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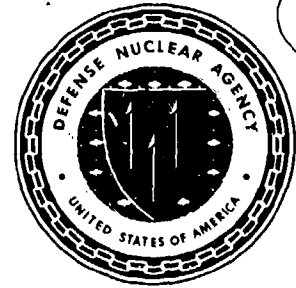
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DNA-TR-93-68

CW Detection Instrument R&D Design Evaluation

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Technical Report

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 931101	3. REPORT TYPE AND DATES COVERED Technical 920701 - 930430

4. TITLE AND SUBTITLE
CW Detection Instrument R&D Design Evaluation

5. FUNDING NUMBERS
C - DNA-001-91-C-0146
PE - 62715H
PR - TA
TA - TA
WU - DH316290

6. AUTHOR(S)
Robert V. Mustacich and Paul M. Holland

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

General Research Corporation
P.O. Box 6770
Santa Barbara, CA 93160-6770

8. PERFORMING ORGANIZATION REPORT NUMBER

CR-93-1346

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Defense Nuclear Agency
6801 Telegraph Road
Alexandria, VA 22310-3398
OPAC/Fox

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

DNA-TR-93-68

11. SUPPLEMENTARY NOTES
This work was sponsored by the Defense Nuclear Agency under RDT&E RMC Code B4613D TA TA 00066 A 25904D.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
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13. ABSTRACT (Maximum 200 words)

This is the "Task 3: CW Detection Instrument R&D Evaluation Report," for the program "Development of a Handheld Chemical Detector Using Microchip GC." The study described in this report covers experimental evaluation of microchip GC and alternative GC approaches for developing a handheld instrument for CWC verification inspections. Shortcomings found in microchip GC technology were examined, and ways to extend microchip GC capability to include critical CWC semivolatile compounds were explored. When this was found not to be feasible due to temperature limitations of key components, alternative miniature GC technology was developed to fill this technology gap. This consists of an innovative ultra-low thermal mass GC with integral heater, whose components are actually smaller than those of the microchip GC. With this new technology, unprecedented temperature programming speed and accuracy have been demonstrated on a wide range of compounds ranging from volatiles to C_{20} hydrocarbons. The advantages of selective detectors coupled to this mini-GC technology are also discussed. A dual flame photometric detector (FPD) which provides simultaneous selective detection of phosphorus- and sulfur-containing

14. SUBJECT TERMS
CW Agent Detection
Correlated Gas Chromatography
Microchip Gas Chromatography
CW Treaty Verification

15. NUMBER OF PAGES
134

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

NSN 7540-01-280-5500

13. ABSTRACT (Continued)

compounds with a single GC column is recommended with the mini-GC in the handheld concept instrument design specification.

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EXECUTIVE SUMMARY

This report presents GRC's Concept Instrument Design Specification and recommendations for the portable, handheld inspection instrument for CWC schedule chemicals. The Task 3 research effort to define the concept instrument and evaluate its functional elements is included as background in this report.

Important considerations in the selection process for the concept design include: an assessment of the operational needs; suitability for handheld operation; detection limits down to the allowable Schedule 1 time-weighted average (TWA) concentrations; and strong selectivity to greatly reduce false positive detections. Gas chromatographic (GC) approaches were evaluated with respect to these considerations and the CWC schedule compounds. The functional elements of these approaches were tested to determine the performance limits of the various technologies with respect to the broad range of chemicals in the CWC schedules.

Our starting concept was to extend the application of the commercially available microchip GC hardware to include the detection of CWC schedule chemicals. This hardware is small and portable, but difficulties were encountered in extending its performance range to include the full range of CWC semi-volatile compounds (compounds with high boiling points and correspondingly low vapor pressures). Such compounds are routinely chromatographed by raising the operating temperature of a GC to effectively vaporize these compounds to allow normal chromatographic operation. Operation of the microchip GC at the higher temperatures required to analyze the full range of CWC semivolatile compounds was found to be beyond the limits of the existing microchip GC components without significant changes in

the fabrication of these during manufacture. Our analysis and experimental testing suggests that the operational range of existing components may be extended into the semivolatile range somewhat by heating the sample inlet lines and injector, but this will not be sufficient to analyze for VX, a key CWC Schedule 1 compound which is representative of low volatility CWC compounds.

The temperature limitations encountered with microchip GC for the analysis of semivolatile compounds led to the need for a supplemental approach which could provide the needed semivolatile analysis with the required speed, small size, low power consumption, detection limits and selectivity needed for the concept instrument. The lack of commercial technologies which could fill this need led to the development of an innovative new approach to fill this critical technology gap. This approach consists of a miniature ultra-low thermal mass GC column with integral heater. The small thermal mass allows rapid heating with low power consumption. The resulting GC has demonstrated a very wide range of semivolatiles analysis, small size, and unprecedented speed. While it was designed to cover the full range of the CWC schedule semivolatile, our evaluation of the technology suggests that most of the CWC schedule volatiles (low boiling point, high vapor pressure compounds detectable by microchip GC) can also be detected with this technology. To distinguish this technology from the microchip GC technology, we dubbed it the "mini-GC," although its packaged size actually appears to be smaller than the microchip GC technology.

In addition to R&D on the underlying GC separation technology, selective detectors were evaluated for the detection of CWC schedule compounds. The original instrument concept utilizing microchip GC involved non-selective thermal conductivity detectors which

are commercially used in microchip GC instrumentation. This type of detector is sensitive to the high levels of hydrocarbons normally present in the environmental background, especially after the vapor preconcentration steps necessary for detection down to TWA levels for the highly toxic CWC Schedule 1 compounds. For this reason, multidimensional chromatography was considered for introducing selectivity to the microchip GC-based approach. In this approach, parallel microchip GCs perform simultaneous separations using different chromato-graphic media. Correlations of the differences in these separations provide additional selectivity over the use of a single microchip GC. Alternatively, the use of an element-selective detector, in particular a phosphorus-selective detector, was also considered. Such a detector is insensitive to the relatively high levels of hydrocarbon background which are present following vapor preconcentration. Phosphorus-selective detection is especially relevant considering the dominance of organophosphorus compounds in the CWC schedules. Selective detectors for nitrogen and sulfur were also of special interest because of the chemical composition of the compounds in the CWC schedules.

Our analysis of phosphorus-, nitrogen-, and sulfur-specific detectors showed that very selective detection of these elements was readily available using commercially available detectors. Further, very low detection limits were also possible using these detectors. An analysis of the CWC schedules showed that phosphorus and sulfur detection capabilities are the most critical for adequate coverage of the schedules. Our evaluation of commercially available detectors indicated that both thermionic and flame photometric detectors (FPD) were capable of low detection limits and selectivity with regard to one or more of these specific elements. Of special interest to this program, a "dual" phosphorus- and sulfur-selective FPD detector is commercially available which provides the complimentary phosphorus and sulfur

detection needs for optimum CWC schedule coverage. This "dual" detector is actually two separate flame photometric detectors which are structurally combined to measure light emissions from a single GC column. The result is a "single" detector package that can be used on a single GC column which provides simultaneous analyses of phosphorus and sulfur with high selectivity and low detection limits. Since a great many of the CWC schedule compounds contain both phosphorus and sulfur, these highly selective outputs from this "dual" configuration will provide coincident results which add to the overall selectivity of the concept instrument. While multidimensional chromatography could also be introduced for added selectivity by the inclusion of multiple GCs in the instrument, it is not apparent that the added selectivity is warranted with regard to the increase in instrument size, complexity, and cost relative to the highly selective, two-dimensional analysis results provided from a single phosphorus and sulfur detection package on a single GC column. For this reason, the use of a single GC with an essentially two-dimensional phosphorus- and sulfur-selective detector is recommended for the concept instrument design. If additional selectivity is warranted in the future, straightforward engineering modifications of the instrumentation can be made to multiply the GCs and detectors in the instrument to provide multidimensional chromatography capability.

The development of this alternative mini-GC technology led to the detailed consideration of three basic concept design approaches: a "baseline" approach in which the mini-GC is used together with the microchip GC to supplement its performance; an approach using the mini-GC only; and an approach using the microchip GC only. The baseline approach represents the earliest evolutionary approach in which the mini-GC was conceived as a supplement to the microchip GC technology. This combination of separate technologies

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results in a concept instrument which is relatively large and complex for a handheld instrument. The concept instrument approach using mini-GC technology only is of minimum size and yet captures nearly all of the detection capability of the large, combined technology approach. The microchip GC only approach illustrates a concept instrument with emphasized volatile capability, but this capability is the least attractive of the concept instrument approaches.

The concept design specification features an innovative ultra-low thermal mass mini-GC with the two-dimensional FPD detector in a very small instrument configuration. This instrument provides very wide CWC schedule detection coverage with an emphasis on the schedule 1 and 2 compounds. We believe that this instrument best fits the expected operational emphasis on schedule 1 and 2 compounds and offers the simplest and most elegant solution combining the miniature technologies required for a handheld instrument. The estimated weight of the prototype is 7.4 kg (16.3 lbs) excluding batteries. An estimated 3.1 kg (6.8 lb) battery belt pack is needed for 4 hour continuous operation of the instrument. Further weight and size reductions that are expected in the fabrication of a pre-production prototype result in a projected 56% reduction in size and a 55% reduction in weight to 3.3 kg (7.3 lbs), excluding the battery pack. This instrument would be capable of unprecedented GC analysis speed, low power requirements, and selective detection of phosphorus- and sulfur-containing compounds at levels which meet or exceed schedule 1 TWAs. This approach will allow a handheld inspection instrument to be fabricated with covers nearly all of the CWC schedule materials while meeting the operational needs of CWC inspectors and enhancing operational flexibility for a wide range of inspection scenarios.

CONVERSION TABLE

Conversion factors for U.S. customary to metric (SI) units of measurement.

To Convert From	To	Multiply By
angstrom	meters (m)	1.000 000 X E -10
atmosphere (normal)	kilo pascal (kPa)	1.013 25 X E +2
bar	kilo pascal (kPa)	1.000 000 X E +2
barn	meter² (m²)	1.000 000 X E -28
British thermal unit (thermochemical)	joule (J)	1.054 350 X E +3
cal (thermochemical)/cm²§	mega joule/m² (MJ/m²)	4.184 000 X E -2
calorie (thermochemical)§	joule (J)	4.184 000
calorie (thermochemical)/g§	joule per kilogram (J/kg)*	4.184 000 X E +3
curie§	giga becquerel (GBq)†	3.700 000 X E +1
degree Celsius‡	degree kelvin (K)	$t_k = t°_c + 273.15$
degree (angle)	radian (rad)	1.745 329 X E -2
degree Fahrenheit	degree kelvin (K)	$t_k = t°_f + 459.67)/1.8$
electron volt§	joule (J)	1.602 19 X E -19
erg§	joule (J)	1.000 000 X E -7
erg/second	watt (W)	1.000 000 X E -7
foot	meter (m)	3.048 000 X E -1
foot-pound-force	joule (J)	1.355 818
gallon (U.S. liquid)	meter³ (m³)	3.785 412 X E -3
inch	meter (m)	2.540 000 X E -2
jerk	joule (J)	1.000 000 X E +9
joule/kilogram (J/kg) (radiation dose absorbed)§	gray (Gy)*	1.000 000 X E +91
kilotons§	terajoules	4.183
kip (1000 lbf)	newton (N)	4.448 222 X E +3
kip/inch² (ksi)	kilo pascal (kPa)	6.894 757 X E +3
ktap	newton-second/m² (N-s/m²)	1.000 000 X E +2
micron	meter (m)	1.000 000 X E -6
mil	meter (m)	2.540 000 X E -5
mile (international)	meter (m)	1.609 344 X E +3
ounce	kilogram (kg)	2.834 952 X E -2
pound-force (lbf avoirdupois)	newton (N)	4.448 222
pound-force inch	newton-meter (N·m)	1.129 848 X E -1
pound-force/inch	newton/meter (N/m)	1.751 268 X E +2
pound-force/foot²	kilo pascal (kPa)	4.788 026 X E -2
pound-force/inch² (psi)	kilo pascal (kPa)	6.894 757
pound-mass (lbm avoirdupois)	kilogram (kg)	4.535 924 X E -1
pound-mass-foot² (moment of inertia)	kilogram-meter² (kg·m²)	4.214 011 X E -2
pound-mass/foot³	kilogram-meter³ (kg/m³)	1.601 846 X E +1
rad (radiation dose absorbed)§	gray (Gy)*	1.000 000 X E -2
roentgen§	coulomb/kilogram (C/kg)	2.579 760 X E -4
shake	second (s)	1.000 000 X E -8
slug	kilogram (kg)	1.459 390 X E +1
torr (mm Hg, 0°C)	kilo pascal (kPa)	1.333 22 X E -1

*The gray (Gy) is the accepted SI unit equivalent to the energy imparted by ionizing radiation to mass of energy corresponding to joule/kilogram.
†The becquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.
‡Temperature may be reported in degree Celsius as well as degree kelvin.
§These units should not be converted in DNA technical reports; however, a parenthetical conversion is permitted at the author's discretion.

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SECTION 1

INTRODUCTION

A handheld detection instrument to detect Chemical Weapons Convention schedule chemicals is being developed by General Research Corporation (GRC) for DNA under contract no. DNA-001-91-C-0146. This report presents GRC's Concept Instrument Design Specification and recommendations for the portable, handheld inspection instrument for CWC schedule chemicals, and concludes our Task 3 effort to define the concept instrument and evaluate its functional elements. Earlier, Task 1 covered target vapor identification and database development, and Task 2 the development of algorithms and performance analysis for the identification of CWC chemicals. In Task 4, we will develop and construct the prototype instrument.

1.1 BACKGROUND.

The proliferation of chemical weapons technology poses a significant threat to peace and stability in the post Cold-War world. This has been recognized by the numerous parties to the Chemical Weapons Convention (CWC) which was signed in January 1993. A key part of this treaty is the provision for on-site challenge inspections for the presence of prohibited Chemical Weapons (CW) and pre-cursor chemicals.

