ORNL/TM-10346
AD

ornl

OAK RIDGE
NATIONAL
LABORATORY

MARTIN MARIETTA

Technology Assessment for the Determination of Chemical Agent Vapors in Demilitarization Facilities

FINAL REPORT

M. P. Maskarinec
M. B. Wise
M. V. Buchanan

Supported by

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
Aberdeen Proving Ground, Maryland 21010-5401

Project Officer: Greg Mohrman

Approved for public release;
distribution unlimited

The findings in this report are not to be construed as an official Department of Army position unless so designated by other authorized documents.

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A04; Microfiche A01

ORNL/TM-10346
AD ____________

TECHNOLOGY ASSESSMENT FOR THE DETERMINATION OF CHEMICAL AGENT VAPORS IN DEMILITARIZATION FACILITIES

M. P. Maskarinec, M. B. Wise, and M. V. Buchanan

Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6120

FINAL REPORT

SUPPORTED BY

U. S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
Aberdeen Proving Ground, Maryland 21010-5401

Project Officer: Greg Mohrman

Date Published: January 1987

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
Under Contract DE-AC05-84OR21400

EXECUTIVE SUMMARY

A survey of analytical methods for the determination of chemical agents GB, VX, and HD was made. Included were methods capable of providing for monitoring requirements at the time weighted average (TWA) and allowable stack concentration (ASC) levels in near real time. A review of the currently used automatic continuous air monitoring system (ACAMS) was made as well as a review of the recently developed atmospheric pressure ionization mass spectrometry (APIMS). This report recommends a strategy for research and development for near term and medium term improvement of the overall monitoring program.

TABLE OF CONTENTS

LIST OF TABLES

BACKGROUND

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is charged with the development of technology for the decontamination and disposal of obsolete chemical weapons. The munitions include rockets, shells, and others, and generally contain the agents HD, GB, and VX. HD, or mustard, is bis-2-chloroethyl sulfide, and is classified as a blistering agent. GB, or Sarin, is isopropyl methyl phosphonofluoridate. VX is O-ethyl-S-(2-diisopropylaminoethyl)methylphosphonothioate. Both GB and VX are nerve agents. Pilot-scale tests are already being conducted at Tooele Army Depot using an incineration process. Because of the extreme toxicity of these compounds, it is necessary to provide monitoring capability at extremely low levels in the workplace, in the exhaust gas (stack), and in the incinerator flue gas. The goals of the monitoring program are to assure that no agent is being released into the environment and to protect the plant workers from accidental exposure. These goals require that the monitoring procedures be not only highly sensitive, but also that they be capable of providing information in real time. With these constraints and goals in mind, USATHAMA commissioned Aerospace Corp. to perform a thorough evaluation of analytical techniques suited for this purpose. This report, published in April, 1983, was a very thorough treatise on the analytical chemistry of these agents and made the recommendation that atmospheric pressure ionization mass spectrometry (APIMS) be developed as the best hope of meeting the monitoring requirements. Such an instrument was designed and constructed, but met with limited success. Therefore, this work was initiated with the following objectives:

1. To review the Aerospace document and its recommendations.
2. To assess any recent additions to the list of potential monitoring technologies.
3. To consider the limitations of the existing APIMS system and identify any possible corrective actions.
4. To consider the possibility of performing all monitoring from a centrally located monitor.

Monitoring requirements. The guidelines for monitoring are based on threshold levels established by the U.S. Army Surgeon General. These are listed in Table 1.

These levels are quite low, and represent a challenge for analytical methods *per se*, but the challenge is magnified by the requirements of instantaneous response in the stack, and less than two minutes in the workplace and flue gas. Furthermore, false positives must be minimized, there must be no false negatives, and the monitor must provide maximum sample time coverage. Finally, the technology must be mature and well suited to commercial production in less than 18 months.

Table 1

Monitoring Requirements for Chemical Agents (mg/M^3)

Compound	Workplace	Stack Gas	Hot Flue Gas
HD	3×10^{-3}	3×10^{-2}	3×10^{-2}
GB	1×10^{-4}	3×10^{-4}	3×10^{-4}
VX	1×10^{-5}	3×10^{-5}	3×10^{-5}
Response Time (Desired)	2 min.	15 sec.	2 min.

This report is organized into three sections. The first section deals with a number of techniques which appear to have applicability to chemical agent monitoring and are therefore mature, but still limited in terms of the current requirements. The second section deals with problems identified in the S-Cubed APIMS and suggestions for corrective actions. The third section deals with considerations of sample transport, sample preconcentration, and sampling problems specific to the matrices of interest. Because of the similarity between this report and the report produced by the Aerospace Corp., techniques will be considered in roughly the same order. Additionally, references to work which are provided in the Aerospace report will not be repeated here.

SECTION I: METHODS WITH POTENTIAL UTILITY BUT LIMITATIONS

Ion Mobility Spectrometry. Ion mobility spectrometry (IMS) relies on the migration of ions through a gas under the influence of an applied electric field. The ions are separated on the basis of mass or mobility and a "spectrum" of ion masses is obtained which is comparable to a mass spectrometer spectrum. Because the ions are migrated through a gas, mass resolution is inherently low. Such a system is therefore prone to interferences, and will produce false positives. Additionally, the sensitivity which can be obtained under the best conditions is a factor of 100 higher than that required for VX monitoring. The response, however, is instantaneous and continuous-very desirable qualities. Thus, the IMS falls into the class of techniques which have possibility as agent monitors if appropriate preconcentration systems can be devised. The Aerospace report concluded that continuous concentrating methods were the only possibility due to the high duty cycle (30 Hz). This is not necessarily the case. The IMS could be used in conjunction with a concentration system such as a solid sorbent tube or wire desorber (described in detail on page 26). If such a system were assembled, the concentrator unit could be configured to provide selectivity improvement as well, and perhaps would overcome the major drawbacks associated with the use of IMS for agent monitoring. Such a system could be configured so that the IMS provides a continuous readout at a higher level while the concentrator collects sample, and the concentrated sample could be introduced at periodic intervals. Thus, the possibility of both high level alarm and TWA monitor exist. The matrices of the stack and hot flue gas should provide no more problems for this technique than any of the alternative methods.

Recommendation: No utility without additional work on preconcentration.

Thin Film Colorimetry. The Aerospace report deals extensively with the optical spectroscopy of the agents, and that discussion will not be repeated. However, several new techniques will be discussed. The first is thin-film colorimetry (1). In this instrument, a thin film (Poroplastic) is used to encapsulate color-forming reagents. The gas sample is allowed to diffuse through this film, and the color change is monitored using a miniature double-beam absorbance spectrometer. The Poroplastic film is an ultramicroporous cellulose triacetate, which is capable of retaining 70 to 90% of almost any liquid. Thus, any chemistry can be used for purposes of detection. In the cited work, diisopropyl fluorophosphate was tested, as a simulant for the nerve agents. The color scheme involved the catalytic hydrolysis of the P-F bond using benzhydroxamic acid, followed by the colorimetric determination of the fluoride ion using zirconium chloride and alizarin. Phosphate ion also provides a colorimetric response in this system, actually enhancing the detection process. The advantages of this system for the detection of agents over previous colorimetric systems are rapid response (due to the high diffusion rate through the film), and little interference from extraneous components. The tested range of the system was 0.5 - 5 ppm, but the ultimate detection limits were not reported. Such a system does have the advantage of operating in an integrating mode, that is, the color produced is the result of total exposure to agent over time. For purposes of an eight hour TWA or ASC, this could conceivably be of use as an adjunct to other monitoring systems. Drawbacks include the need to replace the reagent after an agent challenge, the lack of known color reactions for HD, and the possibility that phosphate could interfere. Agent determination would also be on the basis of one system for each agent. The author suggests that phosphate and fluoride do not penetrate the film, although this must be verified for the stack and flue gas matrices, since high concentrations of these materials will be present.

Recommendation: Unlikely to meet the requirements of sensitivity, but might serve as an adjunct.

