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On-Site Chemical Warfare Agent Identification

Development of a Mobile Chemical Laboratory

J.R. Hancock, C.R. Jackson Lepage, C.L. Chenier, D.S.W. Froese, and M.J. Lukacs

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DRDC Suffield

Defence R&D Canada – Suffield

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Author

Original signed by J.R. Hancock

J.R. Hancock

Approved by

Original signed by Dr. C.A. Weickert

Dr. C. A. Weickert

Head Detection and Identification Section

Approved for release by

Original signed by Dr. P.A. D'Agostino

Dr. P. A. D'Agostino

Chair, DRDC Suffield Document Review Panel

Abstract

In October 2005, the chemical detection and identification group at DRDC Suffield initiated a project to develop and field a prototype mobile chemical laboratory. This laboratory was designed to demonstrate the potential advantages of on-site chemical warfare (CW) agent identification in providing rapid information to an on-scene commander. This paper describes the various elements (i.e. platform, target agents, equipment, methods and people) that were required to deploy such a laboratory, as well as examples of the sample handling, analysis and identification of CW agents and related compounds during CW agent field exercises.

Résumé

Le groupe de détection et d'identification chimique de RDDC Suffield a initié un projet, en octobre 2005, visant à développer et mettre en service un laboratoire chimique mobile prototype. Ce laboratoire a été conçu pour démontrer les avantages potentiels de l'identification d'agents de guerre chimique sur place qui procure rapidement des informations au commandant sur les lieux. Cet article décrit les divers éléments requis (ex. : plateforme, agents cibles, équipement, méthodes et personnel) pour déployer un tel laboratoire ainsi que des exemples de manipulation d'échantillons, d'analyse et identification d'agents de guerre chimiques et leurs composés, durant des exercices pratiques avec agents de guerre chimiques.

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Executive summary

Introduction: The Canadian Forces (CF) and the forces of its allies may be deployed nationally or internationally into theatres where there is a threat of chemical/biological (CB) warfare agents. To operate effectively in these theatres, the CF require chemical warfare agent detection and identification capabilities. Currently CW agent identification in the field uses a limited number of on-site instruments. If more in-depth analysis is required, samples must be packaged and transported to an off-site laboratory which can be thousands of kilometers away. DRDC Suffield initiated a project to demonstrate the potential of using an on-site mobile chemical laboratory (MCL) to support the CF during deliberate operations in a national counter-terrorism deployment.

Results: Beginning in October 2005, the chemical detection and identification group at DRDC Suffield began the development of a MCL using available in-house resources. In May 2006, the laboratory's capabilities were evaluated while working with NATO and the Joint National CBRNE response team during live agent chemical warfare training exercises. The laboratory was able to receive, handle, analyze and identify vesicant and nerve agents collected by sampling teams during training scenarios.

Significance: The MCL was designed to perform rapid on-site identification of CW agents allowing the on-scene commander to make meaningful decisions. The ability to rapidly identify CW agents in less than 60 minutes provided the CF with a capability that was previously lacking in the field.

Future Plans: The MCL was designed to demonstrate the potential of on-site CW agent identification as well as serve as a learning platform for the methods, techniques and instrumentation which could be used in a field environment. With the successful demonstration of the laboratory it is intended to take the lessons learned and design and build a production version of the laboratory to support CF operations.

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Sommaire

Introduction : Les Forces canadiennes (FC) et les forces de leurs alliés peuvent être déployées, nationalement ou internationalement, dans des théâtres où il existe une menace d'agents de guerre chimique et biologique. Les FC requièrent des capacités de détection et d'identification d'agents de guerre chimiques pour être en mesure d'opérer efficacement dans ces théâtres. On utilise actuellement un nombre limité d'instruments installés sur place pour l'identification d'agents de guerre chimiques sur le terrain. Les échantillons doivent être emballés et transportés vers un laboratoire hors site, pouvant se situer à des milliers de kilomètres, si on requiert une analyse plus en profondeur. RDDC Suffield a initié un projet démontrant quel serait le potentiel d'utiliser un laboratoire chimique mobile (LCM) sur place pour soutenir les FC durant les opérations délibérées d'un déploiement national anti terroriste.

Résultats : Le groupe de détection et d'identification chimique de RDDC Suffield a commencé à développer un LCM, en octobre 2005, en utilisant les ressources internes disponibles. On a évalué les capacités du laboratoire, en mai 2006, durant les exercices de formation avec agents toxiques chimiques réels, lors des travaux avec l'OTAN et l'équipe nationale mixte d'intervention CBRNE. Le laboratoire a été capable de recevoir, manipuler, analyser et identifier des agents vésicants et neurotoxiques recueillis par des équipes d'échantillonage durant des scénarios d'entrainement.

Portée des résultats : Le LCM a été conçu pour effectuer une identification sur place rapide d'agents de guerre chimiques qui permet au commandant sur les lieux de prendre des décisions efficaces. La capacité à identifier rapidement les agents de guerre chimiques en moins de 60 minutes fournit aux FC une capacité qui, jusqu'à présent, manquait dans ce domaine.

Perspectives d'avenir : Le LCM a été conçu pour démontrer le potentiel de l'identification d'agents de guerre chimiques sur place et pour servir aussi de plateforme d'apprentissage pour les méthodes, techniques et instrumentation qui pourraient être utilisées sur le terrain. La démonstration du laboratoire ayant été réussie, on envisage de tenir compte des leçons acquises pour concevoir et construire une version finale du laboratoire ayant pour but de soutenir les opérations CF.

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Introduction

February 1941 saw the establishment of a chemical warfare experimental station in Suffield, Alberta. The site was a combined United Kingdom-Canadian station following the loss of a United Kingdom-France joint station in Algeria in 1940. For more than 65 years DRDC Suffield has provided the Canadian Forces (CF) with an ability to conduct independent research and development in chemical and biological defence. Integral to this research has been the ability to detect and identify chemical warfare (CW) agents in a variety of man-made and environmental matrices.

With the end of the Cold War and the entry into force of the UN Chemical Weapons Convention, the threat of battlefield use of CW agents has diminished. However, there remains a concern over the possible use of CW agents by terrorists both domestically and internationally in theatres where the CF might be deployed.

The identification of CW agents has traditionally been carried out in specialized laboratories staffed with personnel trained and experienced in the safe handling of toxic materials. In addition, the laboratories are equipped with analytical instrumentation which can identify the agents in the presence of many background interferents. While these laboratories can provide the highest level of identification possible, there still remains one major drawback. Typically these laboratories would not be located near the site of a chemical incident. Therefore, before the samples can be analyzed, they must be packaged and transported to the laboratory. In a country the size of Canada, this could mean a distance of thousands of kilometres. In the case of retrospective analysis, where the identification is required for political or criminal reasons this time delay may not be significant. For the commander on the scene of a CW incident, the requirement for timely and accurate identification is much more critical. This information could dictate the medical treatment a casualty should receive, or impact the type and duration of decontamination a site requires before it can be returned to civil authorities.

At the scene of a CW incident, decisions on crisis and consequence management would in part be based on information obtained from CW agent detectors. These detectors have rapid response times, are relatively sensitive and easy to operate. Detectors typically generate a response based on a single characteristic of the chemical agent and this lack of selectivity may result in false positive responses. Chemical identification, on the other hand, is based on analysis of the molecular structure of the agent. The advantage therefore is that the level of certainty in the identification is much higher and the number of false positives much lower.