In the interim between the signing of the Chemical Weapons Convention and its projected implementation in 1995 (after ratification), inspection technology for the CWC schedule of treaty controlled chemicals must be readied. Since the treaty specifies that, "where possible, the analysis of sample shall be performed on-site," and the allowable time for challenge inspections under the treaty is limited, this places a premium on rapid, accurate analysis for treaty prohibited materials. It is also expected that challenge inspections will be requested by foreign governments at U.S. sites where proprietary industrial and sensitive military research and/or production are being carried out, and thus the analysis of samples with general purpose techniques such as Gas Chromatography/Mass Spectrometry (GC/MS) might be deliberately used to probe for important information about commercial and military

projects unrelated to chemical weapons. This situation poses significant legal and security questions concerning U.S. industrial competitiveness and national security, and places a high premium on the development of inspection technologies which will provide accurate analyses for treaty prohibited materials *without* revealing the identity of other chemical compounds. Inspections will also involve known chemical weapons storage sites or production facilities where inspector safety will require monitoring and pre-screening measurements for CW agents down to approved Time Weighted Average (TWA) levels well below a part-per-billion (ppb) for some compounds. Combining these operational needs with the wide range of chemical and physical properties of the CWC schedule materials, provides a major technical design challenge.

1.2   TECHNICAL APPROACH.

The present program to develop a handheld chemical detector for CWC inspections is based on miniaturized gas chromatography technology, with emphasis on addressing the operational needs outlined above. GRC's program concept (Figure 1-1) is to translate much of the functional capability of benchtop GC/MS laboratory instrumentation into a handheld miniaturized GC based instrument that can be trained with software to accurately recognize the presence of CWC schedule compounds against complex backgrounds.

Gas chromatography is a powerful tool for the chemical analysis of complex mixtures. The analytical separation of the mixture results from differences in the time for each component in the mixture to flow through and exit the length of a capillary column (narrow tube) under controlled conditions. Here, thin polymeric coatings on the wall of the columns interact with components of the mixtures as they travel the length of the column. Components which spend more time in the carrier gas (as vapor) emerge earliest from the column, and those which interact more strongly with the wall coatings emerge later. This process efficiently separates the components in a sample, and the sequence of components observed by the detector as they emerge from the column is referred to as a chromatogram. The time required for a given component to travel the length of the column is its retention time. Thus, knowing the retention time of a particular targeted component under a given set of conditions

can be readily used to identify its presence in the sample, *without* revealing the identity of any unknown components.
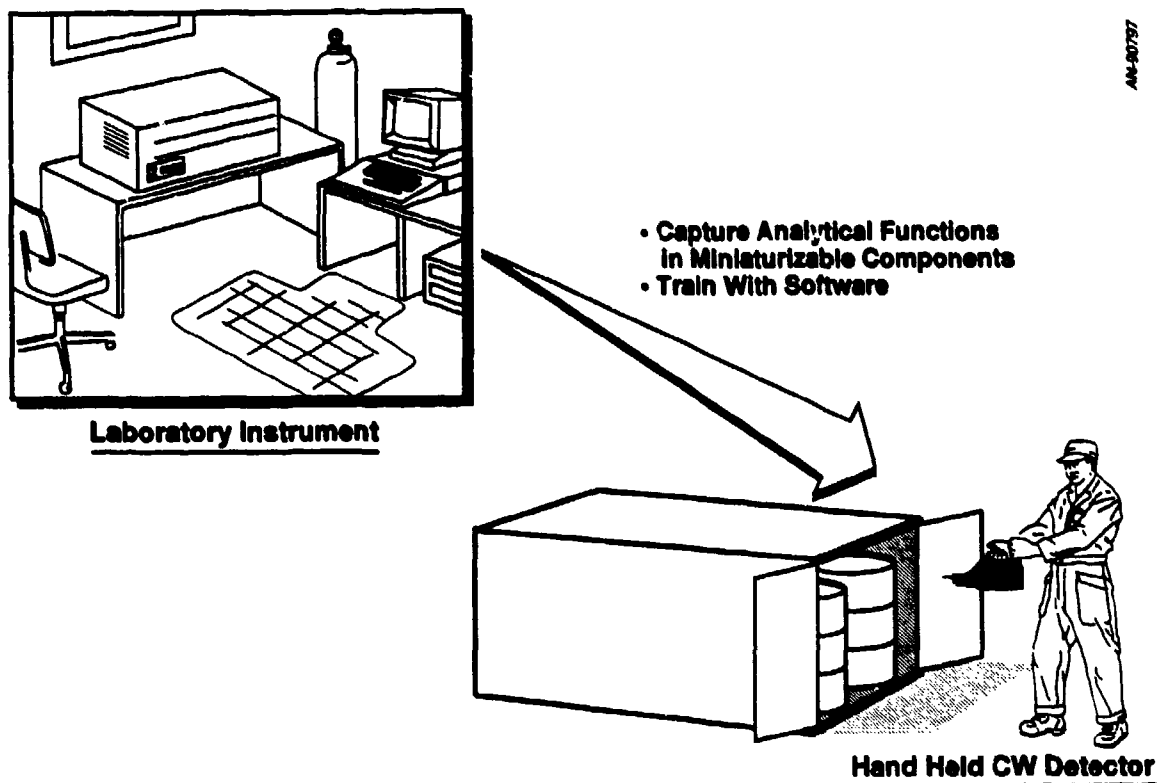
Figure 1-1. GRC's program concept.

GRC's technical design approach is based on the use of miniaturized GC technology coupled with compact specialized detectors and automated signal processing to develop a handheld instrument for use by CWC inspectors. Among the miniaturized GC technologies we have investigated are those based on the use of silicon micromachined components, such as injection valves and detectors (micro-GC), and innovative low thermal mass GC columns with integral heaters (mini-GC). Miniaturized GC technologies are very compact, robust, and consume little power. Also, chemical separations made with miniaturized GC's are typically carried out on time scales of seconds rather than the minutes required for conventional "bench-top" GC. These features make this technology well suited for handheld instrumentation.

Good selectivity will be required to discriminate CWC schedule chemicals against complex and highly variable environmental backgrounds in many inspection scenarios. The technologies we have investigated to address this need are correlated column GC and selective GC detectors. In correlated column GC, the sample is run simultaneously on two GC columns with different types of wall coatings. This results in differences in the separation of sample components on the two columns. Correlating the retention times for the components on the two columns effectively results in an enlargement of the "detection space" with each component now represented by its retention time "coordinates" in a two dimensional plot. This approach can greatly reduce overlap ambiguity between different compounds in complex samples. Another approach to the problem of discriminating CWC schedule chemicals against complex backgrounds is the use of selective GC detectors. Here, certain types of detectors effectively respond only to compounds containing particular elements, such as phosphorus, nitrogen or sulfur. Such compounds are especially prevalent among the CWC schedule materials, and are uncommon in most backgrounds. This approach can also provide a powerful means to discriminate CWC chemicals against backgrounds.

Finally, high detection sensitivity will be needed for CWC schedule compounds, especially those with low TWAs. For this need we have investigated preconcentration technology based on adsorbent traps and thermal desorption. This is relatively mature technology that has been well developed for environmental air sampling applications and previous CW agent detection work. In examining preconcentration technology, our primary effort has been focused on compatibility with CWC schedule compounds, miniaturization of components, and seeking ways to minimize power requirements.

1.3   REPORT ORGANIZATION.

The Concept Definition for the handheld detector is discussed in Section 2. This includes feasibility analysis for using micro-GC and mini-GC technologies for compounds on the CWC schedules. From this a functional and operational diagram of a handheld chemical detection instrument is developed.

In Section 3, the Functional Elements Evaluation is covered. Here, results from laboratory studies and measurements on the various components for the handheld chemical detector are discussed. This includes measurements of micro-GC and mini-GC performance, preconcentrator performance measurements, and results for various CW-selective GC detectors.

The Concept Instrument Design Specification is presented in Section 4 with a discussion of the hardware options and their ability to cover the CW schedule materials. A variety of detailed instrument concept designs are presented and analyzed in depth. These include dual module, enhanced mini-GC, and micro-GC instrument designs. From these, a recommended concept instrument design is specified, with a discussion of the critical design decisions and a summary of functional elements.

Finally, a brief summary with conclusions and recommendations is given in Section 5.

SECTION 2

CONCEPT DEFINITION

2.1 FEASIBILITY ANALYSIS OF USING MICROCHIP GC (μGC).

The feasibility of using a microchip GC (μGC) module capable of 2-D chromatographic analysis of CWC schedule materials is dependent upon several factors: the chromatographic requirements of the individual compounds contained in the schedules of CWC materials; their relative separations on selected pairings of GC column phases to provide the needed selectivity; the potential for additional selectivity through the use of specialized detectors which are selective for phosphorus or sulfur; and the ability to provide suitable signal processing capability for the automated detection of these compounds in gas chromatographic analyses. Example measurements of compounds contained in the schedules were performed by GC/MS in Task 1. These measurements demonstrated the selectivity gains which are possible through 2-D chromatographic analysis. Signal processing methods were then developed and tested in Task 2 which were specifically tailored to the detection of correlated GC measurements of CWC schedule compounds. The combination of these analyses with the GC/MS measurements show that significant differences in the separation performance are readily achievable with commercially available choices of GC column phase pairings which are especially suited for 2-D chromatography of the CWC schedule materials.

In considering the feasibility of using a single μGC module capable of 2-D chromatography, it seemed clear that the GC/MS separations measured for representative volatile compounds in the CWC schedules should be directly translatable to separations by μGC using equivalent columns. This has been confirmed and the data collected with μGC are presented in the Functional Elements Evaluation section of this report. In fact, the basic μGC design lacking a preconcentrator appears to have definite advantages over more conventional GC approaches using preconcentration for the detection of some CWC compounds because of the chemically reactive nature of these volatiles (primarily in Schedules 2 and 3 of the CWC schedules). However, the ability of μGC to detect the least volatile materials in the schedules was an issue which required further investigation.

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Given sufficient thermal stability, virtually any vaporizable organic compound can be analyzed by GC. Most low molecular weight organic compounds have sufficient vapor pressures that GC detectable quantities of vapor are present at ordinary room temperatures. Such compounds are termed "volatiles." In the current schedules of CWC treaty compounds listed in Table 2-1, about half of the compounds are volatiles. Most of the schedule 3 compounds, for example, are volatiles. However, as molecular weights increase, vapor pressures decrease rapidly to the point that GC analyses can be performed only with "thermal assistance." These compounds can be referred to as "semivolatiles," and the thermal assistance can take the form of constant GC operation at elevated temperatures or the use of time-varying "temperature programs." The GC analysis of semivolatile organic compounds using temperature programming is the most commonly used method because of the inherent resolution gained using this approach. Typically, a temperature program consists of initial operation of the GC at low temperatures followed by a gradual ramp of the GC column temperatures to high temperatures. Most of the Schedule 1 compounds and some of the Schedule 2 compounds in Table 2-1 are semivolatile compounds. While most of the compounds in the three schedules in Table 2-1 are relatively polar organic chemicals, the lower vapor pressures of the Schedule 1 compounds are largely a result of their higher molecular weights.

Since the GC requirements for the range of CWC compounds in Table 2-1 can be viewed as a range of temperature requirements, the feasibility issue for µGC becomes the range of temperatures at which µGC can perform analyses. As already mentioned, µGC analyses of volatiles comparable to GC/MS results are presented in the Functional Elements Evaluation section of this report. However, our analysis of measurements with µGC on borderline volatiles and semivolatile materials has indicated that there are significant limitations with semivolatiles analysis by µGC. From GC/MS measurements of semivolatile retention time simulants made in Task 1, it appears that GC temperatures in the range of 150-180 °C may be required for fast chromatography of the less volatile compounds in the schedules. While we expect that the semivolatiles performance of standard µGC hardware

Table 2-1. CWC schedules.

SCHEDULE 1

1.	O-alkyl alkyl phosphonofluoridates
2.	O-alkyl N, N-dialkyl phosphoroamidates
3.	O-alkyl S-2-dialkyl aminoethyl alkyl phosphonothiolates
4.	Sulfur mustards
5.	Lewisites
6.	Nitrogen mustards
7.	Saxitoxin
8.	Ricin
9.	Alkyl phosphonyldifluorides
10.	O-Alkyl O-2-dialkyl aminoethyl alkyl phosphonites and corresponding protonated salts
11.	Chlorosarin
12.	Chlorosoman

SCHEDULE 2

1.	Amiton
2.	PFIB
3.	BZ
4.	Organophosphates having a single methyl, ethyl, or propyl group bonded to the phosphorus atom
5.	N, N-dialkyl phosphoramidic dihalides
6.	Dialkyl N, N-dialkyl phosphoramidates
7.	Arsenic trichloride
8.	2, 2-Diphenyl-2-hydroxyacetic acid
9.	Quinuclidin-3-ol
10.	N, N-Dialkyl aminoethyl-2-chlorides and corresponding protonated salts
11.	N, N-Dialkyl aminoethane-2-ols and corresponding protonated salts
12.	N, N-Dialkyl aminoethane-2-thiols and corresponding protonated salts
13.	Thiodiglycol
14.	Pinacolyl alcohol

SCHEDULE 3

1.	Phosgene
2.	Cyanogen chloride
3.	Hydrogen cyanide
4.	Chloropicrin
5.	Phosphorus oxychloride
6.	Phosphorus trichloride
7.	Phosphorus pentachloride
8.	Trimethyl phosphite
9.	Triethyl phosphite
10.	Dimethyl phosphite
11.	Diethyl phosphite
12.	Sulphur monochloride
13.	Sulphur dichloride
14.	Thionyl chloride
15.	Ethyldiethanolamine
16.	Methyldiethanolamine
17.	Triethanolamine

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can be extended, an analysis of the temperature limitations of µGC was conducted to determine the specific temperature limitations and the extent that they could be remedied.

