproduce between different laboratories due to variations in operating conditions and instrumental parameters. These difficulties may be overcome by using one of a variety of retention index system. In the Kovats system, the retention time of an analyte is related to that of a series of n-alkanes co-injected under the same conditions as the sample. Index systems using phosphorus and sulfur containing standards have also been developed and used during CW agent analyses.

2.6.3.4 Because it is possible for more than one compound to elute with the same retention time, retention indices for a given analyte should be determined on several columns, each of different stationary phase polarity, in order to increase the certainty of the analyte identity. However confirmation of the agent must still be based on the criteria for identification as outline in section 2.6.2.

2.6.3.5 Detection of the components as they elute from the chromatographic column may be performed by a variety of universal and selective detectors. The most common is the flame ionization detector which uses a hydrogen air diffusion flame and responds to almost all organic compounds. When dealing with complex matrices, selective detectors such as the flame photometric detector (which responds to sulphur or phosphorous) and the thermionic or nitrogen phosphorous detector (which responds to nitrogen or phosphorous) are widely used. Although selective detectors provide information on the presence or absence of certain atoms they do not provide structural information. Mass spectrometers and infrared

spectrometers provide this type of information and for this reason are widely used in conjunction with chromatographic separations (for more details see sections 2.6.5 and 2.6.6).

2.6.4 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

2.6.4.1 High performance liquid chromatography (HPLC) is a separation technique in which a multicomponent sample, in the liquid phase, is resolved into it's various components. HPLC is well suited to the separation of polar higher molecular weight compounds or thermally labile compounds that cannot be analyzed by GC. The first step in this technique is the introduction of the sample into a chromatographic column where the separation occurs. Sample introduction in HPLC is accomplished with a switching valve equipped with a fixed volume sample loop. The sample is injected as a liquid plug into the flow stream and swept onto the HPLC column for separation.

2.6.4.2 Separations are based on the physical interactions of the sample components with the liquid mobile phase and a stationary phase. In HPLC the composition of the mobile phase is varied, resulting in mobile phases of different polarity or ionic strength, that may be used to aid separation. The time that it takes a component to travel through the column is known as it's retention time and for a specific column is a reproducible characteristic. If the retention time for methylphosphonic acid under specified conditions is 15 minutes, then any component that does not have a retention time of 15 minutes is not methylphosphonic acid. However the converse is not true, if a component has a retention time of 15 minutes it is not necessarily methylphosphonic acid.

2.6.4.3 Detection in HPLC is typically performed with ultraviolet/visible and refractive index detectors. CW agents do not possess strong chromophores, therefore sensitivity and selectivity remains poor for the detection of these compounds. In recent years flame photometric and thermionic detectors have been used for selective identification with microbore liquid chromatography. Although selective detectors provide information on the presence or absence of certain atoms they do not provide structural information. Mass spectrometers do provide this type of information and are widely used in conjunction with LC chromatographic separations (for more details see Section 2.6.5).

2.6.5 MASS SPECTROMETRY

2.6.5.1 Mass spectrometry (MS) is an identification technique in which sample molecules are ionized, the ionized molecules may then fragment and all ions are separated on the basis of their mass to charge ratio. Assignment of the structure of the original molecule, from the fragmentation pattern, is done by either fundamental interpretation or comparison of the acquired data to that of an authentic reference material. MS sample introduction techniques include: a heated sample reservoir, solids probe are commonly used for pure samples, but direct interfacing to a chromatographic technique is used for multicomponent samples. Sample introduction following chromatographic separation is the most versatile method as it allows the individual components to be introduced sequentially into the MS resulting in mass spectra for "pure" components. Mass separation is generally accomplished with a quadrupole or sector (electrostatic and magnetic) instrument. Detection of the ions is accomplished using either a photomultiplier or a electron multiplier.

2.6.5.2 The most widely used method of ionization is electron impact (EI). Electrons produced within the mass spectrometer impact on sample molecules resulting in analyte ionization. This mode may produce extensive fragmentation resulting in little or no molecular ion information. Chemical ionization (CI), a much less energetic ionization technique, has proven very useful for providing complementary molecular ion information, and for the selective monitoring of trace components in complex samples. CI using methane, isobutane and ammonia as reagent gases have all been applied to the analysis of organophosphorus CW agents and related compounds.

2.6.5.3 The exact mass of a fragment ion can be determined by means of high resolution mass spectrometry using a sector instrument. From this data the corresponding elemental composition can be calculated. High resolution mass spectrometry also permits increased selectivity for the MID detection of trace levels of agents in complex matrices (biological or environmental). Lower sample detection limits are possible for high resolution monitoring of selected ions when compared to low resolution operation, due to the reduction in chemical background.

2.6.5.4 In tandem mass spectrometry multiple analyzers (e.g. sector or quadrupole) are combined in a single instrument. The combination of two or more analyzers means more structural information can be extracted from a sample and greater selectivity maybe achieved than with a single analyzer. Structural information is clearly required for agent confirmation and greater selectivity makes it possible to identify an agent in the presence of a complex background. Table 1 lists the 4 most common used scan modes used in tandem MS.