At the present time, the CF may be called upon to respond to the use of toxic materials (including CW agents) in both domestic and international arenas. Internationally the CF would likely be deployed as part of a coalition under the command of NATO. Within NATO, there is a requirement for deployable analytical laboratories to identify possible CBRN agents [1]. In NATO standardization agreement (STANAG) 4632, the concept of use and capabilities of such laboratories are outlined. A NATO deployable chemical laboratory should be able to identify the traditional chemical warfare agents their precursors and decomposition products as well as a limited number of toxic industrial chemicals.

Domestically, the CF would likely deploy to a terrorist event in support of the civil authorities as part of the National CBRN Response Team. Part of the support could involve the provision of a MCL. Up until the end of 2005 there was no mobile chemical identification capability available to the CF. The national CW agent identification laboratory, located in DRDC Suffield in Alberta, is a fixed-site laboratory capable of providing reach-back identification of CW agents for the CF. In October 2005, the Chemical Detection and Identification Group (CDIG) at DRDC Suffield initiated a project to develop a prototype MCL. The objective behind this project was twofold: to assess whether an on-site chemical agent identification capability would enhance the CF's ability to operate in a chemically contaminated environment and to provide the CDIG with a test platform to study the problems of transferring chemical warfare agent identification technologies from the laboratory to the field.

This report describes the development of a prototype MCL using in-house DRDC Suffield resources. The capability was based on five elements: a suitable mobile platform, people, agent target list, instrumentation, and field appropriate analytical methods. Each of these five elements is described in relation to the final laboratory and examples of on-site CW agent identification during the deployment of the chemical laboratory in field exercises are described.

Mobile Laboratory Platform

At the outset, it was recognized that in order to demonstrate the potential of on-site CW agent identification, it would be necessary to have an appropriate platform from which to carry out the analysis and identification. Such a platform would need to be able to receive, store, handle and analyze toxic samples. In order to meet these requirements several platform options were considered.

One option was to use transport containers which would be capable of storing the various analytical instruments and sample handling equipment. Such containers could be shipped by commercial aircraft to any destination around the country. Once at that location they would require transportation and physical infrastructure (building, power, water, gas) prior to becoming operational. Such flyaway systems have been and continue to be employed by response teams in support of deployed military forces as well as by inspectors for the Chemical Weapons Convention [2, 3]. The main limitation of such systems is that not all sites can provide the appropriate infrastructure to sustain their operation.

Another solution would be to use a functioning transportable shelter with all required instrumentation. Options for such a shelter could include military sea containers or specialized mobile trailers which would have an increased cost and could still require infrastructure at the site of the incident.

The platform selected for the prototype MCL was simplified by the availability of an existing mobile trailer at DRDC Suffield. Figure 1 illustrates a 35 foot trailer that had been used at DRDC Suffield in the 1990s for biological aerosol sampling. The trailer had originally been outfitted to provide a laboratory work area for biological sampling and analysis instrumentation. In addition, it was equipped with running water and an on-board diesel generator as well as the capability of connecting to shore power. Figure 2 illustrates an internal view of the trailer showing the laboratory benches running along both sides and an office area at the far end of the trailer.

A number of exterior and interior modifications to the platform were required in order to meet the needs for CW agent handling. Two fumehood motors, each with a two metre exhaust stack, were installed on the roof of the laboratory. The stacks could be removed and stored during transport of the MCL. The interior modifications included some changes to laboratory services (power, gas, etc) as well as structural changes.

An anteroom located at the main entrance to the trailer was used for sample reception and sample preparation. A one metre fumehood was installed in this room in order to perform initial sample handling and screening with CW agent detectors (typically a chemical agent monitor (CAM) and a portable contamination test apparatus (AP2C)). In this area the samples and accompanying documentation were photographed and detailed information on the sample (type, detector response, originators sample number, etc.) was compiled. It was in this area that the headspace screening of the sample would be conducted using solid phase microextraction (SPME). By performing sample preparation in the anteroom, it was possible to ensure that only low concentrations of CW agents were brought into the main compartment of the laboratory for analysis.

Figure 1. *Mobile Chemical Laboratory platform*

The main compartment contained the analytical instrumentation used to identify the CW agents and related compounds. In this compartment of the laboratory (which can be seen in figure 2) a 1.3 metre fumehood was installed which would hold any subsamples, extraction solvents, etc. In order to operate all of the instrumentation, it was necessary to increase the electrical supply from 60 to 100 amperes with the corresponding modifications to the electrical connections. Once completed the electrical system could provide both 110 and 220 volts, as required.

While developing the concept for the MCL, the CDIG was well aware that techniques and instrumentation which worked in a fixed site laboratory might not work as well in a mobile environment. This prototype offered the opportunity to assess both instrumentation and procedures under field conditions. These procedures included sample preparation requirements, speed of analysis, quality of data, power requirements, physical footprint, and consumables.

Figure 2. *Internal view of the Mobile Chemical Laboratory platform, showing work benches and office area prior to installation of analytical equipment and fumehoods.*

People

Perhaps the most critical component to the success of a project such as the MCL was the people who staffed the laboratory. For the field demonstration, two defence scientists and three chemical technologists were drawn from existing members of the CDIG. All had a background in chemistry and their education ranged from technical school to doctorate degrees. Some individuals had over 25 years experience in the area of handling and identification of toxic materials such as CW agents.

During field operations, a four member crew manned the laboratory, of which two people would perform sample reception, photography, documentation and headspace sampling. Two other people would perform sample analysis, data interpretation, agent identification, and reporting. The experience of the lab personnel allowed each member to carry out any of these functions.

Laboratory personnel also maintained radio communications with the command post. This ensured that information on the arrival of suspect samples and the subsequent agent identification was properly transmitted to the on-scene commander.

The MCL staff had to function as a team. Because of the inherent dangers of CW agents, it was important that each staff member be aware of the safety of every member of the team starting from the time the samples were received in the laboratory until they were neutralized following agent analysis. Members were encouraged to propose changes to the sample handling process in order to make it safer as well as more efficient. DRDC Suffield's analytical laboratory procedures for sample handling and analysis were adapted for use in the mobile laboratory environment. In addition, because samples tended to arrive in batches at the laboratory, analytical methods were modified to increase sample throughput. All these changes were the result of and dependent on the experience and efforts of the laboratory staff.

In addition to providing CW agent identification, the MCL staff also acted as on-site scientific advisors to the on-scene commander. With access to information on toxic materials, their physiological effects, decontamination requirements, etc., the staff provide a unique asset for the on-scene commander during the crisis and consequence phases of an incident.

Agent Targets

When transitioning from a fixed site to a mobile laboratory it was necessary to recognize that, due to limited space for equipment, a mobile laboratory would have a more limited agent analysis capability.

NATO has described in Standardization Agreement (STANAG) 4632 the requirements for a deployable NBC Analytical Laboratory [1]. The document describes a laboratory capable of analyzing nuclear, biological and chemical agents. In practice, this laboratory would likely be composed of three modules to analyze the three different types of agents. In the STANAG, the general capabilities of the deployable laboratory are described, along with the general tasks it would be expected to carry out in support of a NATO mission. Table 1 is a target list of CW agents that the deployable laboratory should be able to identify at the NATO "confirmed" level.