These temperature limitations on current µGC performance are primarily due to condensation of semivolatile vapors on unheated surfaces within the µGC. A measurement of so-called "wall effects" in a µGC inlet system is shown in Figure 2-1. In these measurements, equal vapor concentrations of the normal alkane hydrocarbons ranging from heptane to decane were passed continuously through the sample inlet system and the exiting concentrations were monitored. Losses in the exiting vapor concentrations due to wall effects increase with the molecular weight as shown by the smaller peak areas for nonane and decane. As the flow volume increases, the concentrations increase at a rate dependent upon the vapor pressure. Heptane, the most volatile of the hydrocarbons shown in Figure 2-1, is the least affected and 2 mL of flow is sufficient to overcome the wall losses. In contrast, decane concentrations are severely depressed by wall losses and the data do not even show the expected slope illustrated by the dashed line in the figure.
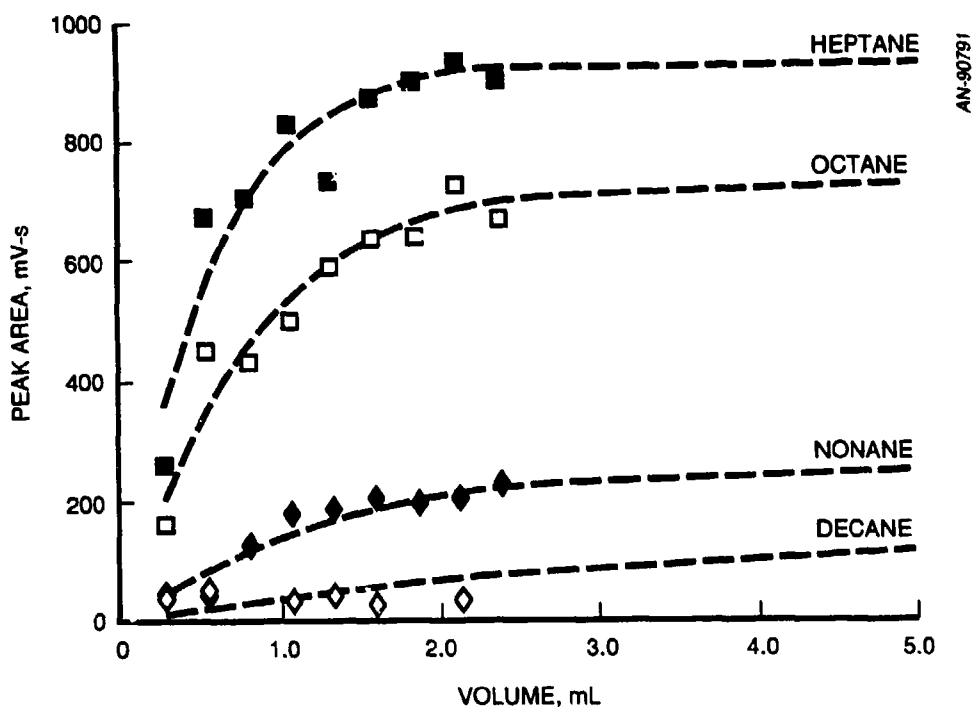
Figure 2-1. Wall effects in sample inlet system in current µGC.

Standard approaches to limit wall losses of semivolatile materials in GC consist of heating the sample transfer lines and any components in the vapor pathway of the instrument. The standard µGC contains lengthy (1-2 ft) unheated lines in the sample inlet system. These could easily be shortened and heated similar to conventional GC transfer lines to eliminate this source of wall effects. However, within the µGC modules there are cold spots in the vapor pathways that use unheated components. While the GC columns are heated in the µGC modules, the silicon micromachined injectors and the microfabricated detectors are not heated. Experimental testing of the injectors suggests that they can be heated very carefully to about 120 °C before the glues become too soft and the part fails. Temperature cycling near this temperature results in part failure. It is believed that the injector can probably be operated in a lower temperature range such as 60-80 °C, but the long-term stability of the injector at such elevated temperatures has not been established. In any event, this temperature range is far below the estimated 150-180 °C range required for the fast GC analysis of the least volatile compounds of interest. Discussions with MTI indicate that a major effort would be required to fabricate a new micromachined injector using different gluing or bonding techniques for high temperature stability. This is not within the current scope of their new product development plans.

Additional cold spots in the vapor pathways of the µGC modules are the thermal conductivity detectors and the regions of unheated GC columns between the column heater and both the injector and the detector. The miniature thermal conductivity detector used in the µGC operates with a detector filament at about 150 °C while the detector body remains at about 80 °C. To operate this detector at much higher temperatures while maintaining this differential required for detector operation is expected to result in the destruction of the miniature detector filament. Thus the operable temperature range is again far below the required 150-180 °C. Similar to the situation with the silicon micromachined injector, a new and different fabrication effort would likely be needed to develop a miniature thermal conductivity detector with higher temperature operation. A better route might be the substitution of a different detector possessing higher temperature operation and selective detection of organophosphorus or organosulfur compounds. However, the temperature limitation of the micromachined injector would still remain.

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Our measurements with µGC demonstrate that analyses of the normal alkane hydrocarbons (e.g., the hydrocarbons shown in Figure 2-1) are limited to about C_{11} (undecane). This is primarily the result of wall effects, but low vapor pressures also become a factor in the direct detection of the heavier hydrocarbons. The breakpoint at the C_{10}-C_{11} range is approximately the point where a conventional line is drawn between volatiles and semivolatiles. One common practices is to regard compounds with vapor pressures less than 1 Torr at ordinary room temperature and standard pressure as semivolatiles. This coincides with the C_{10}-C_{11} limit of the current µGC instrument operating at about 50 °C. It is estimated that an additional 2 carbons of chain length can be gained for about every 20 °C increase in temperature. Given the temperature limit imposed by the injector, this suggests that extending µGC operation to include C_{13} or C_{14} is probably the limit with current µGC technology. With the chromatography requirement for semivolatiles such as VX (near C_{17}), an alternative approach is required.

While conventional GCs easily accomplish the chromatography of semivolatiles such as VX, their use of temperature programmed ovens are not amenable to the small size and low power requirements of a handheld instrument. For this reason, we are developing a small, ultra-low thermal mass GC for the fast analysis of these semivolatile materials.

2.2   FEASIBILITY OF SEMIVOLATILES ANALYSIS WITH MINIATURIZED, LOW THERMAL MASS GC.

The extremely wide scope of CWC compounds ranging from very light volatiles to heavy semivolatiles in Table 2-1 create unusually broad demands on the capability of the chemical detectors. The analysis of the GC requirements and the capability limits of µGC in the previous section indicate the need for an alternative approach for the analysis of the heavier semivolatiles of the CWC schedule. While GC is routinely used for the analysis of semivolatile materials, the conventional approaches are not well suited for a handheld instrument because of the size and power requirements for temperature programming GC ovens. In principle, an isothermal analysis is conceivable for semivolatiles which would save time and power by not requiring temperature programming. However, given the range of semivolatiles which need to be chromatographed, a sufficiently high temperature for the

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timely analysis of the least volatile materials will be far too high for adequate separation and analysis of the lighter semivolatiles. Thus, it appears temperature programming will be needed for coverage of the semivolatiles between C_{10} and C_{20}.

Temperature programming not only provides the means to chromatograph compounds having a wide range of vapor pressures, but also provides a higher resolution approach to covering such a range of compounds. To a first approximation, peak resolution is determined in part by the elution time for a compound. By accelerating the elution of compounds by heating a column, the elution times are shortened and the late peaks are typically much narrower than with isothermal chromatographic analyses. An example of the increased resolution available through temperature programming is shown in Figures 2-2 and 2-3. Figure 2-2 shows an isothermal 40 °C analysis of a 10 component mixture separated with a 0.1 mm i.d. OV-1701 column on a μGC instrument. In particular, notice the increasing broadening of the peaks as the elution times increase. Figure 2-3 shows a μGC analysis of the same mixture using the same GC column but with temperature programming. The temperature program consisted of isothermal operation at 40 °C for 30 s followed by a ramp at a rate of 1 °C/s to 120 °C. The chromatograms are equivalent for the first 30 s showing the high precision and resolution of μGC for fast GC analysis. The compounds eluting after 30 s in Figure 2-3 are significantly accelerated and narrowed by the temperature ramping. Thus, temperature programming both increases the resolution and compresses the required analysis time for a range of compounds. This is especially important in considering a range of semivolatile compounds as wide as C_{10}-C_{20}.

Under subcontract to GRC, Prof. Edward Overton of the Institute for Environmental Science at Louisiana State University (LSU) is assisting our effort with the development of an innovative, low thermal mass "mini-GC" for semivolatiles analysis. The concept mini-GC under development is illustrated in Figure 2-4. The primary component of the mini-GC is the analytical column in the bottom center of the figure. This component is an ultra-low thermal mass GC column of short length and small inside diameter. It consists of a capillary GC column together with a heater wire and a temperature sensor wire. The capillary column and

TEMPERATURE ISOTHERMAL AT 40°C

450
490
598
644
704
711
754 769
846

VOLTS

4

2

0

20   40   60   80   100   120

TIME, seconds
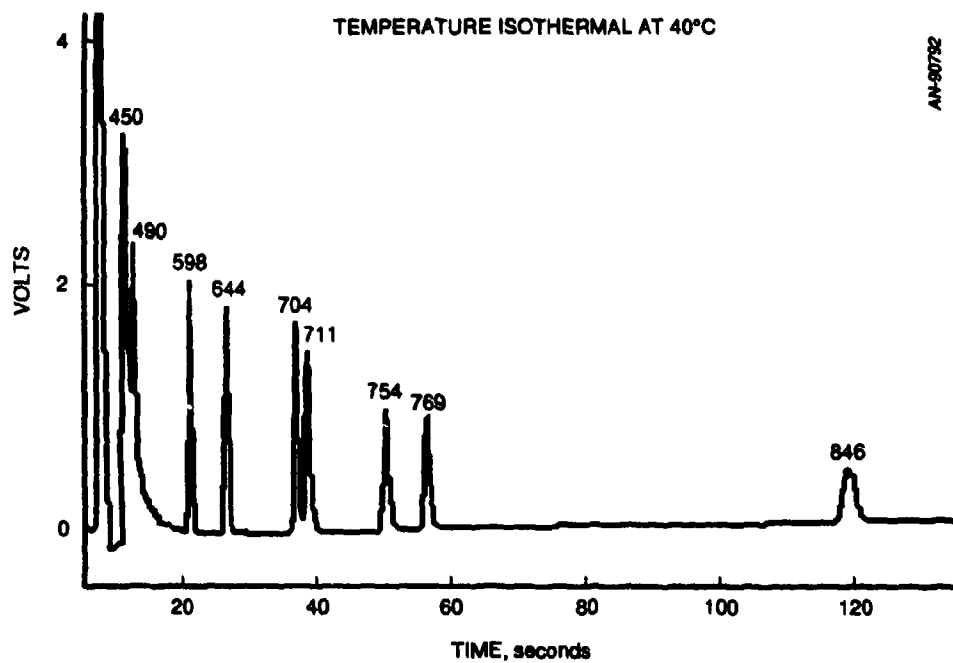
Figure 2-2. Ten component mixture separated isothermally at 40 °C by μGC.

TEMPERATURE PROGRAM:
40°C FOR 30 SECONDS
RAMP @ 1°/sec TO 120°

450
490
598
644
704
711
754
769
846
930

VOLTS

3

2

1

0

20   40   60   80   100   120

TIME, seconds
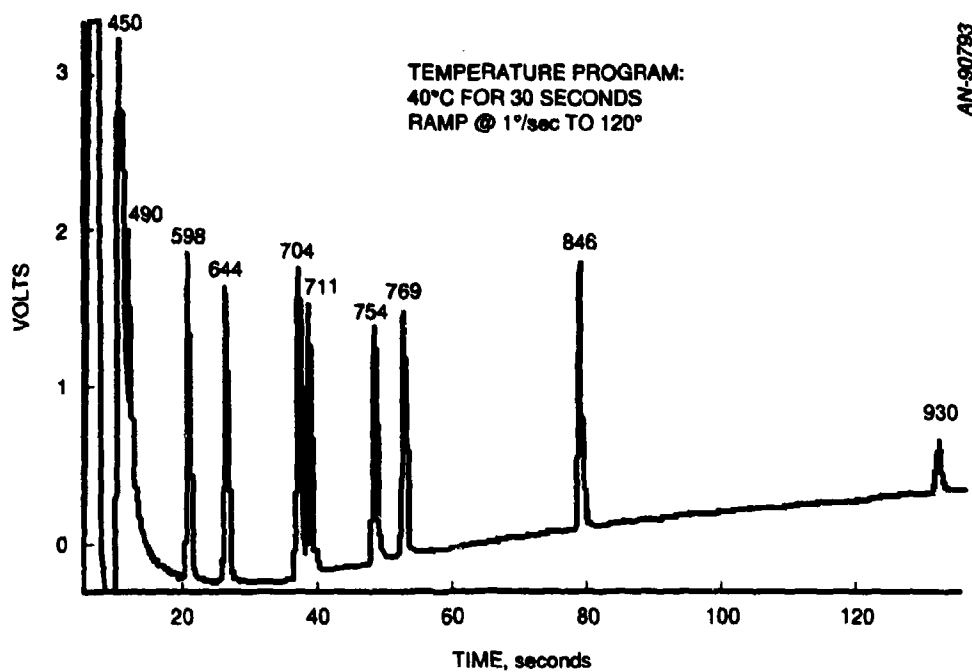
Figure 2-3.   Temperature-programmed μGC separation of the ten component mixture shown in Figure 2-2.

13
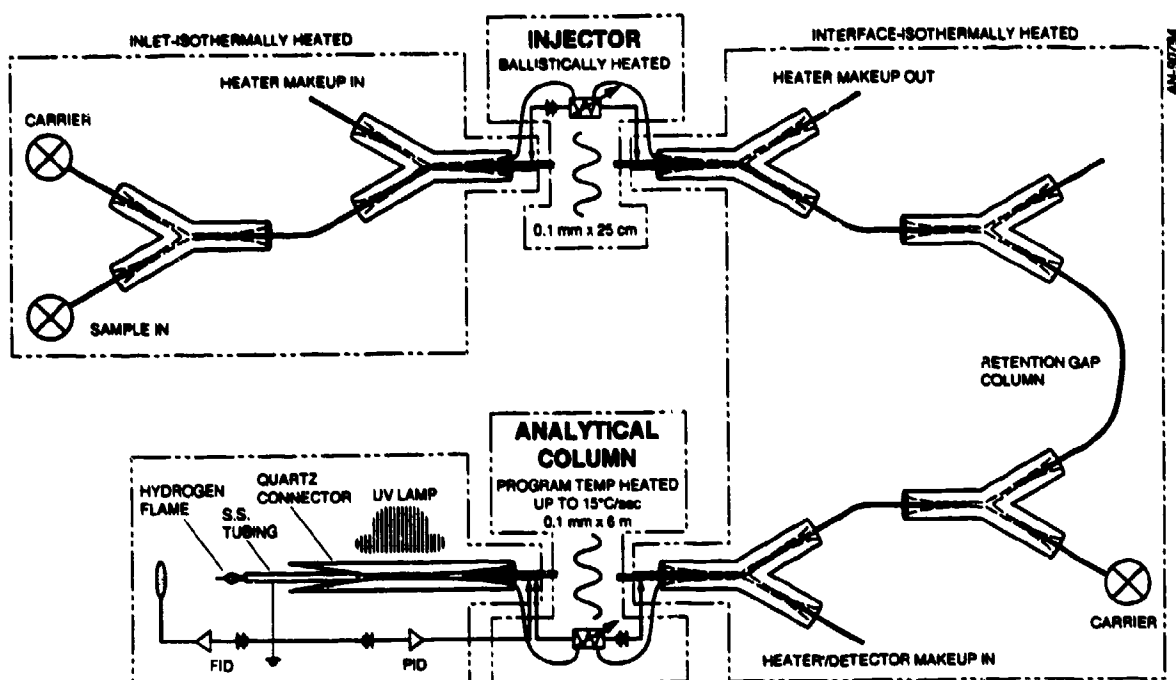
Figure 2-4. Mini-GC instrument concept featuring ultra-low thermal mass analytical column.

the sensor wire can be bundled with the heater wire in an insulating tube, or can be inside the heater "wire" (in this case, a small diameter thin-walled tube, for example). Such an approach minimizes the mass of the GC "oven" needed for temperature programming to the mass of the small tube of an inside diameter of 1 mm or less. Such a low thermal mass makes fast temperature programming possible. The inclusion of a temperature sensor wire provides precise electrical control of the temperature programming.