Frequency-Modulated Laser Infrared Spectrometry (FMLIR). This is a technique which, although relatively immature, shows promise for real-time measurement of the various chemical agents. All work done at this time has been theoretical (2), and no agent testing has been accomplished. FMLIR consists of the modulation of a laser beam, generating two frequency sidebands, and passing this modulated signal through a cell. There will be absorption of the two sidebands if the center frequency falls on the shoulder of an absorptional transition in the molecule of interest. By mixing techniques, a DC signal can be generated which is proportional to the differential absorption, and thus to the concentration of the agent. Therefore, FMLIR represents an elegant method for the determination of very small changes in absorbance in the infrared regime. It is important to note, however, that the measurement is still being made in the infrared, and although the sensitivity figures are impressive, all the constraints of infrared spectroscopy still apply. Foremost among these is the need for absolute water removal. In the referenced work, it is pointed out that all calculations on the signal to noise ratios for the various agents assume negligible contribution to the signal by water absorption, and that the presence of water at even low humidities essentially saturates the system. Effects of other interferences, such as agent impurities and breakdown products, are also considered. These are thought to be of little consequence, although this is probably not realistic. Thus, if the gas sample can be completely dried, this technique will easily attain the required sensitivity for GB and HD, and will closely approach the value for VX. Response time would be essentially instantaneous. However, it is difficult to envision a system for water removal without agent loss, even in the workplace environment. The agents GB and HD could possibly be enriched in a dry stream by adsorption/desorption, or some other form of preconcentration, but VX will likely be lost in such an arrangement. Conversion of the VX to the G-analog would require a second feasibility study on the detectability, although the principle should be appropriate. If, however, there is to be a preconcentration/water removal step in the monitor, the advantages of real-time analysis are lost, and numerous other less esoteric techniques would be comparable. Furthermore, with no data on the use of the technique in any real matrix, the selectivity cannot be adequately assessed. Inherently, selectivity will rely on the presence of materials having absorbance transitions in the region of interest, and it is likely that such interferences will exist, particularly in the stack and hot flue gases. An additional consideration is that simultaneous monitoring for the three agents will be difficult, and the equipment required will be sophisticated.

Recommendation: Further work is not warranted at this time, although there is potential applicability.

SECTION II: CHROMATOGRAPHIC TECHNIQUES

Chromatography implies that a separation in time takes place within a column. A distribution between two (at least) phases causes solute molecules to move at differing rates. The stationary phase can be either a solid (adsorption chromatography) or a liquid (partition chromatography). The mobile phase can be a gas (GC), a liquid (LC), or a supercritical fluid (SFC). In any combination of the above, a time must elapse between the introduction of the sample and the passage of the desired solute through the detection device. Thus, there are <u>no</u> chromatographic techniques capable of meeting the requirements of the instantaneous stack monitor. On the other hand more practical data has been generated using chromatographic methods than any other class of techniques, and this data can be used to make realistic assessments of the possibility of reducing the analytical and sampling time to meet the requirements.

Chromatographic systems all have in common three "modules". There is a sample introduction system (injector), a separation system (column), and a detector module. Depending on the application, there are general considerations in the design of the total system. For the applications covered here, there exist several possibilities. The detector module is the key element in the system, since both sensitivity and selectivity are ultimately defined by the detector. Several possibilities exist for the detection of chemical agents:

1. Flame Ionization Detector (FID): The FID is a nonselective detector, generally responding to compounds on the basis of carbon content. No selectivity, but responsive to all agents. Ultimate sensitivity inadequate, would require sample preconcentration. Useful with GC or SFC, possibly with LC. Inexpensive and rugged.

2. Flame Photometric Detector (FPD): The FPD is the most widely used detector for the determination of the agents HD,GB, and VX, because of its high sensitivity and selectivity for organophosphates and organosulfur compounds. Ultimate sensitivity inadequate, requires sample preconcentration. Useful primarily with GC, but has been coupled with both SFC and LC. Most expensive of the selective GC detectors, but reliable and rugged.

3. Photoionization Detector (PID): The PID uses UV irradiation to ionize solute molecules with subsequent current measurement. Selectivity depends on the ionization potential of the solute, with lower ionization potentials having greater selectivity. Could be used for all three agents. Sensitivity inadequate, although more improvement can be expected here than for the flame based detectors. Primarily a GC detector, although could be used in SFC. Rugged, reliable and portable, and does not require supporting gases. Average cost.

4. Electron Capture Detector (ECD): The ECD is based on the capture of electrons by the solute molecules, causing a

reduction in the background current. Highest ultimate sensitivity of any detector, but response is determined by the electron capture cross section of the solute of interest. Should give high sensitivity with HD, response for the organophosphates is difficult to predict. Selectivity will be lacking, with the detector actually being quite universal. Useful exclusively with GC. Moderately expensive and notoriously unreliable.

5. Redox Chemiluminescence Detector (RCD). This is a relatively new detector, based on the post-column reactions of analytes with nitrogen dioxide on a heated gold catalyst to nitric oxide. The nitric oxide formed is detected by the chemiluminescence resulting from its subsequent reaction with ozone. Has been used for organophosphate pesticides and organosulfur compounds (3). Very high sensitivity and excellent selectivity. Depending on the reaction chemistry, could be used for GC, SFC, or LC. Rather complicated, and although no data on ruggedness is available, reliability is questionable. Expensive to operate.

6. Nitrogen/Phosphorus Detector (NPD): The NPD is based on electron emission from an alkali metal salt after contact with nitrogen or phosphorus containing radicals formed from the solute molecules in a cool flame. Could provide sensitivity equal to the FPD for GB and VX, but unsuitable for HD. Useful only for GC. Inexpensive and relatively reliable.

Many other less extensively used detection schemes are available, although none possess the capability to detect the agents with sufficient sensitivity, with the possible exception of laser-excited fluorescence detection. This technique require the formation of a fluorescent derivative, and the sensitivity and selectivity are dependent on the nature of this derivative. The conclusion reached here is that the FPD offers the best hope for meeting the requirements of agent monitoring currently, and that developments of the PID and RCD offer the possibility to exceed the performance of the FPD. These developments are at least two years away.

In terms of separation technology, the Aerospace report gives a thorough description of the available options, and only an update will be provided here. GC column technology development has been primarily in the area of wide-bore fused silica capillary columns. Commercially available columns of diameter 530 um now provide higher resolving power and similar capacity to packed columns. When installed in conventional instruments, these columns can either provide higher speed or increased resolving power (at the discretion of the analyst). These columns have been shown to be fairly rugged, and can be reproducibly fabricated. They also offer the flexibility required to determine the three agents on the same column, along with any impurities present. Any new gas chromatographic system developed should consider strongly the use of these columns.

Commercially available capillary SFC columns have also been recently introduced. These columns have diameters of 50 - 100 um, and are generally limited in capacity. The arguments put forth in the Aerospace report against the use of capillary GC columns are particularly appropriate here: higher preconcentration factors and increased system complexity. It is interesting to note that packed column SFC has been largely abandoned by the analytical community. Hewlett-Packard had introduced a packed column SFC unit and has now withdrawn the unit from the market. This is largely due to the fact that no analytical advantage exists for packed SFC over HPLC, other than a slight increase in speed, and system complexity is unquestionably greater in the SFC case. The only advantage of SFC over HPLC is the ability to couple with ionization detectors with relative ease.

Major improvements have been made in column technology for HPLC. The advent of particles of 3 um diameter, now available from a wide variety of vendors in a wide variety of bonded phases, has allowed the development of high-speed chromatographic systems. Efficiencies equal to that generated on the analytical columns of yesterday are now obtained in as little as one-tenth the time, and the sensitivity of the detectors has been increased because of the increased concentration of the solutes in the detected band. Unfortunately, the technology for HPLC detection has not kept pace with the column technology, and there is still no detector with adequate sensitivity.

Sample introduction techniques have made no great strides in the period of time following the Aerospace report, and are still largely related to the separation process. In GC, the sample can be introduced as a gas through a sampling loop, as a liquid through a septum injector, or desorbed thermally from a preconcentrator. For SFC, the constraints are that the sample must be injected as a liquid, preferably in the mobile phase. The fact that only very small volumes can be used severely limits this technique for ultratrace analysis. HPLC requires the sample to be introduced in the liquid phase as well, although large preconcentration factors are possible with the use of small precolumns. The process is analogous to that used for thermal desorption GC, with the liquid sample passing through the precolumn, retention of the agents on the precolumn, and then removal of the agents with the mobile phase.