Table 1. COMMON SCAN MODES UNDER TANDEM MS CONDITIONS		
Scan Mode	1st Mass Analyzer Operation	2nd Mass Analyzer Operation
Daughter Scan	Transmit specified ion (parent ion)	Scan over selected mass range
Parent Scan	Scan over selected mass range	Transmit specified ion (daughter ion)
Constant Neutral Loss	Scan over selected mass range	Scanning linked to the 1st mass analyzer scanning such that at any time, the 2nd mass analyzer transmits lower mass ions equal to the neutral mass loss
Reaction Ion Monitoring	Transmit specified ion (parent ion)	Transmit specified ion (daughter ion)

2.6.6 INFRARED SPECTROSCOPY

2.6.6.1 Infrared spectroscopy (IR) is an identification technique in which sample molecules absorb infrared radiation (typically in the 4000 to 400 cm^{-1} range) and the resulting absorbance spectrum is used to uniquely identify the original molecule. Samples are introduced into the IR spectrometer either as a pellet (typically in a KBr matrix), as a thin film between NaCl or KBr plates or in the gas phase either in a gas cell or as the effluent from a GC column. Sample introduction following chromatographic separation is the most versatile method as it allows the individual components to be introduced sequentially into the IR resulting in spectra for "pure" components. Currently two different approaches are used to acquire the infrared spectrum of a component as it elutes from the chromatographic column. The first technique uses a direct deposition mechanism whereby the column effluent is deposited onto a moving ZnSe plate at extremely low temperatures. Condensed phase spectra are collected by either scanning the plate on the fly or in a post chromatographic run mode that allows for increased signal processing and lower detection limits. The second, and more commonly employed technique, uses a gold plated light pipe through which the column effluent flows. Vapour phase spectra are collected on the fly, but with higher detection limits than the former technique. Typically detection limits are in the

20 - 50 ng range for a gold plated light pipe and 1 - 5 ng for a direct deposition instrument.

2.6.6.2 Unlike MS, IR spectra are more difficult to interpret from first principles and confirmation of a chemical agent is generally by comparison of the acquired spectrum to that of an authentic standard. Chemical warfare agents have characteristic infrared absorbances for functional groups which include; P-0-C, P-F, P=O and -CH2-Cl. Most data system software allow the user to preselect narrow wavenumber windows in which the infrared absorbance can be monitored. Proper selection of these windows provides selective detection of CW agents based on their functional groups in the presence of a complex background.

2.6.7 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

2.6.7.1 Nuclear magnetic resonance spectroscopy (NMR) is an identification technique in which sample molecules absorb radio frequency radiation (typically in the 1000 to 10000 cm range) and the resulting absorbance spectrum is used to uniquely identify the original molecule. Assignment of the structure of the original molecule, from the spectrum, is done by either fundamental interpretation or by comparison to that of an authentic reference material.

2.6.7.2 In NMR spectroscopy, the sample is analyzed as a dilute solution. Deuterated solvents such as: D_2O, d_6-DMSO and $CDCl_3$ are used to prepare these solutions with TMS frequently being used as the internal reference. Because NMR does not use a separation technique prior to detection (such as GC in MS and FTIR), samples must be in a relatively pure form to avoid spectral interferences.

2.6.7.3 Instrumentation equipped with multi-nuclear capability (especially ^{13}C, ^{31}P, ^{19}F and ^{1}H) can be useful for identifying chemical agents but detection levels vary depending on the nuclei studied. Using a phosphorous probe and an acquisition time of 8 hours, 10 ppm of a nerve agent can be detected with a modern superconducting NMR. With a proton probe under similar conditions the detection limits would be approximately 1 ppm. The use of selective probes such as^{31}P and ^{19}F provide for selective detection of CW agents in the presence of a complex background. Special NMR techniques or experiments such as multi-dimensional NMR, indirect detection or special probe designs can also increase specificity in complex backgrounds. Where sufficient sample is present, the information obtained by NMR can permit complete structural elucidation of new or previously unreported agents. Two dimensional NMR experiments such as homo- and heteronuclear correlation spectroscopy (COSY, HETCOR, NOESY, ROESY) are now standard methods for the determination of structure.

2.7 PREPARATORY WORK IN PEACETIME

2.7.1 The availability of modern analytical techniques and methods is a prerequisite for the rapid identification of chemical warfare agents. However, the presence of instrumentation and methods does not by itself ensure the confirmed identification of an CW agent, it's precursors or decomposition products. Successful confirmation is dependent on the analysis being carried out by a team experienced in the handling, storage, preparation and analysis of CW agents. Therefore periodically an analyst team familiar with the identification techniques should participate in interlaboratory testing, international round robin exercises and internal quality assurance testing.

2.7.2 In the event of actual chemical warfare, or for laboratory training exercises, it is important that reference compounds and standards be available for immediate use. This means that laboratories should have a synthesis capability in order to produce unique compounds not found in the databases. With the introduction of computer searchable databases increasingly users are creating their own database from spectra acquired during the analysis of samples suspected of being contaminated with chemical warfare agents. These database are then used to match the acquired spectra to authentic reference materials in order to confirm the presence of the chemical warfare agent. It is therefore necessary to ensure that the databases be updated as new spectral information is acquired. It cannot be over-emphasized that proper and careful techniques during sample preparation will greatly reduce the overall analysis time and minimize the potential for the reporting of erroneous results based on the appearance of artifacts, cross-contamination or other interferences.

2.8 QUALITY ASSURANCE AND CONTROL

2.8.1 Increasingly, analytical laboratories are being required to provide documented evidence that the results they produce meet a prescribed standard. Terms such as; good laboratory practice (GLP), quality assurance (QA), quality control (QC) and standard operating procedures (SOP's) are used to describe these standards. In short, it is necessary to demonstrate that accurate records are maintained by a laboratory, in order that experimental results can be verified by tracing the information back to the raw data. In addition maintenance and calibration records are also necessary for the wide variety of instrumentation used in the laboratory.

2.8.2 In order to properly setup and maintain a quality assurance program it is necessary to establish a quality assurance unit (QAU) which is staffed with personnel responsible for reviewing and auditing the records maintained in laboratories in order to ensure compliance with the QA program.

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