The injector assembly in the top center of Figure 2-4 provides a short section of column which is rapidly heated to provide injection onto the analytical column. Here, the injector functions as a small volume "trap" for the injection of vapors onto the analytical column. Such an injector is not a requirement for the temperature-programmed chromatography of semivolatiles since a cool analytical column itself will effectively trap injected volatiles in a narrow band on the analytical column. This eliminates the need for an injector. Instead, the injector can be replaced by a larger preconcentrator trap which releases precon-

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centrated vapor for analysis on the analytical column. The need for a preconcentrator trap containing an adsorbent material is anticipated for the detection of semivolatile compounds because the vapor concentrations are typically very low for these compounds. The remaining parts of the concept mini-GC in Figure 2-4 are plumbing connections between the analytical column, and sample inlet and the example detectors. These regions of the mini-GC are isothermally heated to eliminate wall effects. Heater make-up gas is also illustrated in Figure 2-4 for both the injector and analytical column assemblies. The purpose of the heater make-up gas is to provide a flow of gas between the heater wire and the other column elements to evenly distribute the temperature within the injector and the analytical column. Recent work at LSU suggests that the heater make-up gas is not needed for the current application.

Work at LSU has now progressed to the functional demonstration of the various components of the mini-GC. This is presented in Section 3.3 of this report.

2.3   DEVELOPMENT OF A FUNCTIONAL AND OPERATIONAL DIAGRAM OF A HANDHELD CW DETECTION INSTRUMENT.

Instrument Functional Components for CW Schedule Volatiles Detection. Based upon the feasibility analysis described earlier in this section of the report, the functional and ~ ?rational diagram of the instrument components required for a handheld detector for the ? schedule volatiles can be developed. First, a list of the functional elements is enumerat- ? ?hich meet the requirements for handheld detector components in volatiles detection. These functional elements consist of physical modules which combine to provide the overall funct. ?al performance required by the instrument. Whenever possible, the functional ele. ?.?ts are physically separable modules which provide a modular approach in the design of the instrument. Such a representation is convenient both conceptually and functionally for determining a concept instrument design having ease of maintenance and upgradability as components improve in the future.

The required functional elements for vapor detection are listed in Table 2-2 and can be described as follows. Air samples are drawn through the sample inlet of the instrument by an air sampling pump. We have demonstrated two types of small air sampling pumps in our

laboratory: high volume air sampling handheld personal air sampling pumps, and small pumps internal to the Microsensor Technology Inc. (MTI) instrumentation used for drawing samples into the instrument. In the latter case, vapor samples fill the sample loop in the μGCs micromachined injector assembly which is in the flow pathway of the sample inlet. Under the control of the μGC control electronics, microvalves switch the sample into the flow of the μGC columns. The valve switching is pressure actuated and controlled by the pressure control valving which is also under the direct control of the μGC control electronics.

Table 2-2. Functional elements for CW schedule volatiles.

1.	Air Sampling Pump
2.	μGC
3.	CW-Selective Detector
4.	Pressure Control Valving
5.	μGC Control Electronics
6.	Signal Conditioning Electronics
7.	Signal Processing Electronics/Software
8.	Display/Alarm Generation/Instrument Controls
9.	Data Storage
10.	Off-line Diagnostics/Retraining Software
11.	Rechargeable Batteries
12.	Rechargeable Carrier Gas Supply

In this design, a CW-selective detector having a high sensitivity for organophosphorus is used in series with the μGC's lower sensitivity miniature thermal conductivity detectors since the μGC's detectors are non-destructive. The small signals developed by the μGC's detectors and the CW-selective detector are scaled and digitized by the signal processing electronics. The resulting chromatographic traces are received by the signal processing electronics which analyze the traces for the chromatographic peak contents and CWC compound signature content.

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The display and instrument controls indicate the results of the analysis, recall previous results, indicate instrument status, and perform the other required operations for calibration and operation of the instrument. Removable PCMCIA cards, for example, can provide data storage so that the handheld treaty inspection instrument contains no non-removable magnetic media. Additional software in a remote, portable personal computer (PC) can be used to produce copies of PCMCIA card data if needed, retrain algorithms, and perform diagnostics of the instrument. Additional modules include a small rechargeable cylinder of carrier gas for the chromatography, and rechargeable batteries.

The functional diagram for the CW volatiles detector is shown in Figure 2-5. This figure shows the inter-relationships between the different functional elements of the instrument at the highest level. The opening of valves and the operation of the sampling pump allow the injector's sample loop to fill with sample vapor. The valves are then closed and the sample vapor is injected into the path of the GC columns after the sample loop is pressurized with carrier gas. The μGC control electronics activate the valves in the pressure control manifold which actuate the injector valves to accomplish this injection onto the μGC columns. The μGC control electronics also control the constant temperature of the GC column within the μGC module. The signals from the μGC detectors and the CW-selective detector are conditioned, digitized, and passed to the signal processing electronics by the signal conditioning electronics. The signal processor analyzes the data, communicates with the display/instrument control module and the μGC control electronics. A remote PC is illustrated for advanced, but infrequently needed operations such as algorithm modifications, possible end-of-day data duplication needs for the inspected and inspecting parties, and advanced diagnostics of the instrument.

Instrument Functional Components for CW Schedule Semivolatiles Detection.
The functional diagram and elements list for a handheld CW schedule volatiles detector was developed and described above. A similar development for the components required for CW schedule semivolatiles detection can be developed as follows. Again, these functional elements consist of physical modules which combine to provide the overall functional performance required by the instrument. A modular approach is taken for both conceptual and functional purposes.

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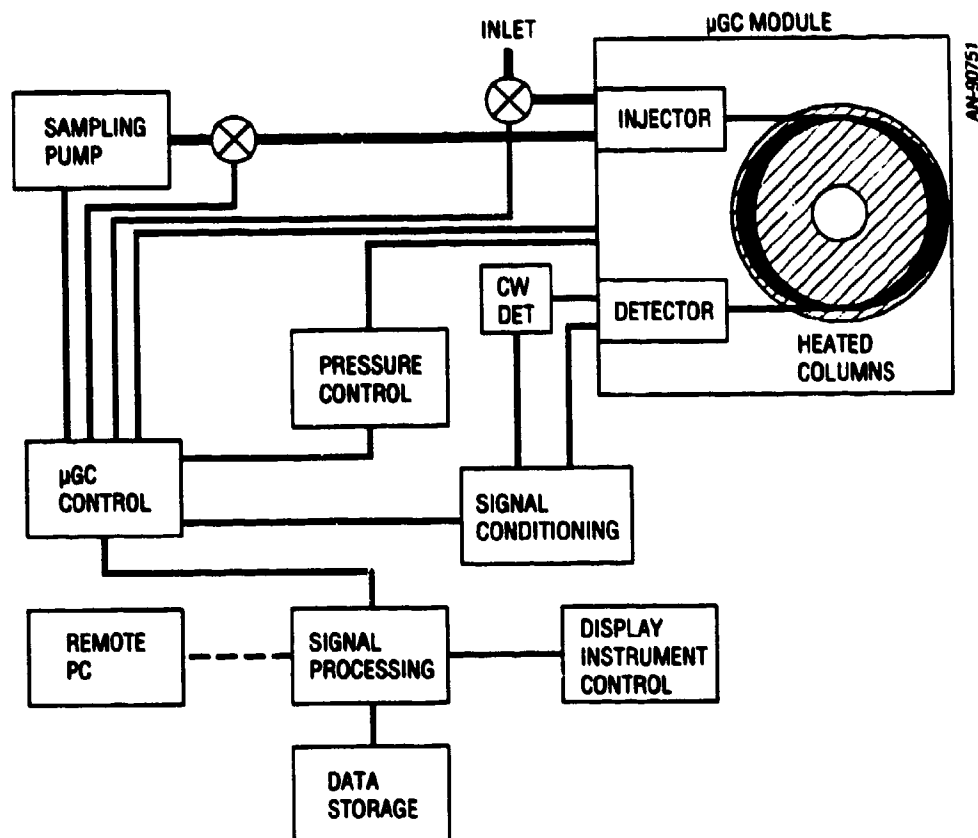
Figure 2-5. Functional diagram for a μGC-based volatiles detector.

The required functional elements for semivolatiles detection are similar to those listed for volatiles detection and are listed in Table 2-3. The main differences are described as follows. A vapor preconcentrator is present in this case to provide the required sensitivity needed for semivolatiles detection. Because of the low volatility of these materials, their low vapor concentrations require preconcentration prior to GC analysis. This is a standard approach with semivolatiles and is the approach used by GC instruments such as the Army's ACAMS and MiniCAMS developments for monitoring G agents, VX, and HD. A sampling pump draws a large volume of air containing vapor through a preconcentrator tube containing an adsorbent material. The vapors in the air are adsorbed on the high surface area adsorbent materials in the traps. These traps are then heated to release the adsorbed vapors into the mini-GC, either onto an injector assembly or directly onto the analytical column. The heating is controlled directly by the mini-GC control electronics. The control of the mini-GC is

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similar to the control of the μGC. The remaining functional elements are essentially the same as for the case of the μGC.

Table 2-3. Functional elements for CW semivolatiles detection.

1.	Air Sampling Pump
2.	Vapor Preconcentrator
3.	Mini-GC
4.	CW-selective Detector
5.	Mini-GC Control Electronics
6.	Signal Conditioning Electronics
7.	Signal Processing Electronics/Software
8.	Display/Alarm Generation/Instrument Controls
9.	Data Storage
10.	Off-line Diagnostics/Retraining Software
11.	Rechargeable Batteries
12.	Rechargeable Carrier Gas Supply

The functional diagram for the semivolatiles detection instrument components is shown in Figure 2-6. That there are many functional similarities and common components can be seen in comparing this diagram with Figure 2-5 for the CW volatiles components analysis. The key differences are as follows. An adsorbent tube preconcentrator is placed in the sampling line between the inlet and the sampling pump. Valves are present on each side of the preconcentrator. Initially air is drawn through the preconcentrator, then the valve to the pump is closed while the trap is heated. After the trap is heated, carrier gas is routed through the trap from the sampling pump (this valve detail is not shown in the figure), through the inlet valve, and into the mini-GC module. The temperature-programmed elution profile from the mini-GC module as detected by a CW-selective detector results in the chromatogram. The remaining functions in the diagram are essentially the same as for the volatiles components described in Figure 2-5.
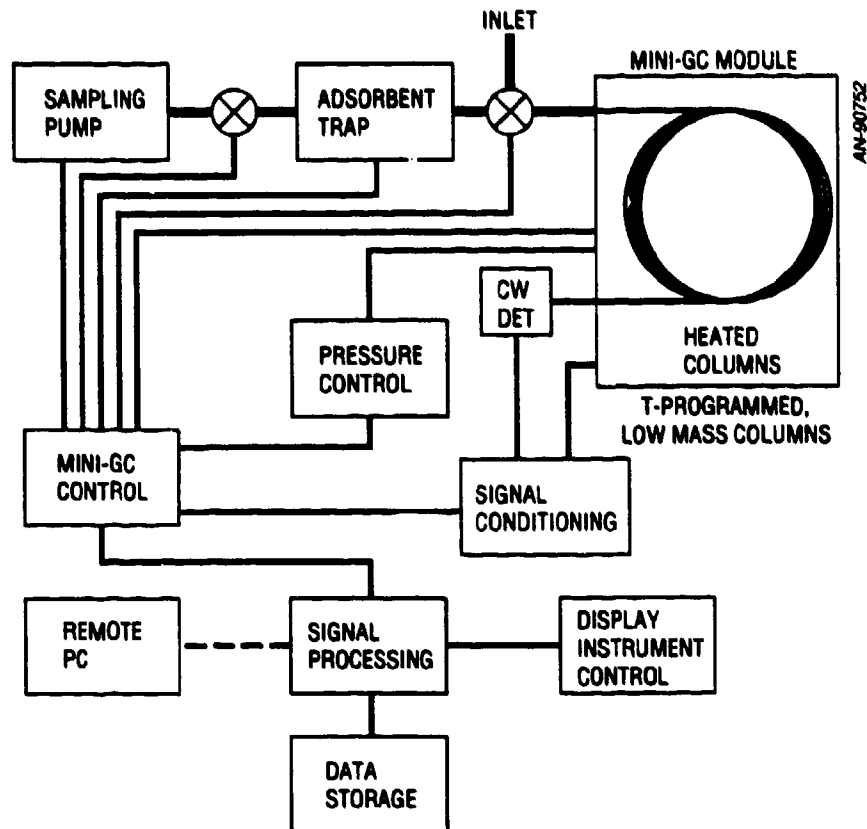
Figure 2-6. Functional diagram for a mini-GC-based semivolatiles detector.