Automatic Continuous Air Monitoring System (ACAMS). Although the ACAMS was not specifically covered in the Aerospace report, this has been the most widely used instrument for the determination of the agents at the TWA levels in near real time. Therefore a discussion of the merits and drawbacks of this system is appropriate here. The discussion assumes that VX will not be monitored directly, but rather as the G-analog after passage through a conversion filter. The merits of direct vs. indirect measurement are apparent, but there seems to be no way to chromatograph VX directly. In terms of the analytical chemistry involved, the ACAMS is relatively crude. However, the unit meets the sensitivity requirements of the various determinations, even the stack, and is lacking in the ability to simultaneously determine the three agents, and in response time. In view of the demonstrated reliability of the unit, it is recommended that alternative but related designs be considered for the purposes of enhancing multiagent capability and improving response time.

The ACAMS uses a sorbent tube to preconcentrate the agent from the sample stream, followed by a gas chromatographic separation with flame photometric detection. There are three problems with multiagent determinations:

1. Sorbent tubes. Different sorbent tubes are used: Chromosorb 106 for the VX and GB, and Tenax GC for HD.
2. Separation. The current packed column cannot resolve GB and the G-analog of VX.
3. Detection. The FPD currently monitors either sulfur or phosphorus, but not both.

It is not clear why these sorbents were chosen, but it should be possible to effectively adsorb all three agents with a single sorbent tube. The tube could contain a single sorbent or a number of sorbents in series. For example, GB and the G-analog of VX are more volatile agents, and would therefore be prone to break through earliest. It would appear that the HD, being less volatile, would be difficult to quantitatively desorb from the sorbent. A possible solution to the collection problem is to use a small amount of Tenax GC, followed by the normal amount of Chromosorb 106. The GB and G-analog would be collected on the Porapak-Q, and the HD on the Tenax. The desorption would be done with the flow in the reverse direction from the sampling, and all three compounds would be efficiently desorbed. There is a precedent for this type of system in the EPA water method for volatile organic compounds. In this method, a three-step trap is used: 3% SP-1000 on Gaschrom-Q for the heavier compounds, followed by Tenax for the more volatile compounds, and finally by Silica gel for the very light materials. This arrangement has the additional advantage of providing higher total capacity for the agents, since breakthrough is much less likely with the higher capacity adsorbents at the end of the trap. In fact, it may be well worthwhile to consider the use of the standard EPA trap in the ACAMS without modification. There has been one additional development in terms of adsorbent development. A new carbon-based material: Carbotrap, has been introduced and touted as an all-purpose adsorbent for adsorption/thermal desorption systems. This material is reported to have capacity well in excess of Tenax, but to be capable of quantitatively desorbing trace quantities of high-boiling compounds. Because of the increased capacity, smaller amounts of adsorbent are used, and direct desorption onto a capillary column is possible. There is currently no experience with this material with respect to agent analysis, although this information could be obtained rather easily.

In terms of the separation, it seems entirely possible to provide adequate separation of all analytes with a commercially available wide-bore capillary column (see earlier discussion in Section II). Such a column will not compromise analysis time or sample capacity, and may actually shorten the separation time. In addition, the increase in efficiency means that the solute bands will be presented to the detector in higher concentrations, lowering the detection limits. Selectivity will also be improved by virtue of the fact that peak resolution will be improved. The net result should be a much more flexible analytical system. The price to be paid is in ruggedness: column lifetime is likely to be much shorter than the current column. However, the improved performance is worth the price of off-the-shelf capillary columns.

By comparison with the first two problems, the simultaneous detection difficulty is trivial to overcome. A second photomultiplier tube will provide the ability to detect sulfur and phosphorus directly, without compromising performance. This modification should be considered immediately.

The second major area of limitation in the ACAMS is the response time. The response time is defined by the time from the initiation of sampling to the FPD response. In addition, it is necessary to consider the additional time until the unit is ready for the next sample. Thus, the turnaround time is dependent on the combination of the following:

1. Preconcentration time
2. Analysis time
3. System reequilibration time

By far the most significant contribution to the turnaround time is the preconcentration or sampling time. This is the time required for the collection of adequate sample for the detection of the agent at the level required. Because of the lower level of detection required, this time is greatest for the agent VX. There are basically two approaches to the reduction of the preconcentration time:

1. Improve the sensitivity of the detector.
2. Increase the sample flow rate.

As mentioned earlier, improvements in the detector sensitivity can be expected from improvements in column efficiency, although these will be modest gains compared to that which is required. It is highly unlikely that intrinsic modifications to the FPD will result in the necessary improvements, since this has been a long-term goal of the instrument manufacturers. Thus the reduction in analysis time which is required will probably come most easily by increasing the sample preconcentration rate. For purposes of discussion, it is assumed that a decrease of 1000% in the preconcentration time would bring the ACAMS into compliance with the requirements for workplace and hot flue gas monitoring, and relatively close to those of the stack. This factor of ten can be accomplished by increasing the diameter of the sorbent tube to 3/8" (from the current 1/8") and increasing the linear velocity by about ten percent. The reason that the current unit uses 1/8" traps is to avoid degradation of the chromatographic process by virtue of thermal nonequilibration of the larger diameter trap, primarily during desorption. This problem can be overcome by including valves at either end of the trap such that sample or carrier gas can either flow through the trap or bypass the trap and proceed directly into the analytical column. While the tube is being heated prior to desorption no carrier or sample flow is directed through the trap. After the trap reaches the desorption temperature, the valves are rotated so that the desorption flow proceeds through the trap, usually in the direction opposite to the sample flow. After the desorption is complete, the trap could be raised to a higher temperature and baked out to the atmosphere while carrier gas flows through the column and the analysis proceeds. The trap can then be cooled down using cryogenics or a simple cooling fan. This is essentially the cycle used in commercial thermal desorption units, and easily amenable to the front end of the ACAMS unit. The addition of the valve arrangement would also allow the ACAMS to be sampling during the chromatographic analysis, improving sample time coverage to better than 80 %. With this and the previously mentioned modifications, the ACAMS could meet the requirements for the workplace and flue gas monitors, would be lacking only terms of the response time requirement for the instantaneous stack gas monitor, would be capable of monitoring all three agents simultaneously, and would sacrifice little, if any, of its inherent ruggedness. The drawbacks would continue to be less than instantaneous monitoring of the stack, and indirect monitoring of the VX as the G-analog.

Recommendation. Pursue actively the modifications listed above.

Multiplex Gas Chromatography. Multiplex gas chromatography, or correlation chromatography (4,5) is a technique closely related to that of the ACAMS. In this experiment, sample gas is used as the carrier gas and is swept continuously onto the head of the analytical column. The analytes of interest are concentrated at the head of the column, as they are at the sorbent tube of the ACAMS, and the entrance to the column is periodically heated ballistically to desorb the compounds. As a result, several analyses are proceeding down the column at the same time. A computer is used to deconvolute the chromatogram and produce an individual report for each sampling interval. This technique differs from that of the ACAMS in that the sample time coverage is essentially 100 %. However, like the ACAMS, the response time is limited to the sum of the preconcentration time plus the analysis time.

The reason for inclusion of this technique in these recommendations is sensitivity improvement. The sensitivity improvement comes from two sources:

1. The ability to signal average multiple sample intervals.
2. The ability to preconcentrate at any interval or flow.

The air sampled has the advantage of serving as the oxidant in the FPD, allowing very high flow rates (up to about 0.4 L/min). The column could be designed to take advantage of this fact and still provide adequate resolution. This system has been applied to automotive exhaust as well as to stack gas analysis. The system has never been used for agent analysis nor has it been tested in ultratrace analysis.

Recommendation. Support development work to determine feasibility and degree of sensitivity enhancement.