Table 1. *Target CW Agents*

COMPOUND	SYNONYM(S)
Vesicants	
H	HD, Sulphur Mustard, Bis (2-chloroethyl)sulphide
Q	Sesquimustard, Bis(2-chloroethylthio)ethane
T	O-Mustard, Bis(2-chloroethylthioethyl)ether
HN-1	Nitrogen Mustard, Bis(2-chloroethyl)ethylamine
HN-1	Nitrogen Mustard, Bis(2-chloroethyl)ethylamine
HN-2	Nitrogen Mustard, Bis(2-chloroethyl)methyl amine
HN-3	Nitrogen Mustard, Tris(2-chloroethyl)amine
L1	Lewisite, Lewisite I, 2-chlorovinyldichloroarsine
L2	Lewisite II, Bis(2-chlorovinyl)chloroarsine
L3	Lewisite III, Tris(2-chlorovinyl)arsine

Nerve Agents	
DFP	Diisopropyl phosphorofluoridate
GA	Tabun, O-ethyl N,N-dimethyl phosphoramidocyanidate
GB	Sarin, isopropyl methylphosphonofluoridate
GD	Soman, Pinacolyl methylphosphonofluoridate
GF	Cyclosarin, cyclohexyl methylphosphonofluoridate
VX	O-ethyl S-2-diisopropylaminoethyl methylphosphonothiolate

NATO Allied Engineering Publication (AEP) 10 describes the NATO concepts and guidelines for the sampling and identification of chemical and biological agents as well as the criteria to be used for the identification of CW agents [4]. While originally designed for fixed site laboratories, these criteria are equally applicable to deployable laboratories. The prototype MCL would be expected to identify CW agents to the NATO "confirmed" level.

The three levels of identification with increasing levels of certainty were defined in AEP-10 as:

PROVISIONAL IDENTIFICATION: A chemical warfare agent may be considered provisionally identified when one of the following criteria has been met:

I The chromatographic retention data acquired for the chemical warfare agent measured using two columns with different stationary phases matches that of a known chemical warfare agent; or

II The chromatographic retention data acquired for the chemical warfare agent with a specific detector (FPD, TID, AED) matches that of a known chemical warfare agent.

CONFIRMED IDENTIFICATION: The identification of a chemical warfare agent is confirmed when one of the following criteria has been met:

I A complete spectrum acquired using a single spectrometric technique (MS, NMR or IR) matches the corresponding reference spectra in a database. If the molecular ion is not present in the mass spectrum, techniques such as chemical ionization must be carried out to confirm the molecular mass of the compound; or

II The chromatographic retention data acquired for the chemical warfare agent during mass spectrometric analysis using selected ion monitoring (minimum of three ions) matches that of an authentic reference standard. The ratio of the three ions must fall within 10% of the values of an authentic reference standard run under identical experimental conditions in consecutive analyses. The ions should have coincident maxima, the same peak width at half height and exhibit a signal to noise ratio greater than three.

UNAMBIGUOUS IDENTIFICATION: Unambiguous identification provides the highest level of certainty required for the development of strategic positions. The identification of a chemical warfare agent is unambiguous when the following criterion has been met:

I The chromatographic retention data acquired for the chemical warfare agent and spectra acquired using two different spectrometric techniques (GC-MS, LC-MS, NMR or IR) match those obtained for an authentic reference standard under identical experimental conditions in consecutive analyses. If the molecular ion is not present in the mass spectrum, techniques such as chemical ionization must be carried out to confirm the molecular mass of the compound.

While these criteria are currently under review by the NATO Sampling and Identification of Biological, Chemical and Radiological Agents (SIBCRA) sub-group, they were used as the guidelines for this project.

Given the limited time available to develop the capability demonstrator it was decided, that for the duration of the field demonstration of the prototype MCL, to focus on identification of the classical CW agents: H, GB, GA, GD, GF and VX. During further development of the MCL, the agent target list could be expanded to include all compounds listed in STANAG 4632.

Analytical Identification Equipment

The decision on what analytical identification equipment would be used in the MCL was based initially on practicality. The instrumentation had to be available in-house at DRDC Suffield and not currently required for any ongoing research project. The MCL platform offered a unique opportunity to assess the capabilities, robustness and limitations of laboratory equipment in a field environment. For this reason it was also decided to use as many different types of instrumentation as possible. From this field experience, the best equipment would be selected for the final fielded version of the laboratory.

A number of potential instruments were identified and the final selection of instrumentation was related to the agent targets (classical nerve and blister agents) that would be analyzed in the MCL. These compounds are volatile or semi-volatile organics which can be analyzed by gas chromatography (GC). While GC can separate the components of a mixture, a means to detect and identify the components is still required. Numerous gas chromatographic detectors are commercially available such as the flame ionization detector (FID) and the flame photometric detector (FPD). These detectors are robust and sensitive and in combination with GC can provide provisional (but not confirmed) identification as outlined in the NATO identification criteria.

The technique of choice for the confirmed identification of organic compounds continues to be electron impact mass spectrometry. With this technique the structure of a compound can be elucidated by either fundamental interpretation of the acquired mass spectral data or by comparison to electronic libraries containing hundreds of thousands of mass spectra. When dealing with a mixture of compounds the combination of gas chromatography and mass spectrometry (GC-MS) provides a powerful tool for the identification of CW agents The applications of GC-MS for the analysis of CW agents has recently be reviewed [5,6]. Both GC-MS and GC-FID/FPD instrumentation were installed in the MCL. The GC-FID/FPD was an Agilent 6890 gas chromatograph equipped with both FID and FPD. The GC-MS was an Agilent 6890 gas chromatograph interfaced to an Agilent 5973N mass spectrometer capable of both electron impact and chemical ionization. The gas chromatograph was modified by replacing the standard oven door with an RVM module which housed a resistively heated GC column.

Another technique which can provide confirmed identification is the combination of liquid chromatography and mass spectrometry (LC-MS). This technique has been increasing used in the analysis of nerve agents and CW degradation products [7,8]. The principal difference between GC and LC is that in GC the sample must be vaporized prior to separation and in LC the sample must be a liquid or dissolved in a liquid prior to separation. Because LC does not require a sample to be vaporized it can be used for the separation of thermally labile or low volatility compounds (e.g. CW agent hydrolysis products). However, the samples must be stable in the solvent used to dissolve the analyte (typically water). The LC-MS installed in the MCL was comprised of an Agilent 1100 LC coupled to a Waters/Micromass LCT Time of Flight mass spectrometer.

The final instrument used in the MCL was an attenuated total reflectance (ATR) infrared spectrometer. The area of spectroscopic detection of CW agents has recently been reviewed by Petryk [9]. The ATR spectrometer used in the MCL was a TravelIR currently sold by Smiths Detection and is similar in operation to other ATR devices such as the HazmatID [10]. With these instruments, a sample of a liquid or solid is placed on the sample stage of the instrument, the infrared spectrum for the sample is acquired, and identification is based on the comparison to an on-board electronic library. One difficulty in this type of analysis is there is no separation of sample components prior to acquisition of the infrared spectrum; therefore if the sample is a mixture, the resulting spectrum will be a combination of the spectra of the pure compounds.