The descriptions contained in the figures and tables in this section are meant to provide a high level description of the components needed for the concept instrument for the purposes of the functional elements evaluation. This evaluation activity in Task 3 is guided by these descriptions to demonstrate the required capabilities for the selected pieces of hardware necessary for this concept of operation. This more detailed analysis of the functional elements serves to establish any additional requirements or necessary modifications, and specify a concept instrument design. This is discussed in the following section of this report.

SECTION 3

FUNCTIONAL ELEMENTS EVALUATION

The purpose of the functional elements evaluation is to repeat certain experimental measurements of the earlier tasks of the program by testing the selected pieces of hardware chosen for the concept instrumentation. The schematic diagrams of the µGC-based hardware for volatiles detection outlined in Figure 2-5 includes such components as µGC injectors, columns, µGC and CW-specific detectors, control components, sampling pumps, and signal processing components. While correlated chromatography for detection selectivity was demonstrated in the first task of the program using laboratory GC/MS, experiments are required to demonstrate that the chromatographic requirements for the CWC schedule volatiles can be met with µGC hardware. µGC performance and the performance of correlated column µGC are examples of key functional elements of the volatiles detection hardware which must be evaluated prior to proceeding with the fabrication of the concept instrument.

Similarly, the functional elements of the mini-GC hardware required for the detection of CW schedule semivolatiles must be evaluated prior to the specification of the concept instrument. The schematic diagram of the low thermal mass mini-GC was shown in Figure 2-6 and includes some of the same components shown in Figure 2-5. New components include the mini-GC module, its control components, and a preconcentrator. As discussed in the earlier section, semivolatiles detection capability has never before been put into a sufficiently small module for use in handheld, fast GC analysis. This new technology development requires demonstration of the components and their integration into a suitable module to meet the needs of the handheld CW detector. The functional elements evaluation of the required mini-GC components are described in a following section.

3.1 MEASUREMENT OF µGC PERFORMANCE.

The feasibility of using correlated µGC modules to detect CWC schedule materials has been a key part of the functional elements evaluation, and was the subject of investigation

earlier in Tasks 1 and 2. In this work, a dual column M-200 μGC manufactured by Microsensor Technology Inc. (MTI) was used to measure representative CWC schedule 2 and 3 volatiles. This instrument has been customized with 4 meter DB-5 and DB-210 capillary columns.

The standard M-200 μGC manufactured by MTI is designed for fast GC analysis of gases and light volatiles at concentrations of 1 ppm and above. It is a dual column gas chromatograph with two chromatographic modules, each having its own injector, GC column, and detector. The injector assembly in the module contains valves micromachined in silicon. The detector assembly (Figure 3-1) is also microfabricated by MTI. The GC columns connecting these two components consist of small bore GC columns which are commercially available. A variety of different column choices exist for designing and optimizing correlated chromatography applications with this dual chromatography unit. The layout of a typical μGC module is shown in Figure 3-2 together with the microfabricated detector. Each module actually contains a pair of GC columns with one column used for reference measurements at the detector. The detector itself is a microfabricated dual thermal conductivity detector (TCD) and the reference GC column provides correction for temperature or pressure fluctuations. The entire module is only 6" long by 4" wide.
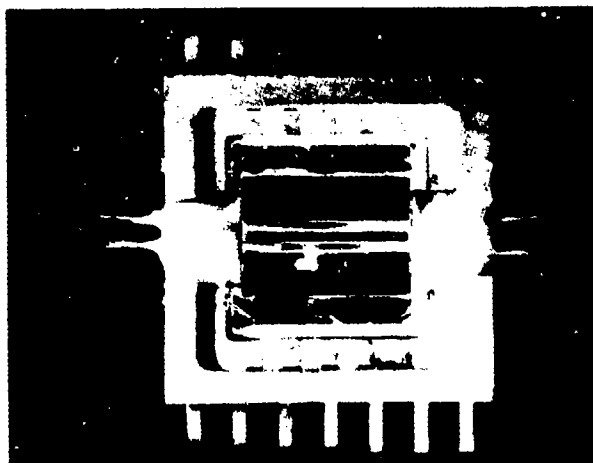
Figure 3-1. Close-up of an MTI microfabricated thermal conductivity detector.
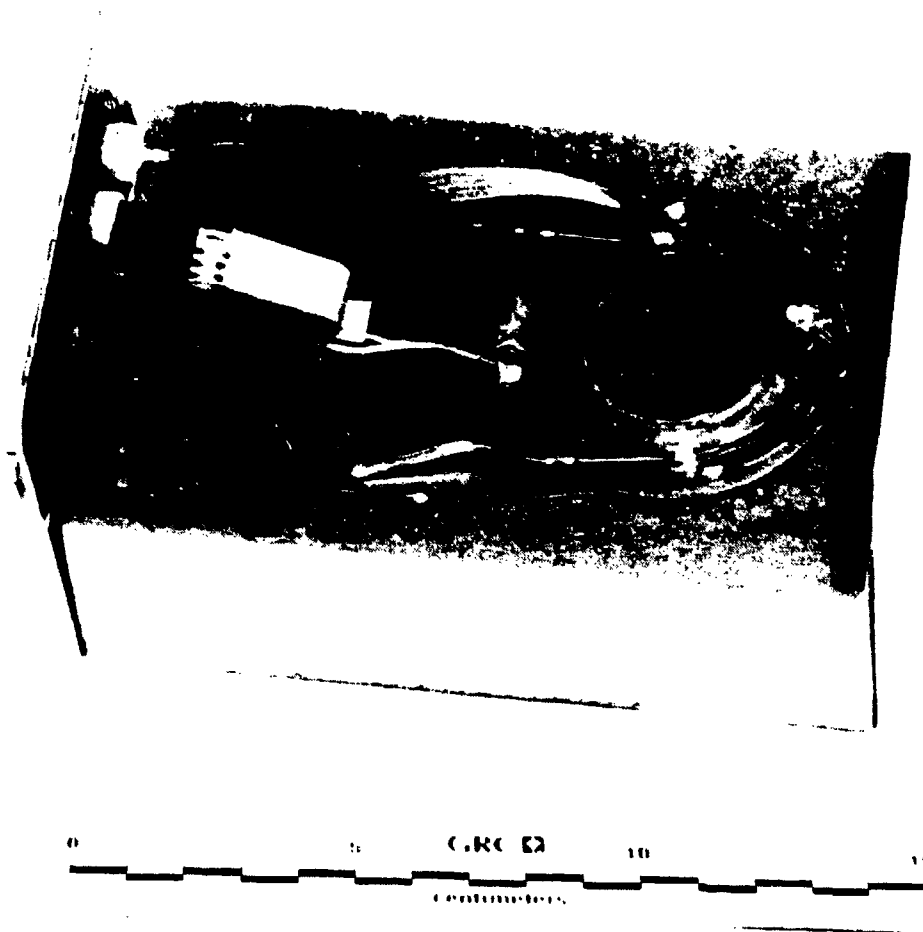
Figure 3-2. Interior of an MTI μGC module.

As shown in Figure 3-2, the injector assembly is potted in a small volume of plastic for ruggedness. The GC columns are also attached to the heater for ruggedizing and temperature control. The small TCD is shielded to reduce noise pickup at the detector. The foam insulation above the TCD has been removed for this picture. The modules manufactured by MTI are housed in metal, and both weight and size could be reduced by repackaging the modules with better insulating materials.

A schematic of the operational components of the M-200 µGC instrument is shown in Figure 3-3. The µGC modules are the two sets of components on the right of this figure.
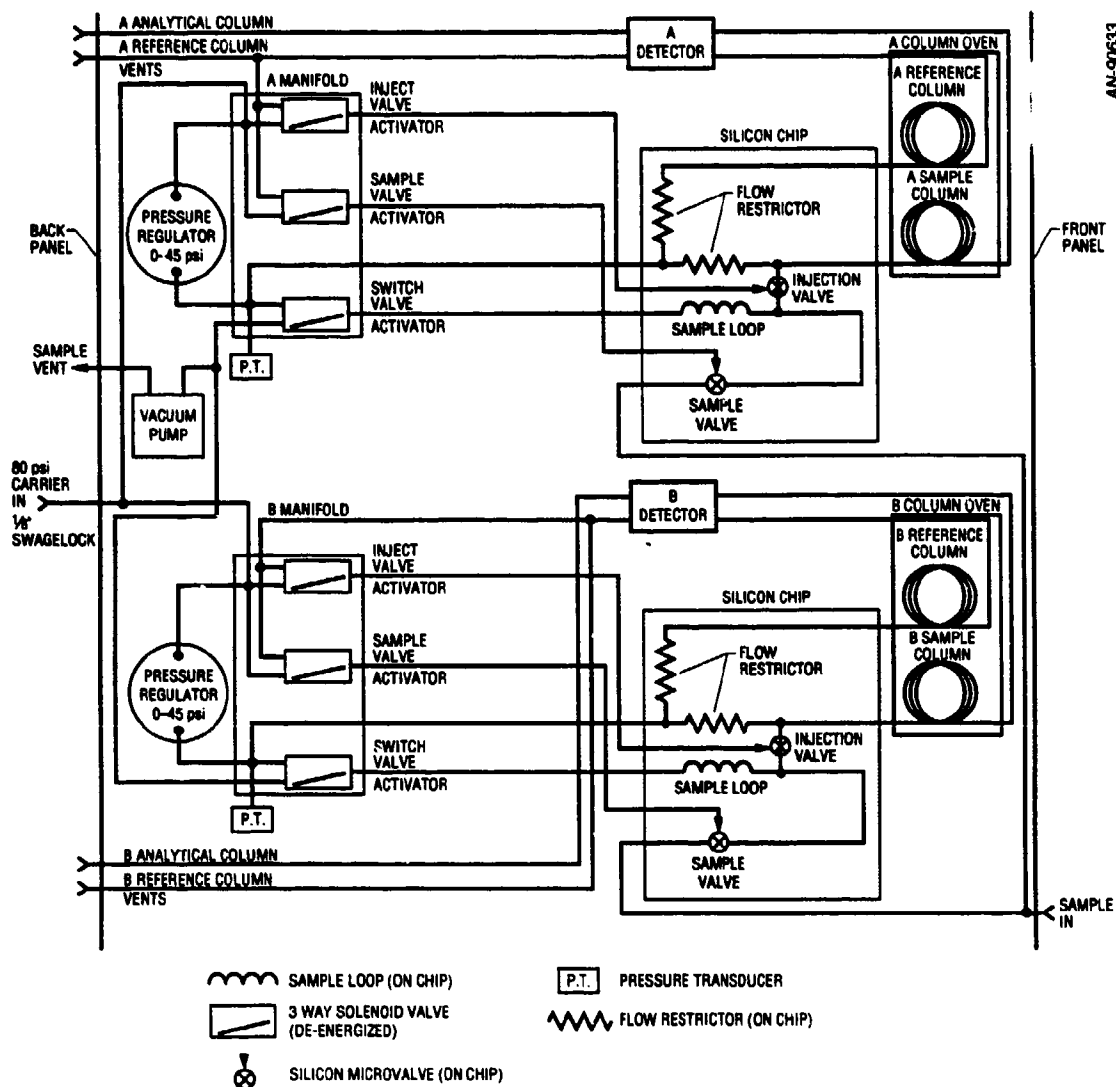
Figure 3-3. MTI M-2000 pneumatic diagram.

This instrument functions as follows. First, the switch valve actuators shown in each pressure manifold (shaded, on the left) open the sample loop line of the injectors to the vacuum pump. This draws vapor samples through the sample loops from the sample inlet on the front panel of the instrument. The sample loop on the silicon injector chip is about 10 µL in volume. After this loop has been filled with vapor sample, the sample valve is closed and the sample

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loop is pressurized with carrier gas (sample switch valve) to a pressure approximately 5 psi above the column head pressure. A flow restrictor on the silicon chip is responsible for the pressure drop between the pressure regulator and the injector valve at the column head. The injector valve is then briefly opened and the pressure differential injects the contents of the sample loop onto the analytical column. The duration of the injector valve actuation is set through the controls on the MTI instrument. Following an injection, the sample loop in the injector is flushed with carrier gas while the chromatographic separations are performed by the µGC columns.

Although the microfabricated thermal conductivity detector is capable of detecting very small quantities, the overall sensitivity of the M-200 is only about 1 ppm. This is primarily due to the small injection volumes which are provided by the sample loop relative to the speed of the detector. The minimum sample volume including the volumes of the inlet lines needed to fill the sample loop is about 200 µL. Of this volume, the maximum injection volume is 0.25 µL from the sample loop itself. The volume of the TCD is about 60 nL/electrode which gives a detection limit of about 10 femtograms. The TCD sampling rate of 100 Hz then requires an injection of approximately 1 pg for observing a peak width of 1 s. Given the ratio of injection volume to minimum sample volume, this is equivalent to 1 ng of vapor in approximately 200 µL of sample which corresponds to the ppm range of sensitivity.

CWC schedule volatiles measurements using µGC. A number of volatile compounds on the CWC schedules were analyzed to demonstrate the feasibility of detecting them using correlated column µGC. Trimethyl phosphite, triethyl phosphite, phosphorus pentachloride, sulfur dichloride, pinacolyl alcohol, and thionyl chloride were selected because they appear on schedules 2 or 3, are commercially available, and exhibit a sufficient range of chemical and physical properties to provide a useful test of the ability of correlated column GC to separate such diverse components in two dimensions. The columns chosen for this work were DB-5, a standard "nonpolar" stationary phase, and DB-210, a partially fluorinated "polar" phase. These very different column types provided a high degree of contrast, with excellent potential for good 2-D separations performance. The GC separations were performed isothermally at 50 C.

Pairs of chromatograms for these measurements are shown in Figures 3-4 to 3-7. It should be noted that with µGC the time scales for these separations are in seconds, rather than the minutes characteristic for ordinary laboratory GC. In order to examine the ability to distinguish the chromatographic signatures of these schedule compounds against background materials, the correlated chromatograms of a variety of industrial type chemicals were also run under the same conditions. These included benzene, toluene, acetone, chloroform, methanol, ethanol, photo resist, and well as the series of normal hydrocarbons which are often used as retention index standards.

A composite of all these chromatograms is plotted in two dimensions in Figure 3-8, where the results exhibit good spread in two dimensions. It can be seen, for example, that the normal hydrocarbons elute especially rapidly on the DB-210 column and are well separated from the other materials. Projection of these composite results onto either of the chromatographic axes, provides an indication of how difficult reliable identifications would become using one dimensional gas chromatography. The correlated chromatography results from this study have also been used in developing a database for recognition of these compounds and the testing of various signal processing algorithms.