SFC/FPD. The technique of SFC has advanced rapidly during the two years since the Aerospace report. There are several commercial manufacturers of SFC units. This report has been aided by consultations with representatives from two of these companies: Lee Scientific and Suprex. As mentioned earlier, all applications of SFC have been based on open tubular (capillary) column separations. The limited capacity of these systems makes them unsuitable for the purpose of determination of the agents.The advantages of an SFC system would be:

1. The ability to interface with a liquid film concentrator (described later).
2. The ability to chromatograph VX directly.
3. Reduced adsorptive losses in the system.

These advantages are balanced by the following negatives:

1. Limited capacity would require very high concentration factors.
2. Collection of the sample as a liquid would allow nonchromatographable components to enter the column.
3. The performance of the FPD is not well documented using supercritical mobile phases as the oxidant.

Recommendation. This technique could be useful in the future as a sample collection/preconcentration system. It offers the possibility of direct injection into the FPD for less specific but very rapid response monitoring purposes. It is not at this time capable of meeting the requirements for agent monitoring.

High Pressure Gas Chromatography (HPGC). HPGC was considered as one of the alternatives to the ACAMS in the Aerospace report. As such, the technique really represents only a modification of these units. However, these modifications will most likely complicate matters with the only return being an increase in speed and perhaps the ability to chromatograph VX directly. Suggestions have already been made as to improvements in the speed of the ACAMS, and the ability to chromatograph VX directly is of little consequence if the compound is lost prior to the inlet. Therefore, it is not likely that the requirements for agent monitoring will be met with this technique, nor that the performance of the ACAMS will be significantly improved.

Recommendation. Do not pursue.

High Performance Liquid Chromatography (HPLC). HPLC column technology has made dramatic advances in the last two years, as pointed out earlier. It is estimated that all of the agents could be separated on a 3 um column in less than 1 minute. The peak concentration of the agents would be very high. However, the limitation of HPLC remains the detector. In the Aerospace report, laser fluorescence and the transport FPD were suggested as possibilities for agent detection in HPLC systems. The usual problems still plague the transport detector: memory, sample loss, noisy baseline. Laser fluorescence requires derivatization, and therefore the selectivity is drastically reduced, since many impurities could react with the derivatizing agent to give fluorescent products. However, the power of HPLC for this purpose lies in the ease of obtaining a very high concentration factor and the ease of automating the sample flow system.

HPLC is, of course, directly able to interface with the liquid film concentrator, which can provide concentration factors of up to 1000. Furthermore, the effluent from the concentrator can easily be passed through a precolumn for further preconcentration. It would be possible to attain concentration factors of up to 100,000 with little hold-up time and a reasonable degree of ruggedness. With this level of preconcentration, less absolute detector sensitivity is required. A possibility is the use of dye-assisted absorbance detection (6), where a dye is used to enhance the absorbance of organophosphorus compounds in a post-column reaction system. However, it must be stated that no detection principle for HPLC exists which will allow advantage to be taken of the ruggedness and concentrating ability of the technique.

Recommendation. Consider any unique detection system in view of the power inherent in the technique. It should be relatively inexpensive to demonstrate feasibility for such a system.

General recommendations on chromatographic systems. Because of the large amount of background information on the ACAMS, as well as its historical record of reliability, all chromatography systems must be judged on the degree to which they outperform the ACAMS. It should be noted that many of the modifications proposed for the ACAMS above are already available in commercial instruments. If this is the case, the "modified ACAMS" may well require little or no R & D, and the cost to USATHAMA would be significantly reduced. Still, it must be reiterated that no chromatographic system will meet the response time requirement of the continuous and instantaneous stack gas monitor.

SECTION III: MASS SPECTROMETRIC TECHNIQUES

The technique of mass spectrometry involves, basically, the ionization of sample molecules, separation of the resulting ions, and detection of the ions using ion counting electronics. The general technique is well developed in the Aerospace report and that development will not be repeated here. However, several comments on that description are appropriate.

First, the assertion in that report that mass resolution is insignificant with respect to selectivity is questionable. It is true that ion current will be higher if all ions are collected together, and that in the case of VX much of the ion current will be distributed over the range of 267-275 amu. However, the measurement of an individual mass is far more indicative of the presence of the compound than is the measurement of total ions over an 8 amu range. The work of Battelle (7) indicates that interferences are obtained even at mass 267 in the presence of burning neoprene. Thus, the ability to obtain higher mass resolution is always of importance to mass spectrometry, particularly when the interferences are largely unknown.

Second, the arguments put forth on the inability of the quadrupole mass filter to provide rugged service without compromising sensitivity or mass resolution are largely unconvincing. Even at the time of that report, quadrupoles were assuming a major role in mass spectrometry, from research grade instruments to routine service units. Their ability to function with inexperienced operators and remain in service was well established. The pumping systems were in place to allow proper maintenance of pressure in the mass analyzer unit, without compromising ruggedness. Finally, these were off-the-shelf items.

Third, the description of MS/MS indicates that a marked loss in sensitivity is the result of adding a collisional dissociation region and second mass filter. The increase in selectivity and decrease in background ion current can in many cases make up for this loss. Far too much emphasis was in general placed on the ion transmission characteristics of the system and too little on the meaningfulness of the actual measurement.

From the standpoint of improvements in mass spectrometric instrumentation since the Aerospace report, there have been many. Quadrupoles continue to be refined and developed with respect to ruggedness, mass resolution, and ion throughput. The atmospheric pressure ionization source has become a viable commercial entity. The general area of MS/MS has exploded with applications, secondary ion mass spectrometry (SIMS) has been shown to provide very high sensitivity for the organophosphorus compounds (8,9), and rugged commercial instruments have appeared. The following is an update on the performance of mass spectrometric instruments for the purpose of nerve agent monitoring.

Secondary Ion Mass Spectrometry (SIMS). SIMS and Fast Atom Bombardment Mass Spectrometry (FAB/MS) are usually reserved for analysis of molecules of very low volatility. Samples are usually prepared by dissolving the analyte in a matrix of low volatility such as glycerol, and bombarded with either ions (SIMS) or neutral atoms (FAB/MS). The unique feature of this technique, from the standpoint of the current problem, is the ability to produce mass spectral data, with its usual high sensitivity and selectivity, from the direct analysis of a liquid sample (8,9). The detection limits obtained with simulants were 1.6 x 10^{-11} g for DMMP and 2.9 x 10^{-10} g for DIMP. These limits were obtained using a non optimized source with direct gas introduction. Even so, the limits are impressive. The real power of the technique, however, would be in the development of a flow-through ion source combined with the liquid film collector. The concentration of the gas sample by a factor of 100-1000 would result in detection limits well below those required for any of the agents, including VX, and may well represent the only available method for the determination of VX in the stack gas. Furthermore, the normal SIMS ion source uses a target matrix. The matrix in this case would be concentrated sulfuric acid, although the matrix is not limited to this acid. In addition, for remote monitoring, filter pads could be collected containing agent vapors, the pads dissolved in sulfuric acid, and analyzed for the agent using SIMS. Sampling using the filters could be either active or passive, but the throughput should be very high. The drawbacks of the technique revolve around the limited numbers of investigators in the area, and the lack of commercial SIMS sources. The possibilities for agent determination cannot, however, be overlooked.

Recommendation. Technique is relatively immature in terms of commercial availability, probably 2-3 years away, but has great potential for solving VX monitoring problems, as well as performing adequately for the other agents. Much depends on the suitability of the liquid film collector as a preconcentrator.

Sciex TAGA 6000. This is a commercially available instrument based on the principles of Atmospheric Pressure Ionization (API) and tandem MS/MS (triple Quadrupole). This instrument was extensively tested in the Battelle work (7) for the purposes of determining chemical agents in battlefield scenarios. The instrument performed very well, meeting or exceeding the criteria for agent determination, both in terms of sensitivity and interference rejection. However, the instrument has a very high cost ($416 K) and may well be too complex for field application. Therefore, since this is the only MS based instrument capable of meeting the objectives, it must be used as a standard by which other mass spectrometric techniques can be judged, as can be done with the ACAMS and other chromatographic methods.