Identification Methods

In general, the identification methods normally employed by the DRDC Suffield CDIG formed the basis of those initially used in the MCL. The identification methods consisted of multiple steps: sample handling, preparation, analysis, identification, and reporting.

Sample handling methods were based on the agent procedures in place at DRDC Suffield. The sample receiving area was stocked with decontaminant, medical countermeasures (HI-6 and reactive skin decontaminant lotion) and chemical agent detectors (CAM and AP2C). All samples that were received by the MCL were immediately placed in a fumehood prior to any further sample handling. Samples were then unpackaged, photographed and documented using either information provided by the sampling team and/or results from the initial CW agent detector screening.

Next, the most appropriate sample preparation method was selected. Sample preparation (the process of liberating the analyte from the matrix and ensuring the sample is amenable to instrumental analysis) is typically the longest step in the identification method. Traditionally, sample preparation uses a solvent to extract the analyte(s) of interest from the matrix. This process can take in excess of 30 minutes per sample.

As rapid identification of CW agents was required, it was decided that initial sample preparation would be performed using a solid phase microextraction (SPME) fiber. The fiber is comprised of a solid support coated with either an absorbent or adsorbent which samples the headspace above a liquid or solid. SPME requires little sample preparation, minimizes matrix interferents and can be very rapid (in the order of seconds). Analysis of the absorbed/adsorbed analytes is typically carried out by GC-MS, where the analytes are thermally desorbed from the SPME fiber into the capillary GC-MS column [11-15]. While headspace extraction using SPME is a versatile technique, it is restricted to volatile and semi-volatile compounds. Within the MCL there was equipment for solvent extraction of less volatile compounds that could be present in contaminated samples.

As was the case for sample preparation, fast sample analysis is also a requirement in MCL operations. While temperature programmed GC-MS runs can typically take 30 minutes, low thermal mass capillary column assemblies have recently been introduced which can be temperature programmed at rates greater than 75°C/min. In such cases, a 30 minute analysis can be performed in less than 5 minutes. Thus, by combining SPME and fast GC-MS, it is possible to achieve rapid CW agent identification in a MCL.

Field Identification Using the Mobile Chemical Laboratory

Once the interior and exterior renovations to the MCL had been completed, the analytical equipment was installed and the laboratory prepared for its initial capability demonstration. In May 2006, it was moved to the Cameron Centre Complex on the DRDC Suffield Experimental Proving and positioned next to Building 93. The initial demonstration was scheduled to take place during a three-week live-agent training exercise (Exercise King Cobra, June 5-23 2006) with the National CBRN Response Team. This team is composed of elements of the DND JNBC Company, the RCMP and the Public Health Agency of Canada. It was proposed that the DRDC Suffield MCL would provide CW agent identification for the team, as well as scientific advice to the response team commander. This exercise would also provide an opportunity to assess how the MCL could be integrated into the operations of the response team.

One of the stated goals of this project was to determine whether an on-site CW agent identification capability would augment the current operations of the National CBRN Response Team in the field. Two examples of sample handling, preparation and analysis are detailed in the following paragraphs, which help illustrate the potential of on-site identification. The first is an example where the MCL confirmed the information that was provided by CW agent detectors. The second is an example where conflicting answers were obtained with different CW detectors and the MCL was capable of providing identification of the unknown substance.

Suspected Mustard Sample

During Exercise King Cobra a sampling team from the National CBRN Response Team collected, from an artillery shell, an aliquot of a liquid sample onto a cotton-tipped plastic swab. The swab was then placed in a screw cap vial and packaged in a series of heat-sealed RCMP evidence bags for transport. Upon receipt in the MCL, the sample package was placed in the fumehood in the sample receiving area for subsequent documentation. Sample labels were printed with a unique identifying number (MCL060621-08). Photographs of the package were taken prior to opening the outermost evidence bag. As each successive evidence bag was opened, the interior of the bag was checked for CW agents with both a CAM and an AP2C and the detector response was recorded. In this case no response was observed on either detector from any layer of packaging.

Figure 3 shows a photograph of the sample data sheet that was included in the evidence bag containing the sample. The original sample number assigned by the sampling team (00006) is visible in the top right hand corner of the figure. When logged into the MCL, the sample was assigned the sample number “MCL060621-08” and a label with this number was affixed to the sample data sheet. In the “Hazards Detected” section of the data sheet, the sampling team has indicated that positive responses for mustard were obtained with a CAM (4 bars in H mode), three way detector paper (red) and the TIMs detector (4 bars in Sulphur mode). From this information, the MCL staff might presume that the sample was sulphur mustard.

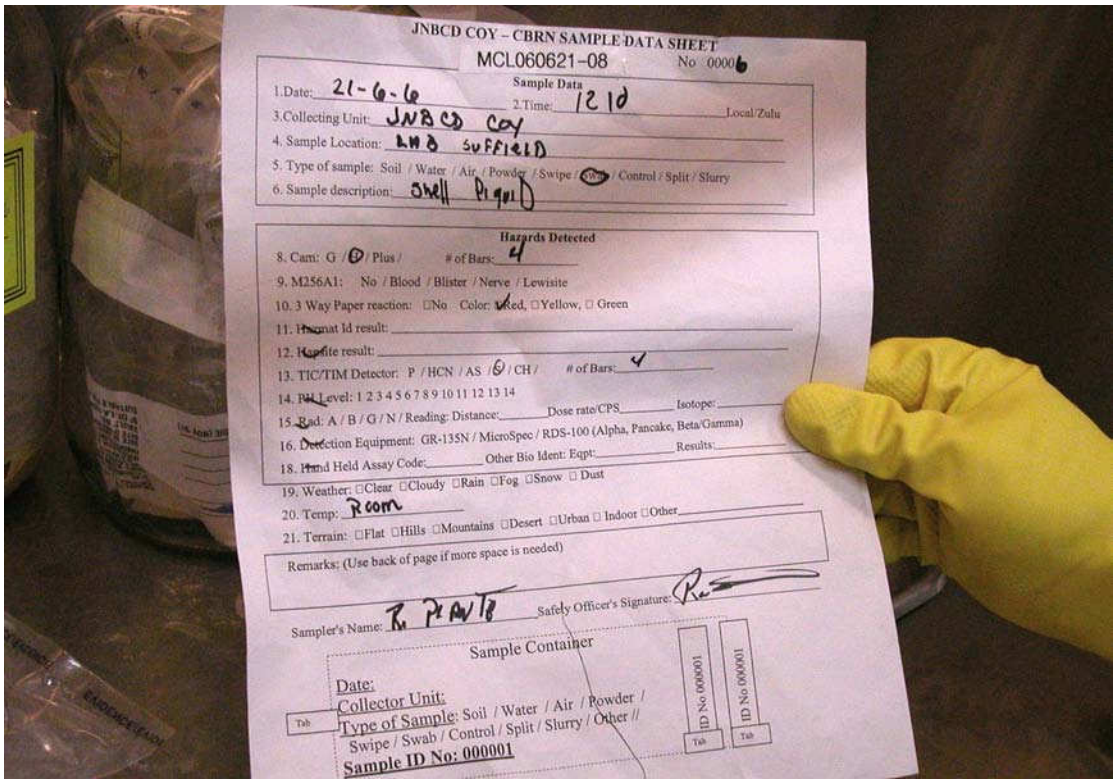

Figure 3. *Sample data sheet for sample 0006 (lab number MCL 060621-08, suspected mustard sample). Information indicates positive responses on CAM, 3-way detector paper and TIMs detector for a mustard type compound.*

Figure 4 shows a photograph of the primary sample container after it had been removed from the evidence bag and labeled with the same MCL sample number as the data sheet. In the photograph the plastic swab can be seen inside the vial which was sealed using an open-top screw cap with a septum. This cap allowed an SPME needle to be inserted into the vial without the vial contents being exposed to the atmosphere. This approach minimized the need for the analysts to directly manipulate potentially toxic compounds. Once inserted into the vial, the SPME fiber was exposed to the headspace in the vial for 1-10 seconds. After this sampling time, the needle was removed from the vial.