3.2   MICROTRAP PRECONCENTRATION AND SAMPLE STABILITY.

The sensitivity of the M-200 µGC modules is limited by the injected volume of vapor which reaches the GC columns. A standard approach for enhancing the sensitivity of GC-based methods is to preconcentrate vapors onto a trap before delivering these concentrated vapors to the injector or GC column. Such an approach has been previously investigated by Prof. Edward Overton and Louisiana State University (LSU) using the MTI hardware. As part of this program, LSU has made special modifications to our M-200 µGC instrument to directly incorporate preconcentration via microtrap preconcentrators.

A diagram of the microtrap modified M-200 µGC is shown in Figure 3-9. The primary change is the addition of a preconcentrator in the sample loop line of each module between the injector and the pressure control manifold. A picture of the small adsorbent trap

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DB-5
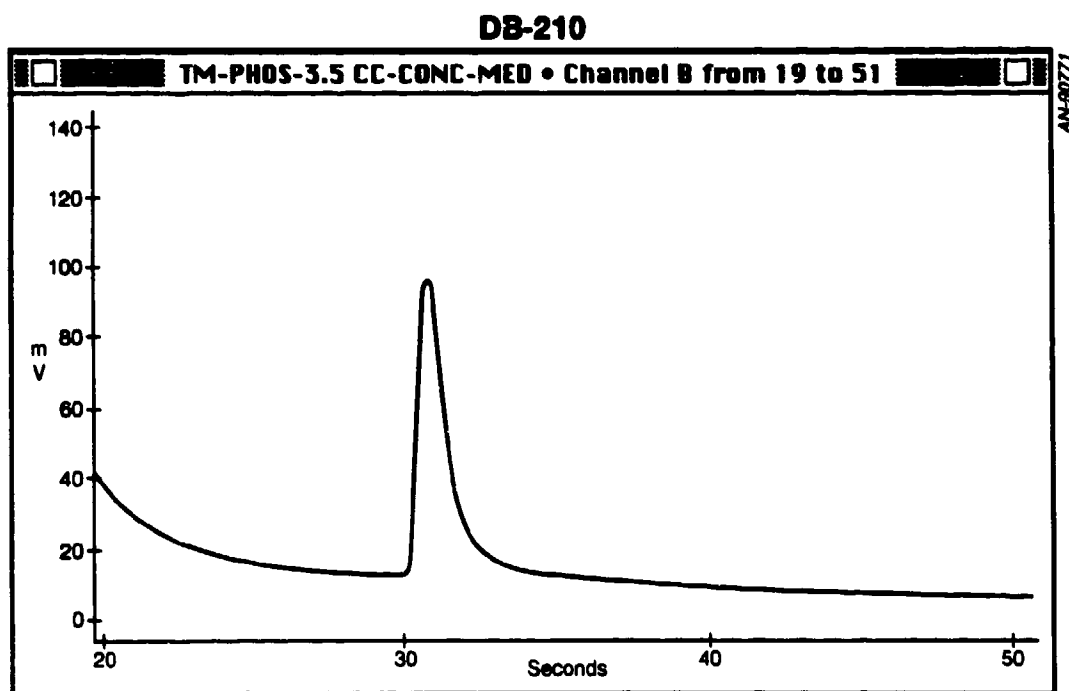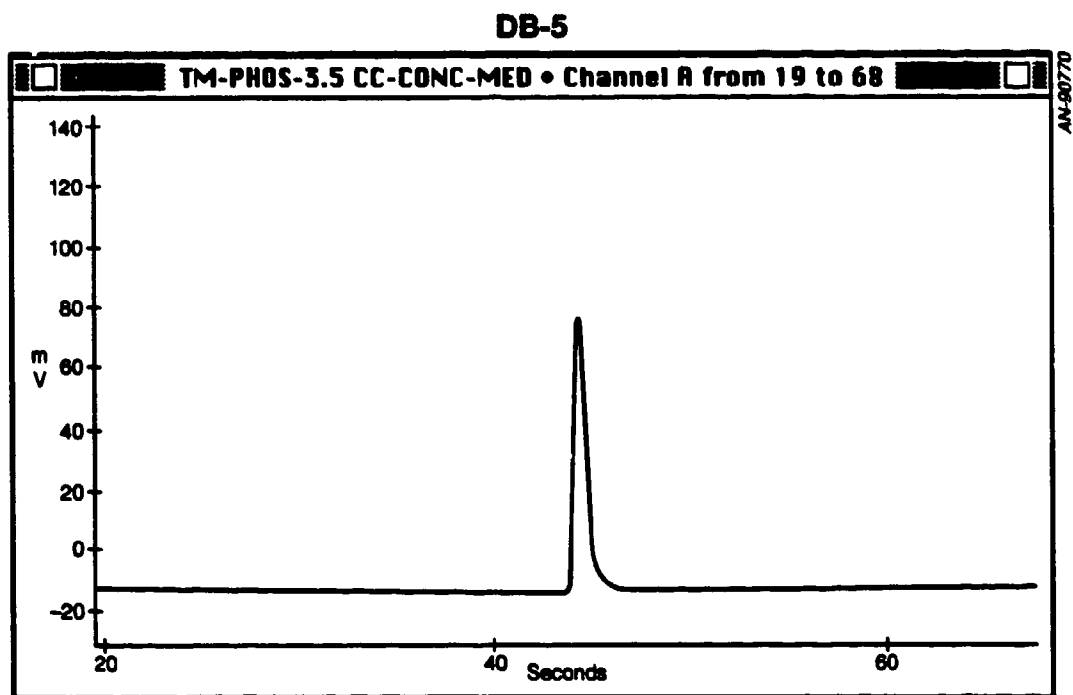
DB-210

Figure 3-4. μGC analysis of trimethyl phosphite on DB-5 and DB-210 columns.

27

DB-5

TM-PHOS-3.5 CC-NOCONC-HI • Channel A from 141 to 211

DB-210

TM-PHOS-3.5 CC-NOCONC-HI • Channel B from 44 to 105
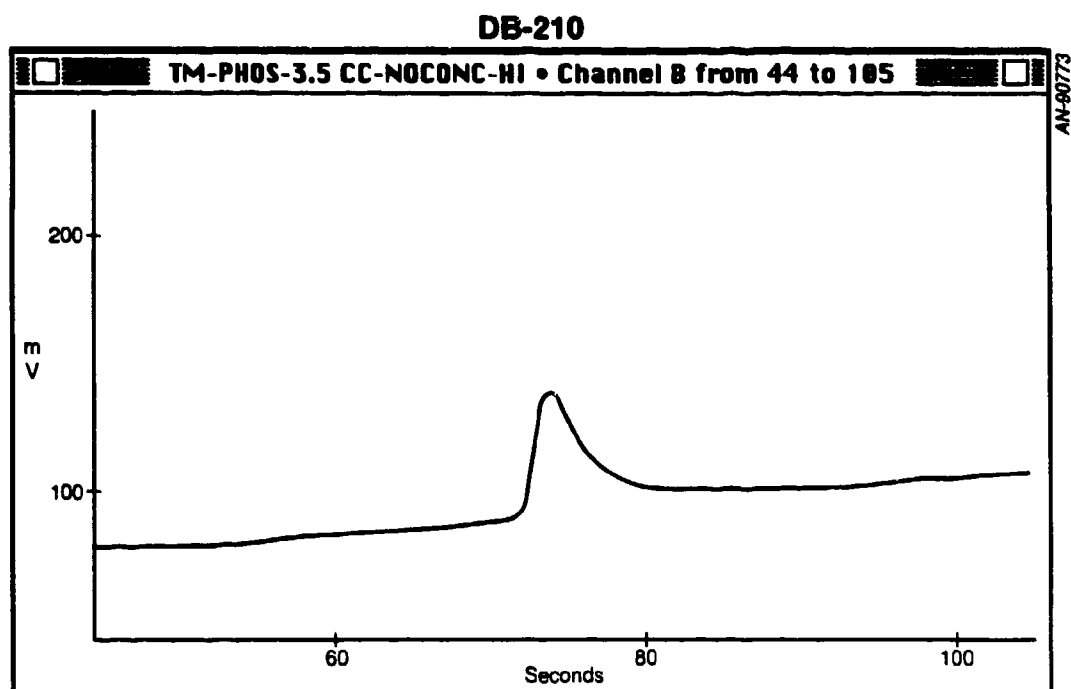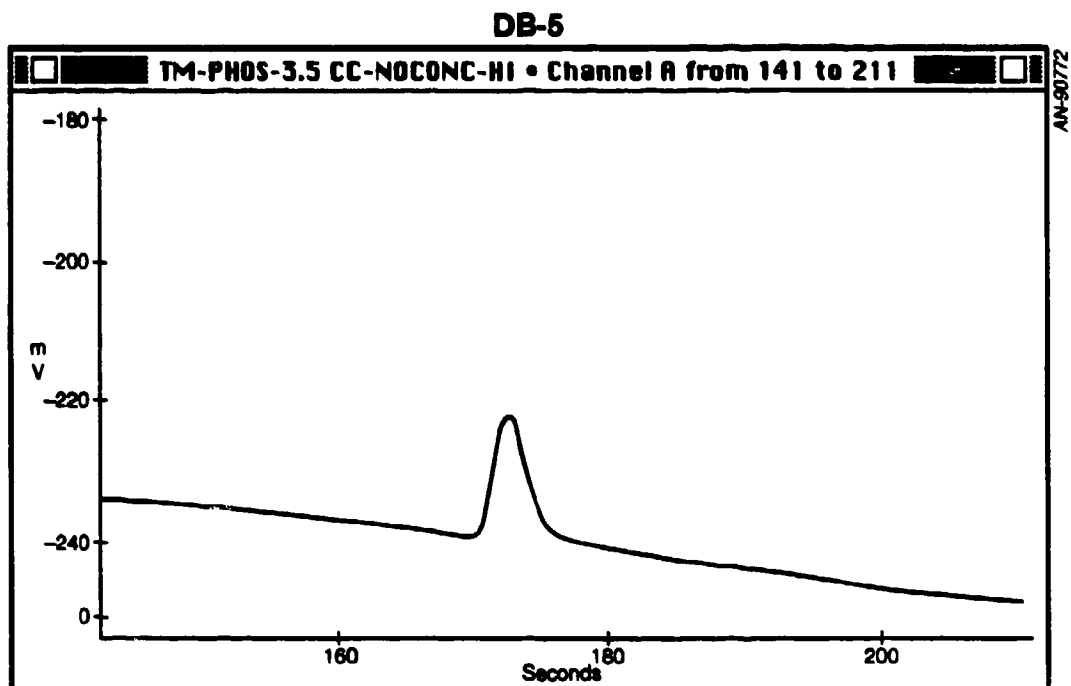
Figure 3-5. μGC analysis of triethyl phosphite on DB-5 and DB-210 columns.

DB-5

PCL5-HI-NOCONC-35CC • Channel A from 24 to 169

DB-210

PCL5-HI-NOCONC-35CC • Channel B from 29 to 151
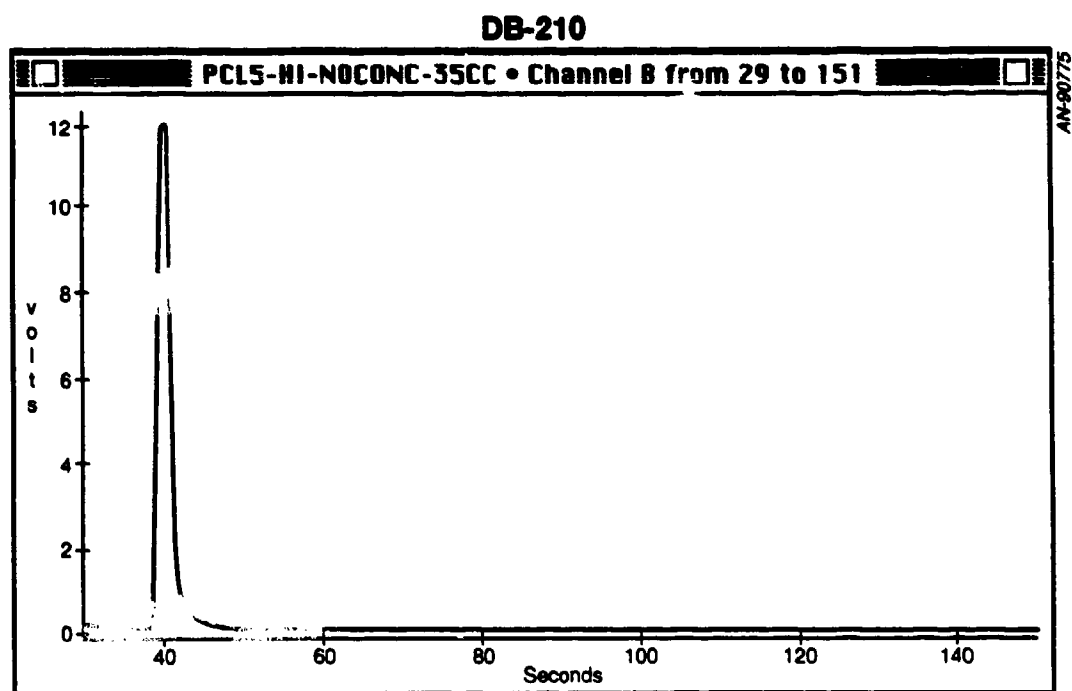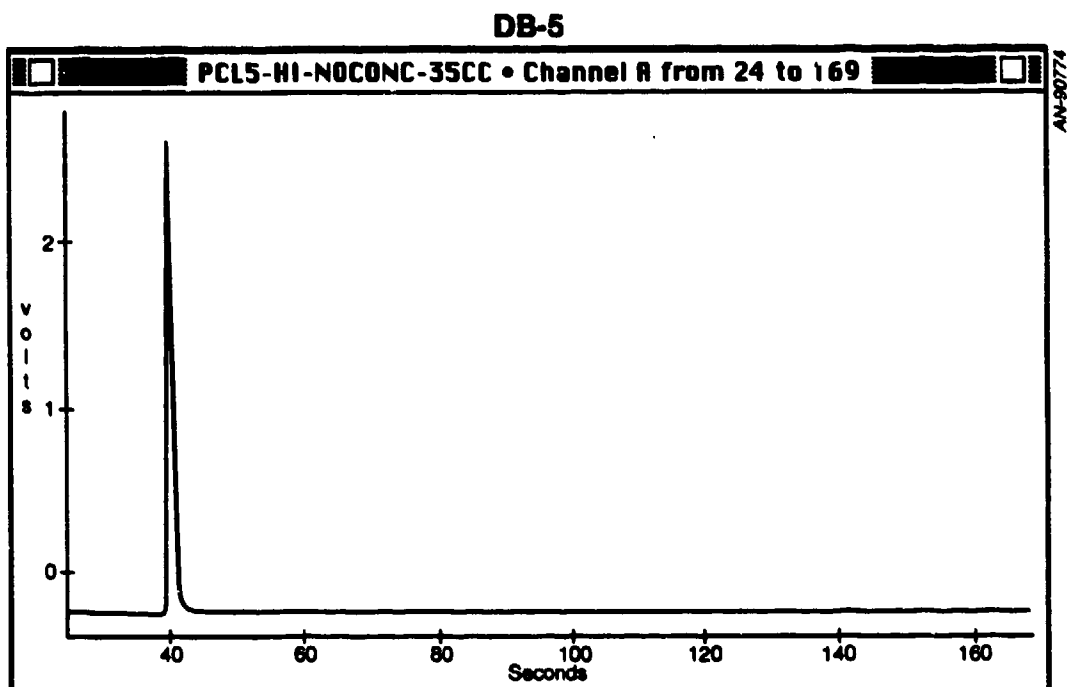
Figure 3-6. μGC analysis of phosphorus pentachloride on DB-5 and DB-210 columns.