It is clear, first and foremost, that design criteria for any APIMS (or, for that matter, any MS unit which could possibly meet the detection requirements) are not at this time available. Therefore, a test of the TAGA 6000 instrument should be conducted at Tooele Army Depot, under realistic demilitarization conditions. This test should be conducted for the purpose of data collection in general as well as an actual performance test of the instrument. The emphasis should be on the evaluation of APIMS and not specifically on the applicability of the TAGA.

In terms of the experimental design, the instrument should be operated in the single sector (single quadrupole) mode for an extended period of time. This will permit an evaluation of the degree of mass resolution necessary for the avoidance of false positives. This information will be required if an adequate assessment of the requirements for a MS analyzer are to be provided. Of course, if a single quadrupole is adequate, the result will be a dramatic price reduction as well as a simplification in operation. An evaluation of the MS/MS arrangement should also be made, particularly in terms of selectivity improvement, and of course, sensitivity. Attention should also be paid to the degree of difficulty in maintaining performance for a multi-sector instrument versus the single sector unit.

The sensitivity considerations are obvious. The data available from previous tests of the TAGA indicate that the detection limits will be satisfactory, even in the stack. This must be verified, not only for the precisely tuned instrument but also for long term stability. Records should be kept on each and every adjustment to the instrument over the time of operation, since it is unlikely that the persons using the instrument at JACADS, for example, will possess the same degree of expertise as the contractor used in this work. The total cost of operation for an APIMS system must include the personnel costs. Furthermore, time spent retuning and recalibrating essentially represents down time, and must be accounted for as such.

While this may seem obvious, it is also important to ensure that the process conditions at Tooele be varied as much as possible to include all likely interferences. If neoprene suits are burned on occasion at the facility, this should be done during the test. All munitions components should be used in the test. Any process conditions which exhibit performance ranges should be varied within those acceptable ranges. Since this test is likely to be expensive, it would seem prudent to have close interaction between the contractor, the Tooele staff, and USATHAMA staff. Careful planning and implementation will result in far more useful data. The data generated in this study should be reviewed and evaluated by competent mass spectroscopists. The primary goal is not to criticize the performance of the TAGA 6000, but to make recommendations on the utility of APIMS in general, and to assess the modifications which can be made to existing instruments for performance improvement in the demilitarization facility environment.

Recommendation. Thoroughly test this instrument with respect to performance in the field. Make every effort to reduce the cost associated with production and to insure that Army personnel will be capable of operating and maintaining the instrument if it is deployed.

Fourier Transform Mass Spectrometry (FT/MS). FT/MS is a highly versatile, extremely sophisticated technique. These instruments exhibit the highest mass resolution (> 1,000,000 at m/z 100) and the widest mass range (> 5000 amu) of any commercial mass spectrometer. In addition, the ability to perform MS/MS and use specific ion-molecule reactions gives this spectrometer a level of selectivity unmatched by any other single sector instrument (10).

In its present state of development, FT/MS is not very compatible with atmospheric monitoring. However, this difficulty could probably be overcome without much effort. The major disadvantages include the high cost of the instrument ($500 K) and the complexity of the system. In addition FT/MS requires a large superconducting magnet which must be constantly cooled with liquid nitrogen and liquid helium. Because of the large physical size of the magnet and the temperature control requirements of the computer, the current generation of spectrometers is not well suited for industrial monitoring.

Recommendation. FT/MS may well provide the sensitivity and selectivity needed for the determination of the chemical agents in the demilitarization environment. However, the instrument is expensive, requires extensive maintenance and operator skill, and is not compatible with the industrial environment. It is also not immediately suitable for atmospheric monitoring. Unless the superconducting magnet can be replaced by a small permanent magnet, this technique will not be useful in the next 2-3 years.

Ion Trap Detector (ITD). The ion trap detector is a relatively recent development in mass spectrometry. The low cost (< $40K) and small physical size are particularly attractive. In addition, this mass filter is quite simple from a mechanical standpoint and apparently requires very little maintenance. Both the mass range and resolution are similar to a quadrupole mass filter.

Most ion trap detectors are currently being employed as detectors for gas chromatography and not as routine mass spectrometers. However, the ITD inherently operates at relatively high pressures, thus making it attractive as a possible mass filter for atmospheric monitoring. Unfortunately, at the present time, there are no atmospheric pressure ionization sources available for the ITD and it is questionable whether or not it will indeed be possible to couple API with such an instrument.

Recommendation. In terms of cost, size, and simplicity, the ITD is an attractive possibility for atmospheric monitoring mass spectrometry.

The technology has not yet been developed to combine API with an ITD but it may be possible in the near future. This instrument should be considered as a mass filter for APIMS but due to the stage of development, it should not be given as high a priority as quadrupole or time-of-flight based instruments.

Laser Based Multi-Photon Ionization Mass Spectrometry. Multi-photon ionization is a powerful means of selectively ionizing certain compounds present in a mixture. Ions are formed by irradiating the molecules of interest at a wavelength that enables them to absorb energy. By pumping enough photons of the correct frequency into the molecule, the excited electron may reach an energy level greater than the ionization potential and will be removed, thus forming a positive ion. Since the wavelength of light required to do this depends on the structure of a molecule, only the molecules of interest will be efficiently ionized. These ions can then be detected by a mass spectrometer for additional identification.

The advantages of MPI as an ion source for mass spectrometry include the increased selectivity and, usually, a reduction of the number of fragment ions formed relative to electron impact ionization. However, the use of MPI for atmospheric monitoring has not been thoroughly investigated. Also, the need for a high-power laser would require significant maintenance and increased cost of the system.

Recommendation. Multi-photon ionization is attractive on the basis of selectivity. The maintenance requirements are a major concern. This technique should be considered with lower priority than API mass spectrometry.

Bruker MEM Mobile Mass Spectrometer. The MEM is a rugged, quadrupole based, atmospheric monitoring mass spectrometer. This system is fully portable (can be carried in a truck) and can be operated in fairly harsh environments. In its present configuration, this spectrometer can detect 1 ppb of material without preconcentration. This system also has a complete data system and electronics for continuous monitoring of 20 substances with automatic alarms for pre-set concentration levels. Cost of this instrument is $140K.

Without modification of the pumping system and sampling line, it is unlikely that the required limits of detection could be met without some type of preconcentrator. This instrument, however, does demonstrate the usefulness and ruggedness of a quadrupole based instrument for atmospheric monitoring.

Recommendation. The MEM is a commercial implementation of a quadrupole based atmospheric monitoring mass spectrometer. With modification it might be possible to reach the required detection limits. The use of such a system should be given high priority although having a system designed specifically for agent monitoring should receive highest consideration.

SECTION IV: SAMPLING/PRECONCENTRATION TECHNIQUES

Because several analytical techniques are capable of monitoring the agents at a level of about 10^{-2} mg/m^3, it is important to assess methods for the preconcentration of gas samples prior to analysis. There are several documented approaches for the preconcentration of samples using a variety of techniques. This section of the report summarizes our opinions on the use of some of these systems.

Liquid film preconcentrator/collector. This system represents a unique approach to preconcentration. The gas sample is passed through a tube containing a small amount of flowing liquid i.e. a wetted wall column. Sample material is condensed/extracted into this liquid, which provides the opportunity to achieve large concentration factors. This concept has been successfully applied to the monitoring of agent BZ (11). The use of a liquid for transport of the sample concentrate is an additional advantage of this system. There should be no difficulty in transporting VX to the analyzer, as is the case in the gas phase. The drawbacks are that presentation of the sample in the liquid phase may require modification of the measurement equipment, and that the possibility of hydrolysis in the liquid phase is significant, particularly in the stack and hot flue gases. For the case of HD and GB, the advantages of the system are somewhat marginal, and perhaps outweighed by these disadvantages, but for the case of VX, the liquid film collector is a reasonable approach. As is the case with all preconcentration technologies, the reasonableness of this system depends on the choice of analytical procedure. The obvious marriage of this concentrator with the SIMS technique reported on earlier cannot be overlooked. The liquid would in this case, be sulfuric acid, which would flow directly into the ion source of the SIMS instrument. This system is projected to provide sensitivity well in excess of the requirements, with a high degree of selectivity as well. This is not to say that the only application for the liquid film collector is in combination with SIMS. The unit is the best hope for sample introduction to any technique requiring a liquid sample.