The SPME holder was then transferred to the analysis area of the laboratory where the sample was analyzed by SPME-GC-MS. In this procedure the SPME needle was inserted into the heated injection port (200°C) of the GC-MS and the SPME fiber was extended. The analytes on the fiber were thermally desorbed and transferred by the GC carrier gas to the capillary column. The column was then temperature programmed from 40°C to 250°C at 75°C/min. As the analytes eluted from the column, their mass spectra were acquired by the mass spectrometer.

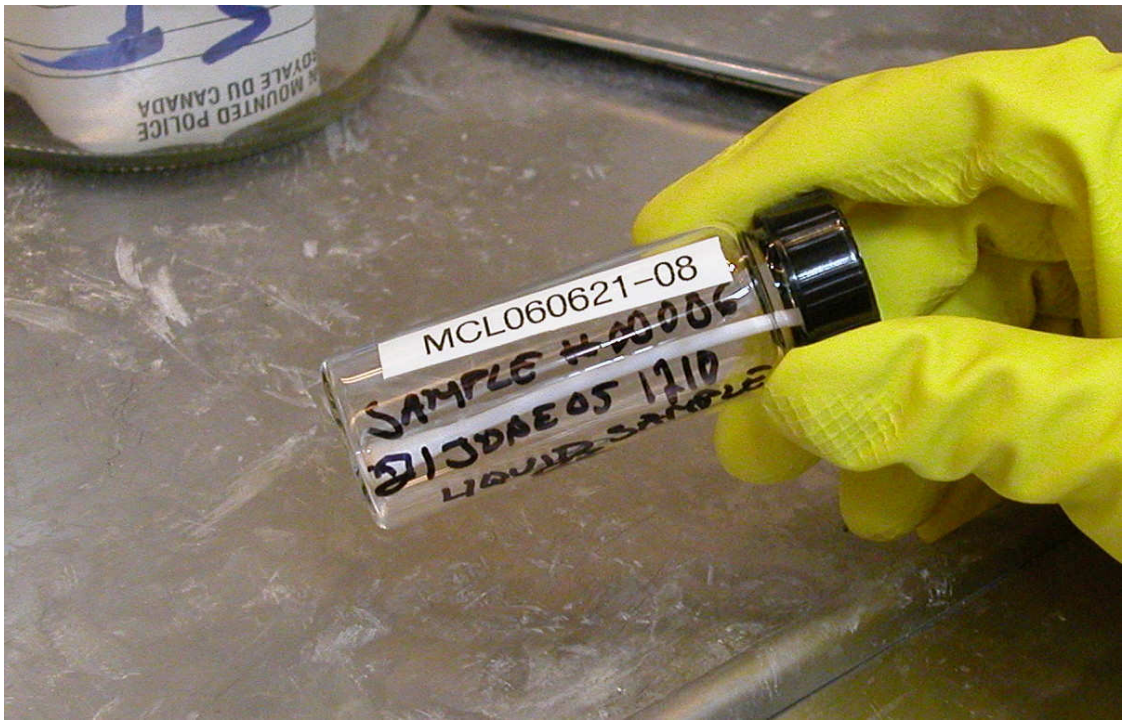

Figure 4. *Primary container (headspace vial) containing cotton tipped plastic swab suspected of containing mustard.*

Figure 5a illustrates the total ion current chromatogram acquired during the SPME-GC-MS analysis of the headspace contained in sample MCL060621-08. The major peak in the chromatogram has a retention time of 3.9 minutes which corresponds with that for a standard of sulphur mustard. Figure 5b illustrates the electron impact mass spectrum acquired for the peak at 3.9 minutes. This mass spectrum contains ions at m/z 158, 109 and 63 and on visual inspection, is similar to that obtained from an analytical standard of sulphur mustard. The resulting mass spectrum was also found to match that for sulphur mustard found in the NIST library.

From the acquired data, it was possible to identify sulphur mustard, at the NATO confirmed level, as the principle component in the headspace of sample MCL060621-08. This finding is in agreement with the detector responses acquired by the sampling team.

Figure 6 illustrates the Chemical Analysis Report that was submitted to the response team commander for sample MCL060621-08. It contains both the laboratory sample number as well as the sample number assigned by the sampling team. Additional information on the sample type and any descriptors used by the sampling team are also included. The report indicates that mustard was identified at the NATO confirmed level in the sample using SPME-GC-MS. In addition it indicates that the sample was also screened for the CW agents; GA, GB, GD, GF, HD and VX.