29

DB-5
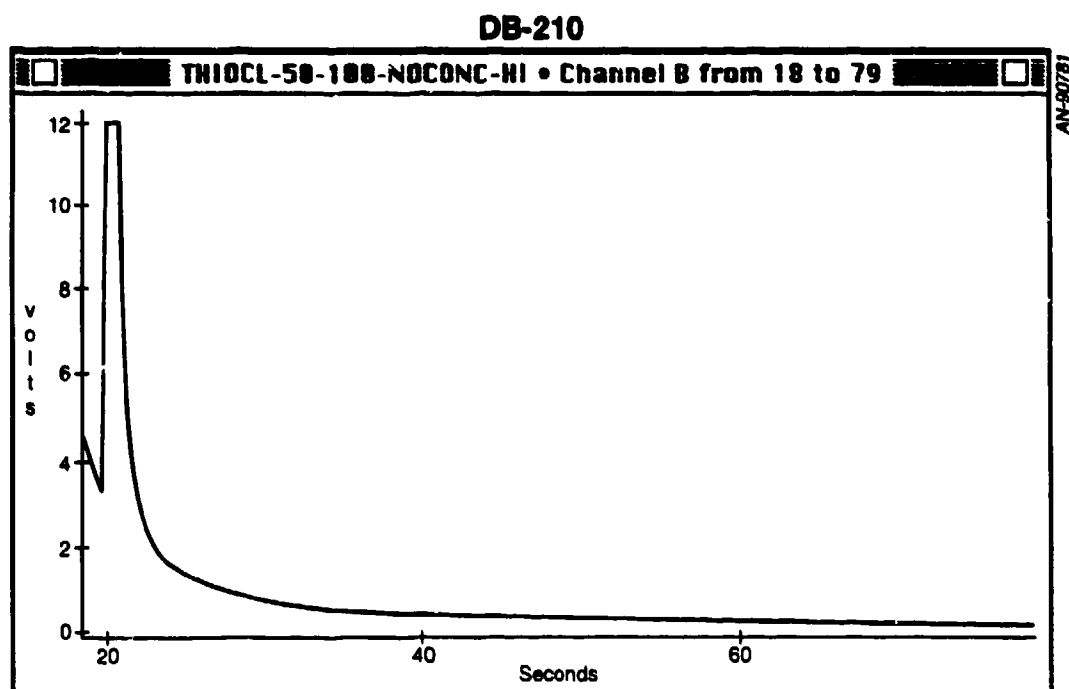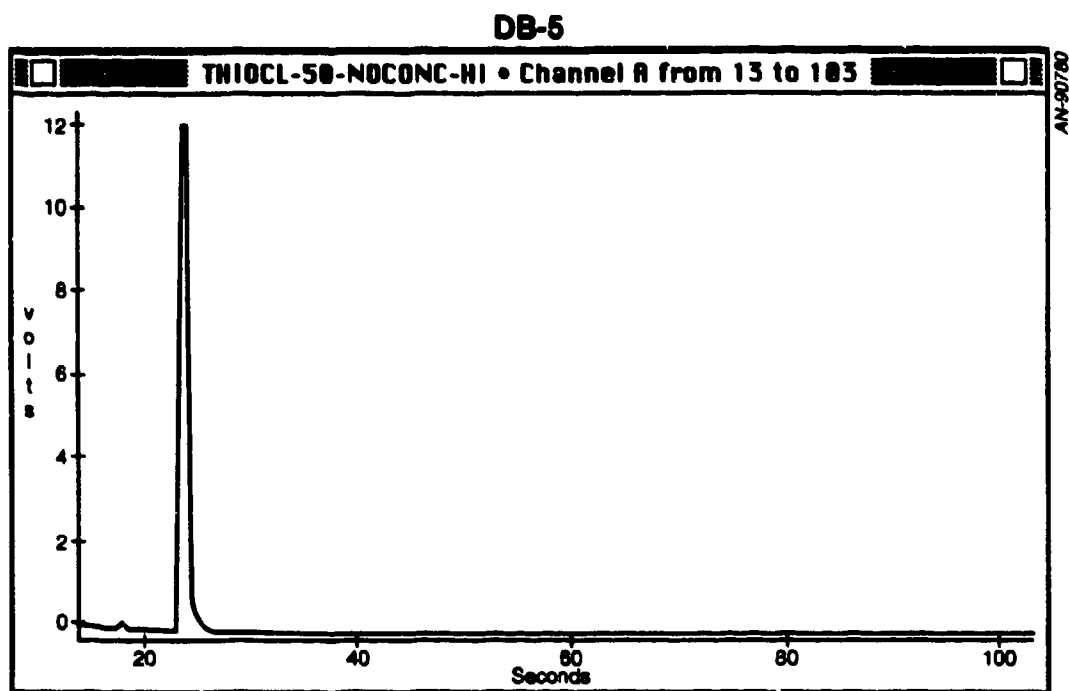
DB-210

Figure 3-7. μGC analysis of thionyl chloride on DB-5 and DB-210 columns.

30
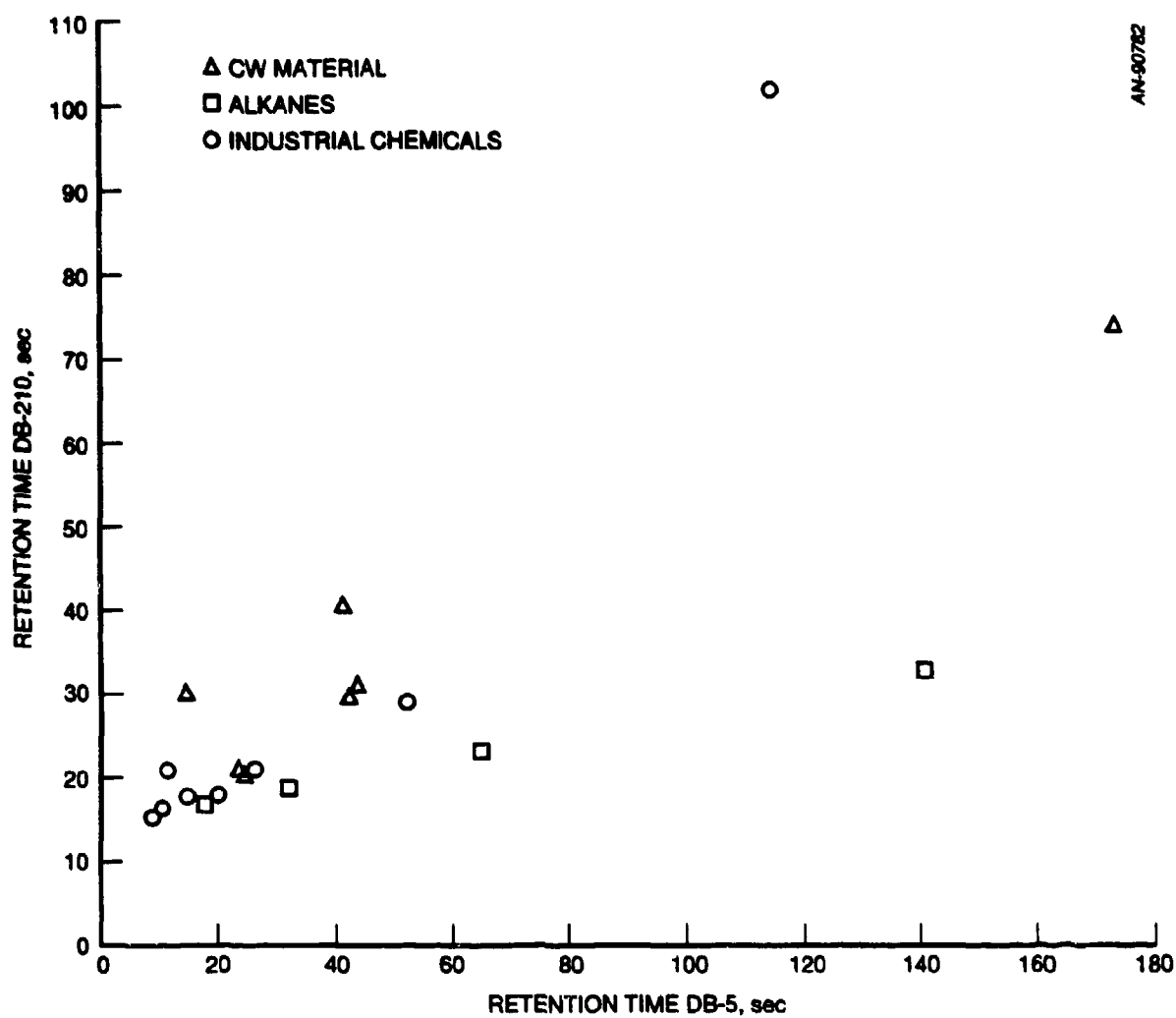
Figure 3-8. Correlated chromatogram for a variety of CW materials, hydrocarbons, and industrial chemicals.

31
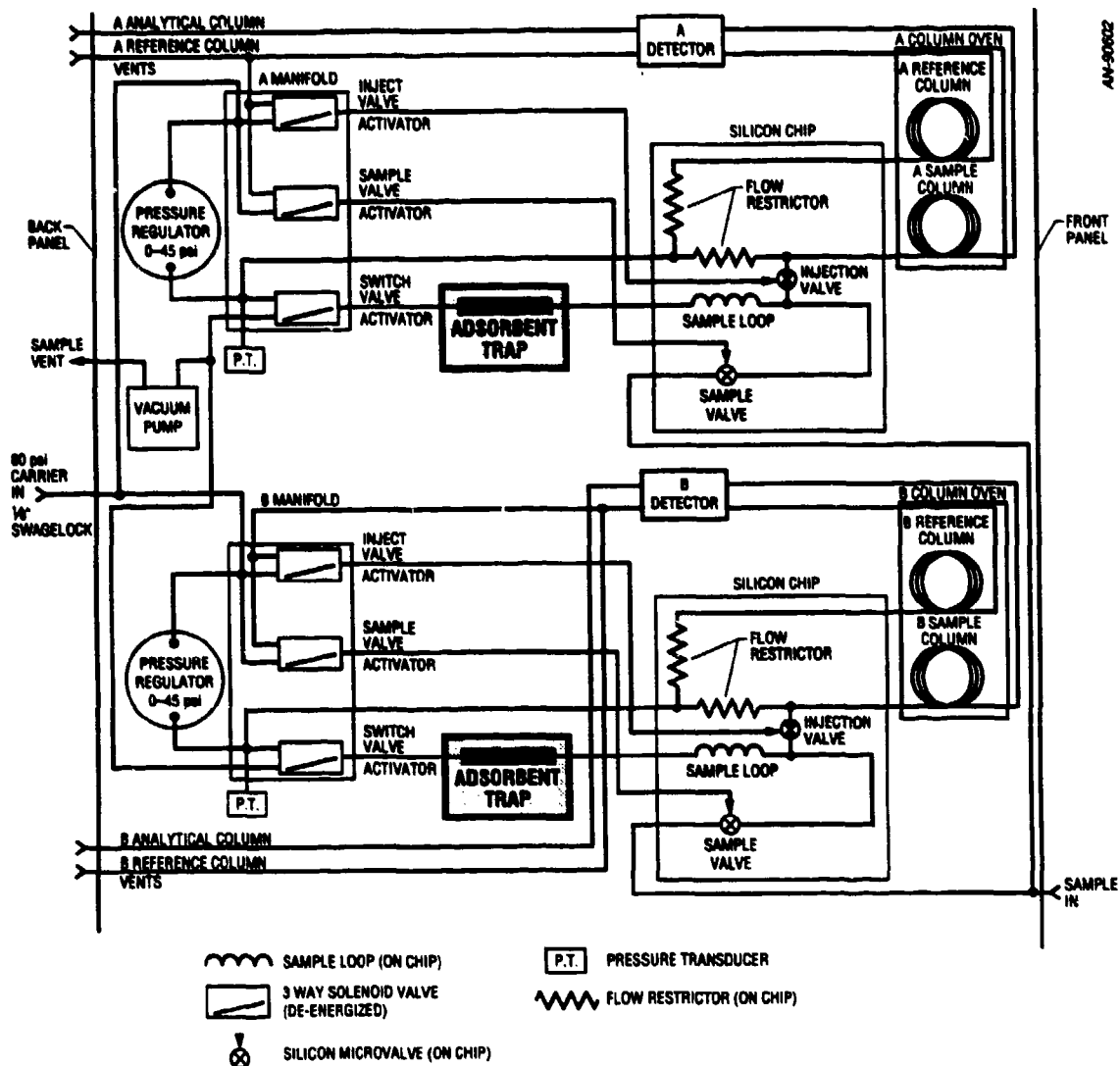
Figure 3-9. MTI M-200 pneumatic diagram showing microtrap modifications.