Recommendation. Continue development of the technique. Perform studies using VX as soon as possible.

SFC/Sorbent preconcentration. As mentioned earlier, supercritical fluid chromatography in its present state of the art is not appropriate for the analysis of the chemical agents. However, the technique of supercritical extraction may well have advantages for sampling/preconcentration. LDC, Inc. has announced the availability of a supercritical fluid extraction unit which is designed to be interfaced with SFC. This unit might allow the use of SFC for extraction from solid sorbent cartridges with direct introduction into an FPD. Alternatively, the supercritical fluid could be made up of CO_2/ methanol (99/1), and used for desorption from sorbent tubes. The CO_2 would immediately evaporate, leaving the agents in the methanol and providing an additional concentration factor of 100. The advantages of such a system also include the ability to efficiently remove the agents from any sorbent without thermal problems, and the ability to use large sorbent tubes.

As mentioned later in this report, such a system could be used for routine, nonselective monitoring for the purpose of prioritizing sample streams for a more sophisticated central monitoring technique. This device is expected to be in the shipping stage by mid to late 1986. No firm cost is yet available.

Recommendation. Follow LDC announcements and test the extractor when available if cost is reasonable.

Sorbent preconcentration/thermal desorption. As discussed earlier, the response time of the GC analysis is primarily limited by the need to sample large volumes of air. Several options exist for decreasing the percentage of cycle time required for sampling. These include increasing the diameter of the trap, increasing the linear velocity of the sample gas, and others. A more detailed description of these options is given here. It is important to note that these considerations apply regardless of the nature of the measurement technique,as long as the sample introduction is in the gas phase.

The most straightforward means of decreasing sampling time is increasing the linear velocity of the sample gas through the trap. In this case, the primary limitation is pressure drop. It would appear that only modest improvement can be made with the current trap configuration.

A geometric alteration in the configuration of the current trap appears to be the most useful means of reducing sampling time with current equipment. As mentioned earlier, an increase in the diameter of the trap will provide the capability of increased mass flow rate. Assuming only that the diameter is changed, and that the pressure drop remains constant, the relationship between diameter and mass flow is quadratic. The relationship between trap length and mass flow is approximately linear. Therefore, a trap with diameter of 1/2 in. would allow mass flow of 16 times that of the current 1/8 in. trap. This reduction in sampling time alone would bring the technique close to the requirements for all situations. However, other conditions can now be altered. In a trap of any kind, a third geometric consideration is important -- particle size. The particle size is to some extent limited to that which is commercially available, but in this case a wide range is available. The relationship which is critical is the ratio of particle size to diameter, which should be kept at least ten for the maintenance of performance. The relationship of particle size to mass flow is also quadratic, assuming the distribution of the particle size remains constant. Thus, an increase in particle size by a factor of two in the previous calculation would allow an additional reduction in sampling time of a factor of four. The required time for sampling would be reduced to less than 15 seconds for the worst case--VX. The use of such a trap would require the redesign of the front end of the units now in use, but this redesign is relatively simple and inexpensive. The suggestion made earlier in this report -- the use of additional solenoid valves, would be the primary modification. In this case, the trap would be in the sampling line during the actual trapping; the trap would be heated to the desorption temperature with the ends sealed from any flow, and the desorption would be accomplished via the carrier gas after valve switching. Alternatively, several commercial adsorption/thermal desorption units are available at less than $5000. Most of these units could be directly connected to existing ACAMS. These include units manufactured by Tracor, Envirochem, Metrex, and Chrompack.

Recommendation. These modifications should be investigated as soon as possible.

Wire loop adsorber/thermal desorber. An innovative approach to the collection of semivolatile organic compounds has been suggested by Sciex, Inc. Here, rather than using a solid sorbent, a collection device consisting of a coated conical wire is placed in the sample stream. After an appropriate sampling period, the wire is resistively heated and the components desorbed for further analysis. Because of the inherently low pressure drop, very high sampling rates are possible. In addition, the "sorbent" has extremely small thermal mass, allowing rapid heating and cooldown cycles. This approach has merit in three areas: 1) the collection of agent vapors, 2) the separation of the agents for simultaneous determination, and the conversion of VX to the G-analog.

Collection of agent vapors using such a system would allow the concentration factors to be very large indeed. The sampling tube would be about 1/2 in. in diameter and would permit flow rates in excess of 100 L/min. Collection of a 20 L sample would require only 12 seconds. Desorption and analysis could be done essentially instantaneously, and a cycle time of less than 30 seconds should be easily attainable. With the use of two sample tubes, sample time coverage could be greater than 80%. Furthermore, only minimal sample pretreatment would be required (cooling of the flue gas). It is likely that the stack gas could be sampled directly, since water condensation would have little or no effect on collection efficiency. This is due to the fact that the coating on the wire is likely to be a hydrophobic material. In addition, much of the water and other interferences would be removed. Finally, the relatively large concentration factors would bring the sensitivity of a variety of techniques down to the required levels.

Use of the wire desorber as a separator column for the simultaneous determination of the agents could be achieved by selecting the coating on the basis of agent capacity. The resistive heating rate of the wire can be thought of as the analogy to temperature programming in gas chromatography, and the coating can be thought of as the stationary phase. By selecting the coating material and mass of coating properly, the agents could be made to desorb sequentially. The analogy here is not strictly to elution chromatography, but to the frontal chromatographic system of the sorbent trap. Thus, in the best case, efficiency would be limited to perhaps 1000 theoretical plates. The selectivity factor would need to be fairly large for complete resolution, although this is certainly possible. If this can be done, it will be possible to couple the collection device directly to a flame photometric detector, producing a simple, rugged, selective, and sensitive monitoring device which could be produced for about $15000.

The final utility of the wire collector is as a conversion unit for VX. For transport of VX, conversion to the G-analog is probably necessary. In the ACAMS modified for VX, this is accomplished using a high volume filter impregnated with silver fluoride. The constant replacement of the filter becomes a maintenance problem. If the wire collector were used in place of the filter, a silver wire could be treated with a fluorinating agent (the simplest example being HF) _in-situ_, so that the conversion reagent is constantly and reproducibly regenerated. In the simplest case, the wire would be fluorinated, the sample collected, the sample desorbed, and the wire regenerated. The use of such a system should greatly facilitate VX transport and analysis.

Recommendation. When the Taga 6000 is tested at Tooele, the utility of the wire adsorber should be studied as well, since the only commercial version of this desorber is manufactured by Sciex.

SECTION V: CRITIQUE OF THE API RF MASS ANALYZER

Summary. The design and performance of the API RF mass analyzer constructed for USATHAMA by S-Cubed, Inc. has been reviewed. The following conclusions and recommendations are based on a critical evaluation of the information contained in the monthly reports and final report by S-Cubed, as well as an oral presentation on the project by Aerospace Corporation.

Because of what appear to be overwhelming technical problems with the entire API RF mass analyzer constructed by S-Cubed, it is recommended that additional development of that particular system not be continued at this time. However, because of the potential of API MS as a viable means of instantaneously detecting nerve agents, continued evaluation of this technology as a whole should be pursued. Efforts in the short term should be particularly focused on the testing and evaluation of commercial API MS instrumentation currently on the market. Additionally, long term research and development of less expensive API MS units should be considered if the present technology provides satisfactory results.

It is clear that if further development on API MS is to be considered, explicit design criteria must be developed based on experience with the technique on-site at Tooele. The data set should be carefully reviewed by qualified mass spectroscopists in order to assess the reliability, availability, and overall performance of APIMS. This approach will prove cost effective in the long run by providing critical information for subsequent designs.

The API RF Mass Analyzer constructed by S-Cubed, Inc. for the detection of nerve agents in air is plagued by a number of serious problems. These problems are the result of the design of the atmospheric pressure ionization source, the ion optics, and the type of mass filter used. The combined result is an instrument that has very poor selectivity and inadequate sensitivity for its intended purpose. Specific problems with the API RF mass analyzer are outlined below. Possible corrective actions are outlined in the next section.