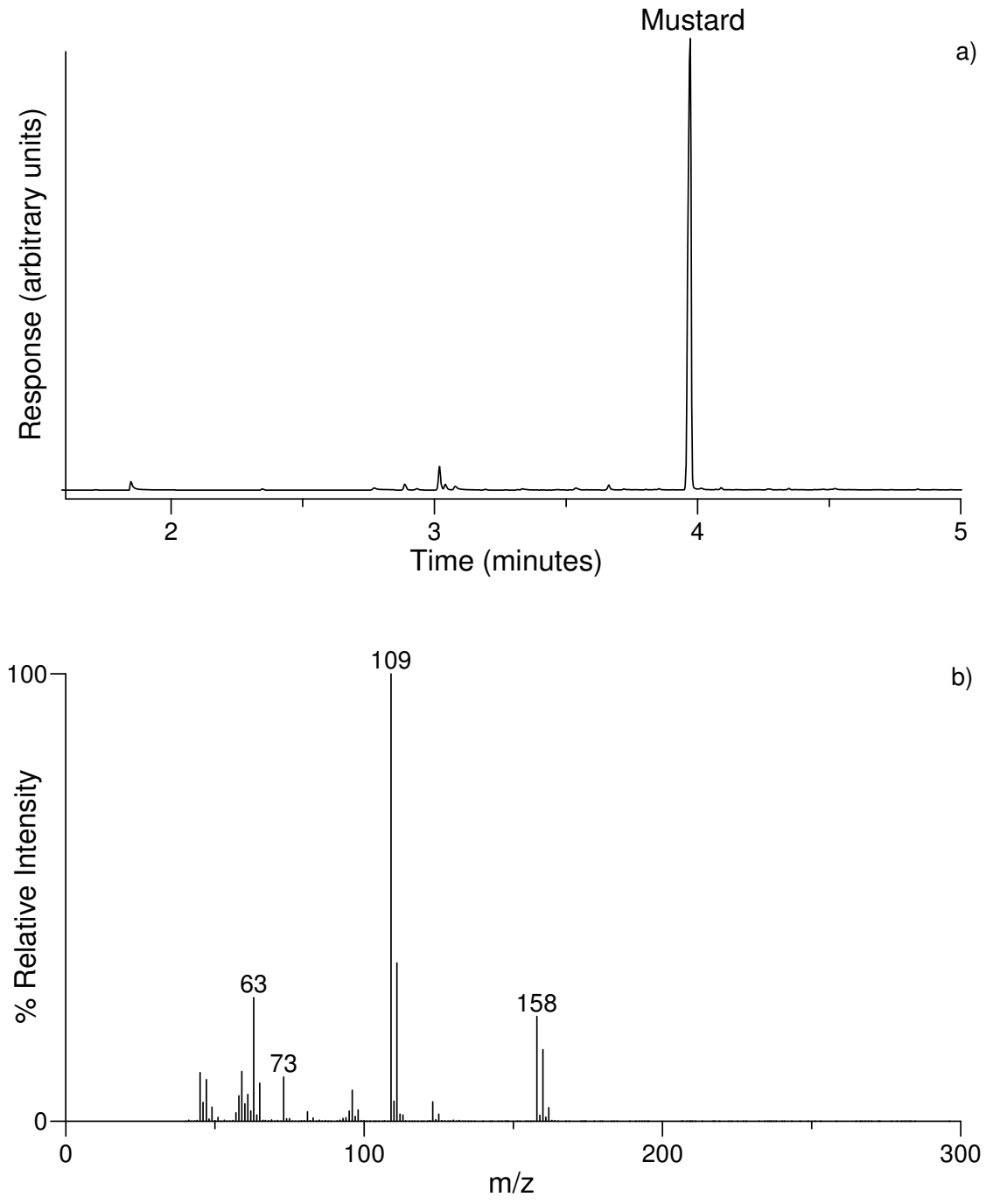

Figure 5. *SPME-GC-MS headspace analysis of a suspected mustard sample (MCL060621-08). a) Total ion current chromatogram acquired using a temperature program of 40°C(90s)/75°C/min/250°C(30s) and b) electron impact mass spectrum acquired for major component at 3.9 minutes.*

Chemical Analysis Report

ORIGINATOR'S ID# 00006	**MCL ID# MCL060621-08**
Originator's Sample Description: Shell liquid	
Receipt Time: 13h00 2006/06/21	Sample Type: swab
Report Time: 14h41 2006/06/22	

Compound Identified: Mustard

NATO Level of Identification: Provisional ☐ Confirmed ☑ Unambiguous ☐

Identification Techniques: SPME-GC-MS

Agents Targeted

☑ Tabun (GA)	☑ Cyclosarin (GF)
☑ Sarin (GB)	☑ Mustard (HD)
☑ Soman (GD)	☑ VX

Comments:

Analyst Signature: Date: 2006 June 22

Figure 6. *Chemical Analysis Report for laboratory sample number MCL060621-08.*

Suspected Nerve Agent Sample

The second example was a clear liquid provided to the MCL by the RCMP as part of the Joint National CBRN Response team during Exercise King Cobra. This sample was packaged in a series of heat-sealed RCMP evidence bags and upon receipt was placed in the MCL fumehood for documentation and processing. CW agent detectors were used to monitor for contamination in each layer of packaging as it was opened. Figure 7 shows a photograph of the sample data sheet provided with the sample. The original sample number assigned by the sampling team (AN3) is visible in the top right hand corner of the figure. When logged into the MCL, the sample was assigned the sample number "MCL060621-04" and a label with this number was affixed to the sample data sheet. According to the information provided on the sample data sheet, an ECAM (enhanced CAM) exposed to the sample generated a 5 bar response in G mode, indicating a potential nerve agent of either the G or V-class. The sampling team also recorded a green colour response from 3-way detector paper, indicating a possible V class nerve agent. Based on the data available from two sources, the MCL staff might presume that the sample could contain a V-class nerve agent.

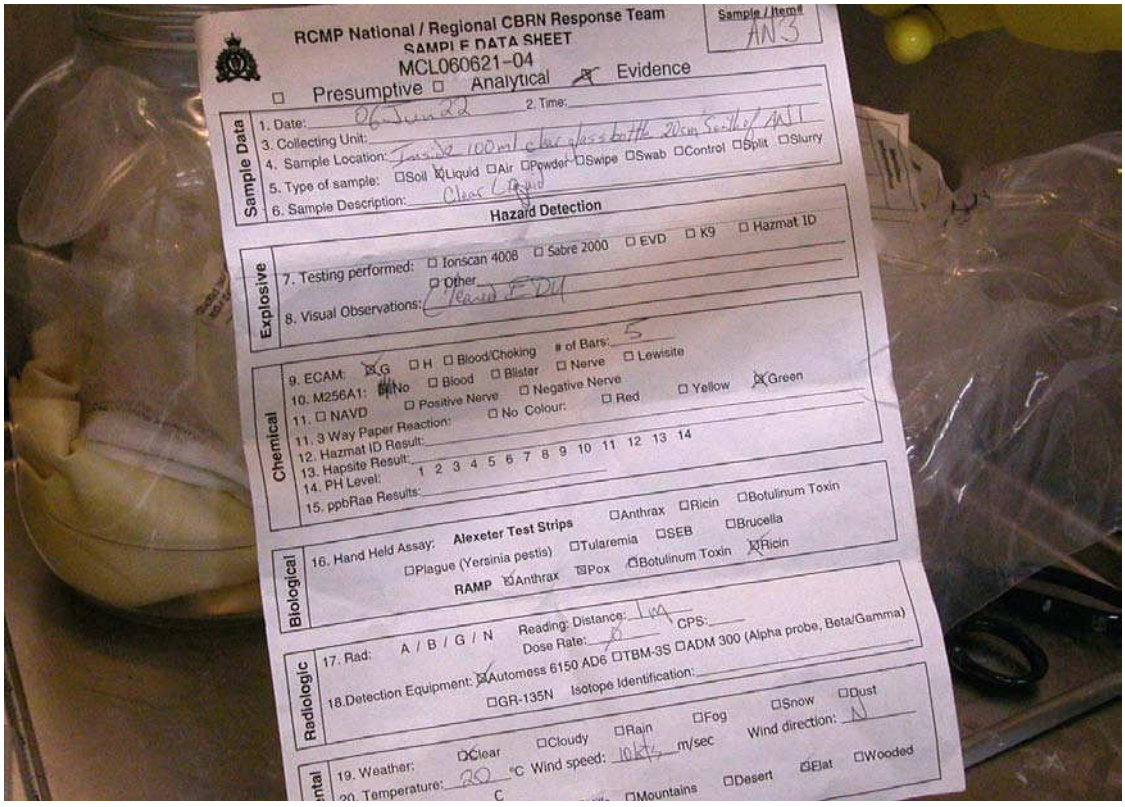

Figure 7. *Sample data sheet for sample AN3 (lab number MCL060621-04, suspected nerve agent sample). Information indicates positive responses on CAM and 3-way detector paper for nerve agent type compound.*