Pulsed Valve Atmospheric Pressure Ionization Source. The atmospheric pressure ionization source/pulsed valve assembly represents one of the most serious problems with the instrument. Although the concept is reasonably sound and could be of significant use in the future, pulsed valve API is not at this time an established technology and has not been demonstrated as a reliable and reproducible means of generating ions and introducing them into the source of a mass spectrometer. In particular, uncertainties associated with ion-molecule reactions, ion-loss mechanisms, and ion transport through the valve orifice, make it virtually impossible to predict the performance of the ion source in the environment required for chemical agent monitoring. For example, it was demonstrated that simply by altering the position of the ^{63}Ni foil (used for ionization) within the pulsed valve, significantly different ionic species were formed. Placement of the foil near the valve nozzle favored formation of lower molecular weight cluster ions, while placement of the foil farther away favored the formation of higher weight cluster ions due to the increased number of ion-molecule collisions. Other factors including source temperature, source pressure, relative humidity, interfering compounds, and contamination of the ^{63}Ni foil should also have significant effects on the ionization characteristics which would lead to unpredictable instrument response. These factors have not been properly addressed.

Although the major problems associated with the transport of ions through the valve nozzle were apparently overcome, the build-up of contaminants on the valve nozzle and poppet could eventually lead to charging of the surfaces and reduced ion transmission. To minimize this problem would require operation of the valve body at elevated temperatures which at this time does not seem to be compatible with piezo-electric valves.

The formation of the water clusters in the ionization source is in itself a serious problem that could be difficult to overcome. These cluster ions are formed as the result of 1) the long residence time of ions in the atmospheric pressure side of the valve, and 2) additional formation of clusters in the ion-beam expansion region as the ions are pulsed through the valve nozzle into the mass spectrometer. Ion clusters of the molecular weight formed in this source create a serious background interference problem that makes the trace level detection of chemical agent virtually impossible. Additionally, these cluster ions constitute a large portion of the ion current which may tend to reduce the number of analyte ions generated and transmitted through the pulsed valve. Efforts to reduce clustering have thus far been ineffective and it is likely that significant research and design changes will be required to minimize this problem.

Ion Optics: Source and Transmission. The design of the ion extraction optics and ion transmission lenses is very basic. Discussion with Aerospace Corporation indicated that no significant effort was made to optimize the extraction and transmission efficiencies.

RF Mass Analyzer - Bennett Tube. From the spectra published in the reports by S-Cubed, Inc., it is obvious that the resolution of the mass analyzer is quite poor. This results in peaks that are 5-10 amu wide at half height in the mass region of interest. Combined with the problems of cluster formation, it is impossible to separate the peaks due to the simulant (DMMP) ions from those due to the water clusters. Even in the absence of the water clusters problem, resolution as poor as that demonstrated for the Bennett tube, makes the instrument highly susceptible to matrix interferences that could result in false positive readings. To minimize this problem, a mass resolution of at least unit mass (Resolution=200 at mass 200, mass of the peak divided by the peak width at 1/2 height) is necessary.

API RF Mass Analyzer - Possible Corrective Actions. In order to optimize the performance of the existing API RF mass analyzer, the following corrective actions are recommended.

1. The resolution of the mass filter must be increased from 30 to at least unit mass (200 at mass 200). According to the theoretical calculations given in the Aerospace report, this is not possible with an RF mass filter (Bennett tube). Therefore, the mass filter must be replaced with a higher performance mass filter such as a quadrupole or time-of-flight. Both of these mass spectrometers are rugged and reliable for long term operation. In addition, the pumping requirements and support electronics are comparable to those needed for the S-Cubed, Inc. API RF mass analyzer.

   To further increase selectivity if necessary, a triple-quadrupole (MS-MS) mass analyzer could be used. This allows a single characteristic to be selected from a complex matrix by the first

MS stage and fragmented in the second stage for positive identification. SCIEX Corporation, for instance, has demonstrated the usefulness of such an arrangement for detection of chemical agents in the presence of battlefield contaminants, [(7) and earlier discussion].

2. The overall sensitivity of the spectrometer must be increased by a factor of approximately 100 if the detection limit for VX is to be reached. An improved lensing system for optimum ion extraction and transmission could be designed using existing computer programs. This would result in reduced ion loss in the source, better ion transmission, and ultimately an increase in sensitivity. However, it is highly unlikely that this alone would achieve the required sensitivity due to the presence of background ions generated in the source. Redesign of the ionization source to minimize cluster ion formation and unwanted background signals is therefore necessary.

3. Due to the lack of prior research in the area of pulsed valve API sources, it is very difficult to identify corrective actions that will have a significant chance of minimizing cluster ion formation while maintaining high efficiency formation of chemical agent ions. Some possible changes in design and operating parameters include:

    a. Operation of the valve at reduced pressures (1 torr) to decrease the number of ion-molecule interactions that favor cluster formation.
    b. Operation of the valve at an elevated temperature to increase cluster decomposition.
    c. Reduction of the residence time of ions in the high pressure side of the valve through the use of two pulsed valves in series. By pulsing a volume of gas from the first valve (atmospheric pressure) into the second valve (where it is ionized) a few milliseconds prior to introducing the ions into the spectrometer, the residence time of the ions would be decreased in the ionization region of the valve, thus reducing the number of ion molecule reactions and decreasing cluster formation.
    d. Placement of the ^{63}Ni ionizing foil in the nozzle of the pulsed valve. This would also decrease the time available for cluster ion formation.
    e. The addition of a neutral buffer gas, such as argon, to the molecular beam could result in enough collisions to break-up clusters.
    f. Electric fields in the molecular beam region could also be used to break-up cluster ions; however, this could result in an undesirable increase in the kinetic energy spread of the ions, causing a loss of mass resolution.

g. An adjustable skimmer nozzle should be used and optimized for decreased cluster transmission.

Because of the wide range of parameters that must be investigated and optimized, an iterative approach must be used which will require extensive research time. It is quite possible that even with significant additional effort, the problems with the pulsed valve API source cannot be minimized to the degree necessary. Therefore, it is recommended that if API mass spectrometry is to be evaluated further, a more conventional API source and mass filter should be used.

Estimated Time and Costs for Optimizing* the Current API Mass Analyzer

1. Replacement of the Bennett tube with a quadrupole mass filter.

   Estimated Time: 4-6 months
   Estimated Cost: $85,000

2. Optimization of ion optics.

   Estimated Time: 3 months
   Estimated Cost: $30,000

3. Optimization of pulsed valve ion source.

   Estimated Time: 6-8 months
   Estimated Cost: $200,000

4. Testing and evaluation of optimized system.

   Estimated Time: 2-4 months
   Estimated Cost: $45,000

   Estimated time start-finish: 12-16 months
   Total estimated cost: $350,000

*This optimization study is aimed at <u>maximizing</u> the performance of the existing API mass analyzer but does not guarantee that the required performance criteria could be met. The serious nature of the problems in the ion source do not favor complete success.

API RF Mass Analyzer: Final Recommendation. The APIMS mass analyzer constructed by S-Cubed, Inc. suffers from numerous problems which prevent it from meeting the required performance specifications. Although the overall system performance could almost certainly be improved through alterations in the basic design, it may be very difficult, if not impossible, to reach the performance level necessary for the proposed applications. Since the likelihood of success is questionable and the costs of optimization are substantial, it is recommended that further work on the current API mass analyzer be discontinued.

SECTION VI: TRANSPORT LINE TECHNOLOGY

Consideration of a Central Monitoring Facility. Since one of the best approaches to the monitoring of the agent vapors appears to be the use of a very expensive instrument (TAGA 6000), it is necessary to assess the degree to which samples can be transported to such a device for analysis. Using the TAGA 6000 as the detection device, it has been reported that GB and VX can be transported at least twenty feet without significant loss (7), although this work was done at much higher levels than the TWA or ASC concentrations. It is likely that if VX is to be transported to a central monitor, it must be done either in the liquid phase or after conversion to the G-analog. There are advantages and disadvantages to either approach. The use of the liquid film collector for VX (described earlier) would almost certainly increase the likelihood of presenting a representative sample to the detector, while at the same time effecting a concentration step. However, the sample would be presented in the liquid phase - a significant divergence from the normal inlet system for the TAGA 6000, but appropriate for the SIMS technique. Conversion to the G-analog would allow presentation in the gas phase, but the conversion efficiency would be suspect and the filters would require maintenance.

Perhaps a more severe restraint on the use of a central monitor is the requirement for sample time coverage. The sample time coverage, t, in % is given by the inverse of the number of points to be sampled (N):

$$t = 1/N$$

Thus, for 80% sample time coverage only one point can be sampled. The time between samples (T), is given by:

$$T = rt/N,$$

where rt is the response time of the monitoring instrument. For an instrument monitoring 10 sample points sequentially with a response time of 30 seconds, the sample time coverage would be 10% and the time between samples at a given point would be 5 minutes. Thus, it appears that an additional compromise is needed if the monitoring instrumentation is to be located centrally.

An alternative to the sequential monitoring of a large number of sample points is the use of priority sampling via a "stream selector method." This method would be simple and rapid, sacrificing selectivity. The signal generated using this method would be used to develop a priority for the central monitor. Thus, the more expensive monitor would serve a confirmatory purpose, rather than a routine monitoring purpose. Such a system would have the advantages of:

1. Much greater sample time coverage
2. Independent measurement methodology
3. Decreased reliance on the central monitor, extending its maintenance interval.

The stream selector method could consist of a large sorbent tube connected directly to an FPD, with the only selectivity coming from the rate at which the tube is heated. Given the relatively simple nature of the chromatograms, such an approach should be sufficient for the identification of the appropriate stream to monitor. Other possibilities exist, including the use of any of the preconcentration techniques covered earlier with the FPD as the detection technique.

Recommendation. Test sample transport at the levels necessary for detection at the TWA, particularly for VX.

VX monitoring using 2-diethylaminoethanethiol (DEAT). Because of the low volatility and high degree of adsorptivity of VX, any analytical method for this compound must take into account the possibility of sampling and sample transfer losses. These problems exist in the bubbler system, where it is difficult to get the VX into the solution, as well as in the sorbent sampling tubes, where a small conversion filter is used to produce the G-analog at the sample entrance. Even in a direct measuring device, such as IMS or APIMS, it may be difficult to quantitatively deliver the VX to the ionization region. As a possible solution to this problem, it may be useful to consider monitoring for DEAT as well as VX. DEAT is known to be an impurity in VX and is always present at some level (usually about 10 %). Very little data is available on this compound. However, the data which is available allowed the calculation of vapor pressure and heat of vaporization. The vapor pressure calculated is 2.8 mm at 25°C. This compares with 2.9 and 0.0007 mm for GB and VX respectively. The latent heat of vaporization is 68 cal/g, comparable to that of the agents. It must be emphasized that these calculations are the result of the use of data of unknown quality, and are therefore somewhat suspect. The values obtained do, however, seem reasonable. Thus, the volatility of DEAT is substantially greater than that of VX, and similar to that of GB. While the level of this compound would be 10 % of that of VX, the gas phase concentration will always be three orders of magnitude higher. This has been shown to be the case (12). Monitoring the atmosphere for DEAT could therefore be considered as an early warning signal for the presence of VX. Properties bearing on the detection of this compound include good chromatographic behavior and the presence of sulfur in the molecule. It is quite likely that this compound can be measured using the ACAMS in the GB mode with a sulfur filter on the FPD. While the presence of this compound does not necessarily confirm the presence of

VX, it would indicate a high probability of contamination. In addition, a system capable of monitoring DEAT would also be capable of monitoring diisopropyl aminoethanethiol, which is the result of the conversion of VX to the G-analog. While no data exists as yet on the fate of this compound after conversion, if the compound is released from the filter it would have analytical significance. Furthermore, the simultaneous measurement of DEAT and the G-analog would provide additional confirmatory evidence in the current monitoring system for VX. Since the chromatography of the two compounds is similar, addition of a sulfur filter to the ACAMS should be the only instrumental alteration.

REFERENCES

1. Nichols, L.D. Thin-Film Colorimetry for Miniature Chemical Agent Detection Systems. Phase I Study. Report USAFSAM-TR-83-43. November, 1983.

2. McMillan, R.W., and Gallagher, J.J. Feasibility Study For the Use of Frequency Modulated Laser Infrared Spectroscopy in Chemical Agent Monitoring. Final Technical Report to USATHAMA, December, 1985.

3. Seivers Research Institute, commercial information, 1986.

4. Phillips, J.B. Multiplex Gas Chromatography. Anal. Chem. 52 (4) 468-478, 1980.

5. Gordon, R.J. A Multiplex Gas Chromatograph for Real-Time Gas Analysis. Final Report. SBIR Phase I. Contract No. ER80147. 1985.

6. Trujillo, A., Gnanasambandan, T., and Freiser, H. Determination of Organophosphorus compounds by Dye-Assisted Chromatography. Anal. Chim. Acta, 162, 333-338, 1984.

7. Corporate Author. NBC Reconnaissance System: Final report. Batelle Columbus Laboratories, 1985. CRDC-CR-85-.

8. Todd, P.J. and Groenewold, G.S. Temporal Behavior of Secondary Ion Emission form Analyte/Liquid Matrix Samples. Anal. Chem. 54, 895-899, 1986.

9. Groenewold, G.S. and Todd, P.J. Detection of Gaseous Organophosphorus Compounds using Secondary Ion Mass Spectrometry. Anal. Chem. 57, 886-890, 1986.

10. Marshall, A.G. Accounts of Chemical Analysis, 18, 316, 1985.

11. Lucero, D.P. and Kolakowski, J. A Continuous Isokinetic Gas/Mist Sampler for Flue Stream Extractive Analysis. Final Report USATHAMA.

12. Classified document.

DISTRIBUTION LIST

	No. Copies
Defense Technical Information Center Cameron Station Alexandria, VA 22314	12
Commander U.S. Army Toxic and Hazardous Materials Agency ATTN: AMXTH-CO-P Aberdeen Proving Ground, MD 21010-5401	2
Defense Logistics Studies Information Exchange U.S. Army Logistics Management Center Fort Lee, VA 23801	2
Greg Mohrman USATHAMA DRXTH-TE-A, Bldg. E-4585 Aberdeen Proving Ground, MD 21010-5401	20
M. V. Buchanan Oak Ridge National Laboratory Building 4500-S P. O. Box X Oak Ridge, TN 37831-6120	2
Central Research Library Oak Ridge National Laboratory Building 4500-N P. O. Box X Oak Ridge, TN 37831-6286	1
Document Reference Section Oak Ridge National Laboratory Building 9711-1 P. O. Box Y Oak Ridge, TN 37831	1
M. R. Guerin Oak Ridge National Laboratory Building 4500-S P. O. Box X Oak Ridge, TN 37831-6120	10
Laboratory Records Oak Ridge National Laboratory Building 4500-N P. O. Box X Oak Ridge, TN 37831-6285	3

DISTRIBUTION LIST (Cont'd)

	No. Copies
Mr. J. A. Lenhard, Assistant Manger Energy Research and Development U.S. Department of Energy, Oak Ridge Operations P. O. Box E Oak Ridge, TN 37831	1
D. L. Manning Oak Ridge National Laboratory Building 4500-S P. O. Box X Oak Ridge, TN 37831-6120	2
M. P. Maskarinec Oak Ridge National Laboratory Building 4500-S P. O. Box X Oak Ridge, TN 37831-6120	10
ORNL Patent Office Oak Ridge National Laboratory Building 4500-N P. O. Box X Oak Ridge, TN 37831-6258	1
M. B. Wise Oak Ridge National Laboratory Building 4500-S P. O. Box X Oak Ridge, TN 37831-6120	2
Technical Information Center U.S. Department of Energy Oak Ridge, TN 37831	146

For DOE/TIC 4500 distribution
under UC-4 Category.