Figure 8 shows a photograph of the vial that was used as the primary container for the sample. The vial was labeled "AN3" by the sampling team and the MCL labeled the sample "MCL060621-04" to correspond with the label on the sample data sheet. The vial was constructed of clear amber glass with a standard solid screw cap meaning that the vial would need to be opened in order to gather a SPME headspace sample. When the vial was opened, a CAM and a TIMs detector were used to monitor the contents. The CAM produced a 4 bar G mode response (replicating the sampling team's observation) as well as low reactant ion peak (RIP) indication. This low RIP signal is not uncommon in G mode and along with the 4 bar response could indicate the presence of a G or V agent. When checked with a TIMs detector, no response was obtained on the phosphorous channel. If this was a volatile nerve agent, a positive response would be expected. However, for a compound such as VX which has a low vapor pressure, it is possible that no response would be observed. The TIMs detector also produced a 3 bar response on the HCN channel. This channel, while normally used for blood agents, also gives some response to nitrogen containing compounds. This was the first indication that the might not contain G or V agents.

Figure 8. *Primary container for sample AN3 (lab number MCL060621-04). Vial contained clear liquid suspected of being a V-class nerve agent.*

Due to the fact that the sample vial was fitted with a solid screw cap instead of an open-top screw cap with a septum, a 30 second SPME headspace sample had to be collected from the opened vial. Figure 9a illustrates the total ion current chromatogram obtained during the SPME-GC-MS headspace analysis of sample MCL060621-04. It indicates the presence of numerous compounds, with the major component having a retention time of 1.9 minutes. This retention time does not correspond with that for the targeted G or V nerve agents. This was strong evidence that the sample did not contain any of the classical nerve agents. However it did not rule out the possibility that this could have been some other organophosphorous compound such as a pesticide. The full scanning mass spectrum acquired for this major component is illustrated in Figure 9b. The highest mass ion in the spectrum is observed at m/z 101, suggesting that this could be a nitrogen containing compound (as also suggested by the TIMs detector response). When this mass spectrum was searched against the NIST database the best match was triethylamine, a nitrogen- containing compound with a molecular mass of 101 Daltons.

Figure 10 illustrates the Chemical Analysis Report that was submitted to the response team commander for sample MCL060621-04. It contains both the laboratory sample number as well as the sample number assigned by the sampling team. Additional information on the type of sample and any descriptors used by the sampling team are also included. The report indicates that triethylamine was identified at the NATO confirmed level in the sample using SPME-GC-MS. In addition it indicates that the sample was also screened for the CW agents; GA, GB, GD, GF, HD and VX.

These examples illustrate how through the use of a capability such as the MCL, it is possible to either confirm the results obtained with chemical detectors or to correctly identify compounds which may have produced false positives with these detectors. The ability to rapidly identify CW agents and related compounds can influence an on-scene commander's decision for medical countermeasures, decontamination or level of personnel protective clothing required.

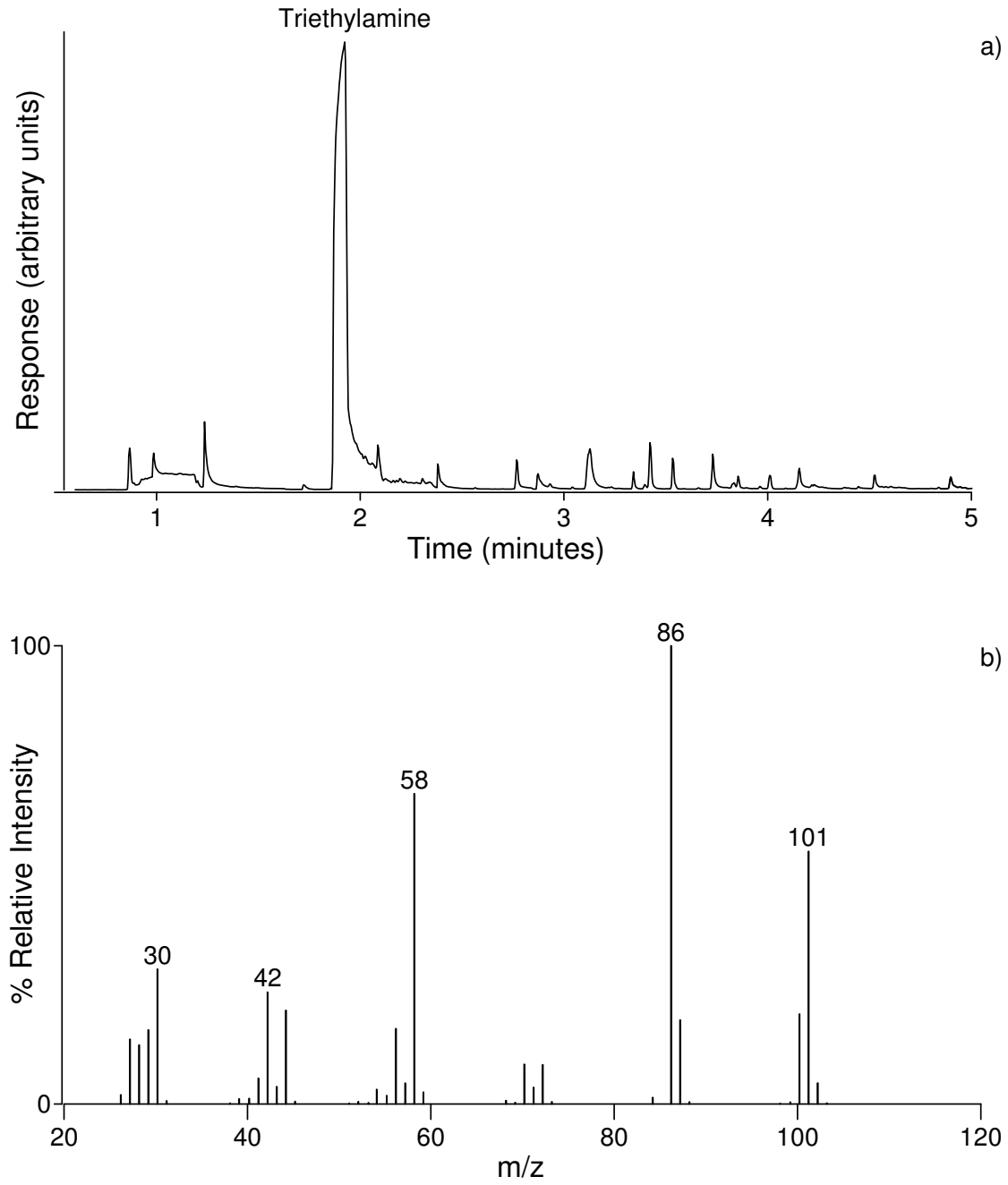

Figure 9. *SPME-GC-MS analysis of the headspace above a suspected nerve agent sample (MCL060621-04). a) Total ion current chromatogram acquired using a temperature program of 40 ℃(90s)/ 75 ℃/min/250 ℃(30s) and b) electron impact mass spectrum acquired for major component at 1.9 minutes.*

Chemical Analysis Report

ORIGINATOR'S ID# AN-03	**MCL ID# MCL060621-04**
Originator's Sample Description: **Clear Liquid**	
Receipt Time: 1232	Sample Type: **liquid**
Report Time: 1430	

Compound Identified: **Triethylamine is major component**

NATO Level of Identification: Provisional ☐ Confirmed ☑ Unambiguous ☐

Identification Techniques: SPME-GC-MS

Agents Targeted

☑ Tabun (GA)	☑ Cyclosarin (GF)
☑ Sarin (GB)	☑ Mustard (HD)
☑ Soman (GD)	☑ VX

Comments:

From RCMP Sample Datasheet suspect G agent (CAM) and VX (3-Way paper).

Did field testing indicate Soman??

Analyst Signature: Date:

Figure 10. *Chemical Analysis Report data sheet for laboratory sample number MCL060621-04*

Conclusions

This technical memorandum has described the concepts behind the development of a prototype MCL. This laboratory was designed and built using existing in-house resources at DRDC Suffield with the principal elements being a suitable platform, people, a list of agent targets, analytical identification equipment and methods.

The MCL was deployed during the summer of 2006 in order to demonstrate to the CF the potential of on-site CW agent identification, through live CW agent training. During these exercises, the laboratory provided on-site CW agent identification and the MCL staff also acted as on-site scientific advisors to the on-scene commander. With access to information on toxic materials, their physiological effects, decontamination requirements, etc., these people provide a unique asset for the commander in crisis and consequence management.

Examples have been presented of the capability of a MCL to either confirm the results obtained with chemical detectors or to identify compounds which produced false positives with these detectors. A second Technical Memorandum will describe the operation of the MCL in the field, and the problems encountered with the existing platform design, as well as detailed information on the sample handling and analysis methods used during live CW agent exercises.

References

1. NATO STANAG 4632 Deployable NBC Analytical Laboratories, Edition 1, 2004, UNCLASSIFIED

2. Heyl, M. (1996). Globetrotting with a Modular GC/MS Laboratory. *Field Analytical Chemistry and Technology* 1 (1), 3-12.

3. Mogl, S. (2005). Chemical Weapons Convention Chemicals and Analysis, Sample Collection Preparation and Analytical Methods. M. Mesilaakso (Ed.), *Sampling and Analysis in the Chemical Weapons Convention and the OPCW Mobile Laboratory*, pp 7-31, Sussex, England, John Wiley and Sons.

4. NATO Allied Engineering Publication (AEP-10), Volume 1, Edition 5, 2000, UNCLASSIFIED.

5. Hooijschuur, E.W.J., Kientz, C.E. and Brinkman U.A.T. (2002). Analytical separation techniques for the determination of chemical warfare agents**,** *Journal of Chromatography A***,** 982 (2), 177-200.

6. Wils E.R.J. (2005). Chemical Weapons Convention Chemicals and Analysis, Sample Collection Preparation and Analytical Methods. M. Mesilaakso (Ed.), *Gas Chromatography/Mass Spectrometry in Analysis of Chemicals Related to the Chemical Weapon*, pp 249-281, Sussex, England, John Wiley and Sons.

7. Black R.M. and Read R.W. (2005). Chemical Weapons Convention Chemicals and Analysis, Sample Collection Preparation and Analytical Methods. M. Mesilaakso (Ed.), *Liquid Chromatography/Mass Spectrometry in Analysis of Chemicals Related to the Chemical Weapons Convention*, pp 283-320, Sussex, England, John Wiley and Sons.

8. D'Agostino P.A. (2005). Recent advances and applications of LC-MS for the analysis of chemical warfare agents and their degradation products – A review, *Trends in Chromatogr.,* 1, 23-42.

9. Petryk M.W.P. (2007). Promising Spectroscopic Techniques for the Portable Detection of Condensed-Phase Contaminants on Surfaces, *App. Spec. Reviews,* 42 (23) 287-343.

10. Ong K.W., Baldauf, F.C.Carey, L.F. and Amant, D.C. (2003). Domestic Preparedness Program: Evaluation of the Travel*IR* HCI™ HazMat Chemical Identifier, ECBC–TR-355, Research and Technology Directorate, Aberdeen Proving Ground, MD., USA.

11. Schneider J.F., Boparai, A.S., and Reed L.L. (2001). Screening for Sarin in Air and Water by Solid-Phase Microextraction-Gas Chromatography-Mass Spectrometry, *J. Chrom. Sci.,*39 (10), 420-424.

12. Kimm G.L., Hook, G.L., and Smith P.A., (2003). Application of headspace solid-phase microextraction and gas chromatography-mass spectrometry for detection of the chemical warfare agent bis(2-chloroethyl) sulfide in soil, *J. Chromatogr. A.,* 971, 185-191.

13. Hook G.L., Kimm, G., Betsinger G., Savage, P.B., Swift, A., Logan, T., and Smith, P.A., (2003).Solid phase microextraction sampling and gas chromatography/mass spectrometry for field detection of the chemical warfare agent O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX), *J. Sep. Sci.,* 26, 1091-1096.

14. Smith P.A., Jackson Lepage C.R., Koch, D., Wyatt H.D.M., Hook, G.L., Betsinger, G., Erickson, R.P., and Eckenrode, B.A., (2004). Detection of gas-phase chemical warfare agents using field-portable gas chromatography-mass spectrometry systems: instrument and sampling strategy considerations, *Trends in Anal. Chem.,* 23 (4), 296-306.

15. Smith P.A., Sng, M.T., Eckenrode, B.A., Leow, S.Y., Koch, D., Erickson, R.P., Jackson Lepage, C.R., and Hook, G.L., (2005). Towards smaller and faster gas chromatography-mass spectrometry systems for field chemical detection, *J. Chromatogr. A.,* 1067, 285-294.

List of symbols/abbreviations/acronyms/initialisms

DND	Department of National Defence
MCL	Mobile Chemical Laboratory
CW	Chemical Warfare
DRDC	Defence Research and Development Canada
SPME	Solid Phase Microextraction
GC-MS	Gas Chromatography-Mass Spectrometry
LC-MS	Liquid Chromatography-Mass Spectrometry
ESI	Electrospray Ionization
NATO	North Atlantic Treaty Organization
STANAG	Standardization Agreement
CAM	Chemical Agent Monitor
ECAM	Enhanced Chemical Agent Monitor
CBRN	Chemical Biological Radiological and Nuclear
RIP	Reactant Ion Peak
TIMs	Toxic Industrial Materials
CDIG	Chemical Detection and Identification Group
AEP	Allied Engineering Publication
SIBCRA	Sampling and Identification of Chemical Biological and Radiological Agents
AP2C	Portable contamination test apparatus
HCN	Hydrogen cyanide

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   Development of a Mobile Chemical Laboratory

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In October 2005, the chemical detection and identification group at DRDC Suffield initiated a project to develop and field a prototype mobile chemical laboratory. This laboratory was designed to demonstrate the potential advantages of on-site chemical warfare (CW) agent identification in providing rapid information to an on-scene commander. This paper describes the various elements (i.e. platform, target agents, equipment, methods and people) that were required to deploy such a laboratory, as well as examples of the sample handling, analysis and identification of CW agents and related compounds during CW agent field exercises.

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