("microtrap") configured in the LSU-modified M-200 instrument is shown in Figure 3-10. With this addition the unit can still be operated exactly as before, or sample vapors can be drawn onto the microtrap and then the microtrap heated to desorb sample and increase the vapor concentrations in the sample loop. In the preconcentrator mode, the effective sensitivity of the instrument is increased by a factor of 20-50x. This increases the sensitivity of the overall instrument to the 20-50 ppb range. The relatively modest sensitivity increase observed is due to the small injector volume.

However, when coupled to a second larger adsorbent trap preconcentrator in series with the microtrap in a "staged" trapping scheme, much larger preconcentration factors can be achieved. Experiments conducted using absorbent tube traps (4 mm i.d.) show that air volumes on the order of one L/min can be easily drawn through the larger trap. When thermally desorbed, these release preconcentrated vapors into a few mL of carrier gas which can then flow into the microtrap. The microtrap then releases the resultant vapors into a fraction of a mL in the injection loop. Experiments directly coupling a large absorbent trap to the microtrap equipped μGC, showed that preconcentrator enhancement factors of 2800x can be achieved for hydrocarbon test compounds relative to direct injection into the sample loop without the preconcentrator.

In the case of volatile CWC schedule 2 and 3 materials, our experimental results show that chemical stability under sampling conditions becomes an important issue, especially for some of the more chemically reactive precursor chemicals. This situation may not be widely appreciated since chemical warfare agents themselves are known to be stable under a wide variety of sampling conditions.

Our experiments showed, for example, that triethyl phosphite samples prepared in dry nitrogen in inert (Teflon) air sampling bags could no longer be detected after a few minutes. This lead us to directly sample these materials by sampling air near partially open containers (in a fume hood). Furthermore, some of the volatile precursor materials that we tested proved to be unstable on both the Carbotrap and Tenax GC adsorbents used in the microtraps. This was demonstrated by comparisons of integrated intensity of the detected compound with and
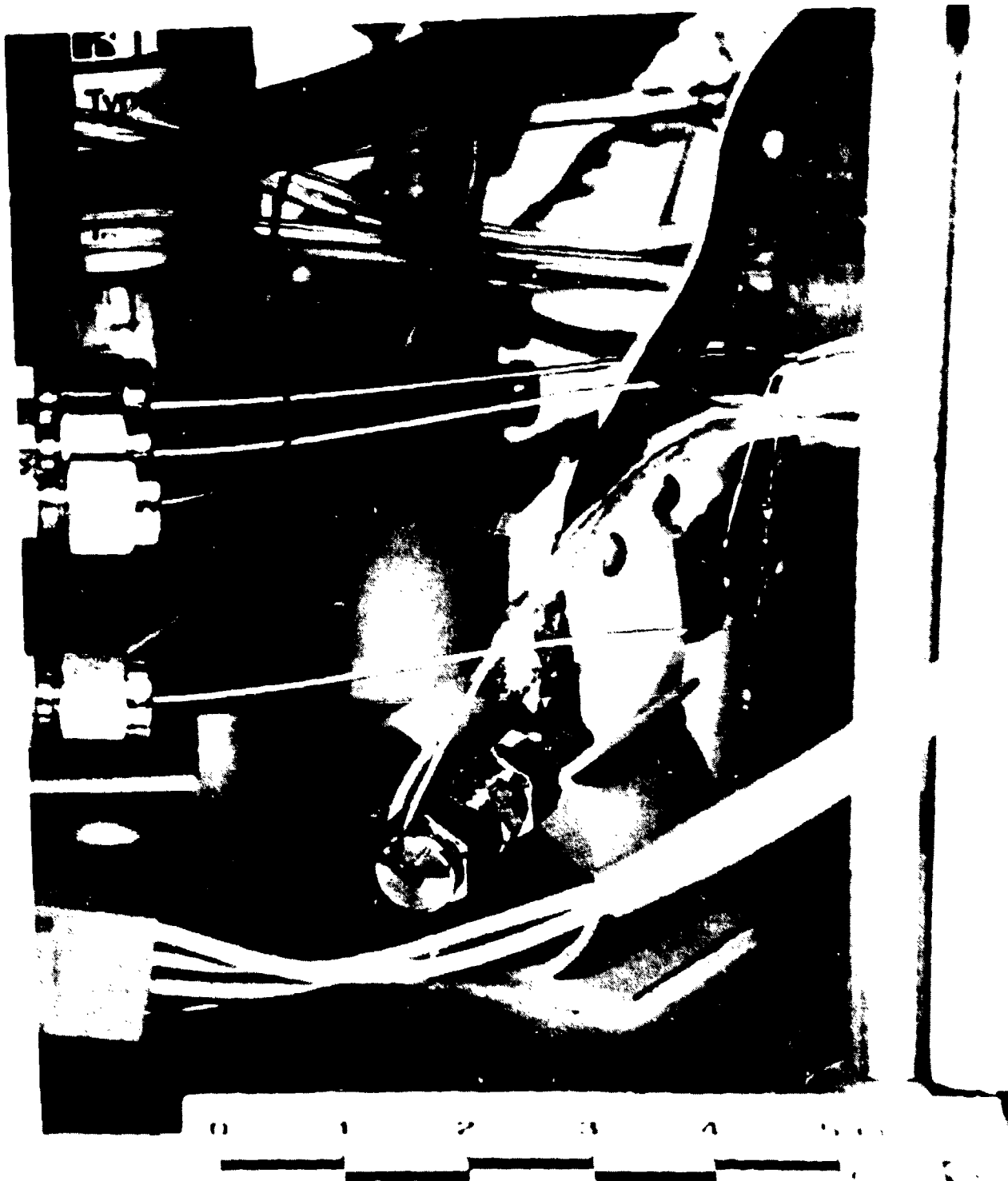
Figure 3-10. Close-up photograph of a microtrap assembly in a modified M-200.

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without use of the microtrap preconcentrators. In the cases of phosphorus pentachloride and thionyl chloride, the compounds were either absent or detected at reduced intensities with the microtrap preconcentrator.

Together these results demonstrate that some of the volatile precursor chemicals on the schedules are chemically too reactive for adsorbent trap preconcentrators to be used. Direct sampling (bypassing the preconcentrators) shows these compounds to have both high enough vapor pressures and sufficient stability for direct analysis by μGC. However, the use of a preconcentrator for the semivolatiles (dictated by their low vapor pressures and TWAs), would make the detection of some schedule 3 volatiles difficult using a single GC module with a preconcentrator.

3.3   MEASUREMENT OF LOW THERMAL MASS MINI-GC PERFORMANCE.

The feasibility of semivolatiles analysis by an innovative low thermal mass mini-GC with integral heating was presented in Section 2.2 of this report. The extremely wide scope of compounds required for CW treaty inspection push the GC analysis requirements beyond the capabilities of current commercial μGC, even after extending the performance with some minor design improvements. While conventional GC is routinely used in the laboratory as a primary method for the analysis of semivolatiles, the large size, power requirements, and long analysis times have not been amenable to the use of GC in a small instrument for fast analysis. We subcontracted LSU to fill this technology gap for our development of a low thermal mass GC with the required semivolatiles analysis capability. This development was government funded and represents a significant breakthrough in GC technology. Their mini-GC concept for an ultra-low thermal mass, fast GC with integral heating is shown in Figure 2-4 of Section 2.2 of this report. The functional elements evaluation for this concept is presented in the following paragraphs.

The feasibility analysis in Section 2.2 presented the requirement for fast temperature programming by the concept mini-GC. This fast temperature programming is required in order to chromatograph a broad range of semivolatile compounds in a short time span. Our

requirements call for semivolatiles chromatography spanning approximately C_{10} to C_{20}. As described earlier, the temperature of the mini-GC is controlled by a resistive heating of a heater wire or the heating of a small, thin-walled tube. The repeatability of the chromatographic measurement is critically dependent upon the reproducibility of the heating of the GC column. This is true of all temperature programming methods regardless of column or oven sizes. The large thermal mass of laboratory instruments necessitates slow temperature ramps with fans to even the temperature distribution within the oven. Electrical temperature sensors and feedback control are used to control the temperature ramp. This same approach is used in the concept mini-GC by the inclusion of a temperature sensing wire.

The precision of the temperature programming by the concept mini-GC can be seen in Figure 3-11. In these measurements, the temperature determined by the sensing wire in the mini-GC column is shown for a variety of different temperature ramps. Following isothermal operation at 50 °C, the mini-GC was linearly ramped by the heater wire under feedback control to 300 °C at speeds ranging from 1 °C/s to 9 °C/s. Note the linearity of the temperature ramps and the lack of any temperature overshoot at the completion of the ramp. This is possible because of the very low thermal mass of the mini-GC and the resulting fast response to temperature control. Further, the low thermal mass of the mini-GC allows a very rapid cooling of the column by simple air convection once the power is turned off from the heater wire. This is needed for repetitive rapid analysis cycles by a handheld instrument. Ordinary GC ovens require minutes to cool while the mini-GC cools in 10's of seconds to a usable starting temperature.

The speeds of the temperature ramps shown in Figure 3-11 are extraordinary. Standard GC ovens are typically capable of rates approaching 1 °C/s, but typically have trouble sustaining these rates past the initial 50-100 °C of temperature increase. MINICAMS, produced by CMS Research Corporation of Birmingham, AL, provides an example of a GC oven which has been reduced in size for faster temperature programming. Its oven can be heated at 3 °C/s over a 150 °C temperature range for the analysis of semivolatiles. In contrast, the mini-GC can be heated very rapidly over wider temperature excursions with great precision because of its uniquely low thermal mass. Importantly, the power require-

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ments are small because of the small thermal mass of the mini-GC "oven," the interior of a short length of small diameter tubing.
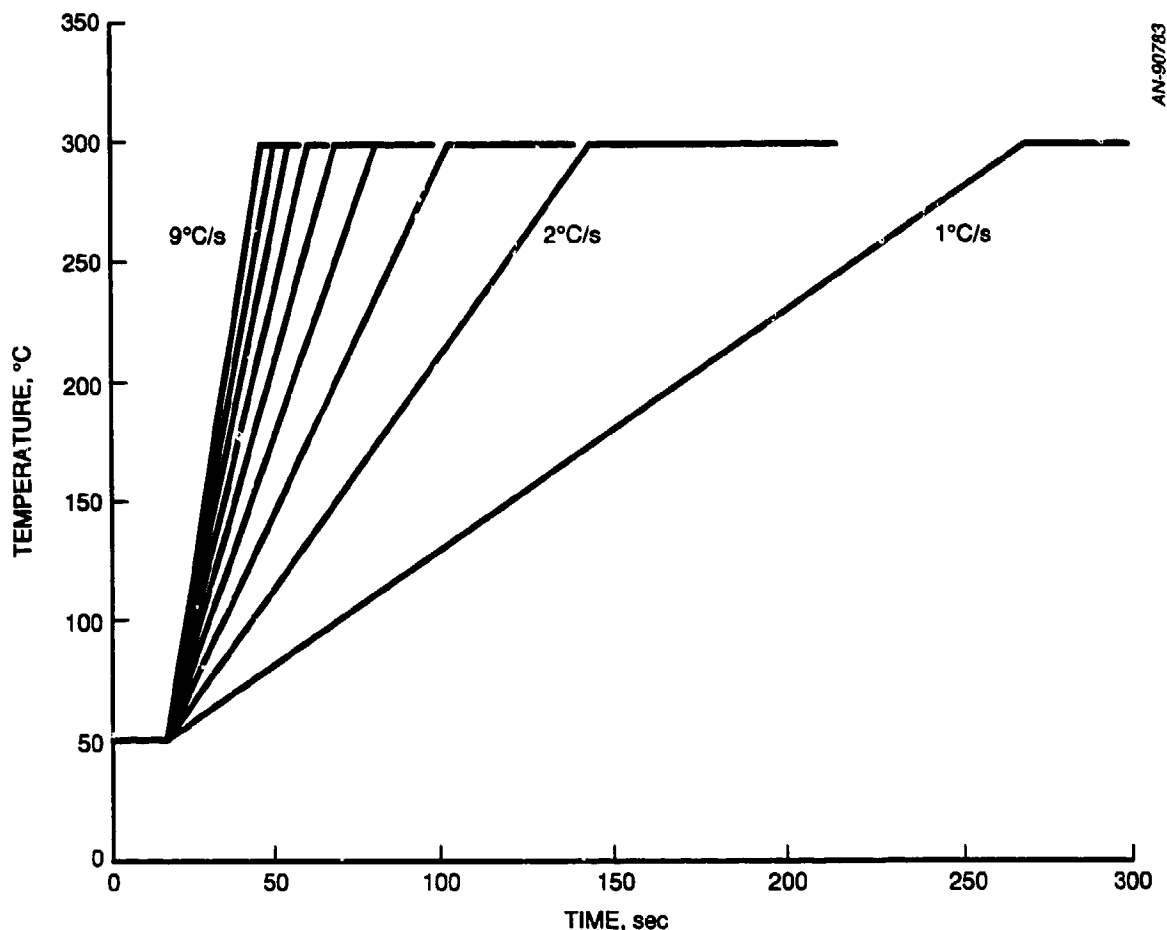
Figure 3-11. Mini-GC temperature ramps as monitored by the sensor circuit.

An evaluation of the mini-GC concept was performed at LSU using a capillary GC column combined with the temperature sensor and heater wires in a small diameter Teflon tube. Hydrogen was used as a carrier gas and a flame ionization detector was used to measure the chromatographic effluents from the mini-GC column under different temperature programming conditions. A set of normal paraffin waxes (saturated hydrocarbons) was used to demonstrate the analysis range of the mini-GC. Figure 3-12 shows the chromatogram for the set of paraffins. The temperature conditions were isothermal at 30 °C for 10 s followed by a 1 °C/s ramp to 250 °C. The temperature was held constant at 250 °C once the final

temperature was reached (analogous to the temperature ramps illustrated in Figure 3-11). Excellent chromatographic analysis coverage below C_{10} all the way to C_{20} is observed. The approximately equal spacing of the paraffins is typical of a linear temperature ramp for this set of compounds. Included in Figure 3-12 are two chromatograms of diesel fuels having characteristic fingerprints in the C_8-C_{20} range. These diesel fuels are complex mixtures familiar to the LSU laboratory which were analyzed by mini-GC to demonstrate the ability of the mini-GC to rapidly analyze a complex mixture of semivolatiles.
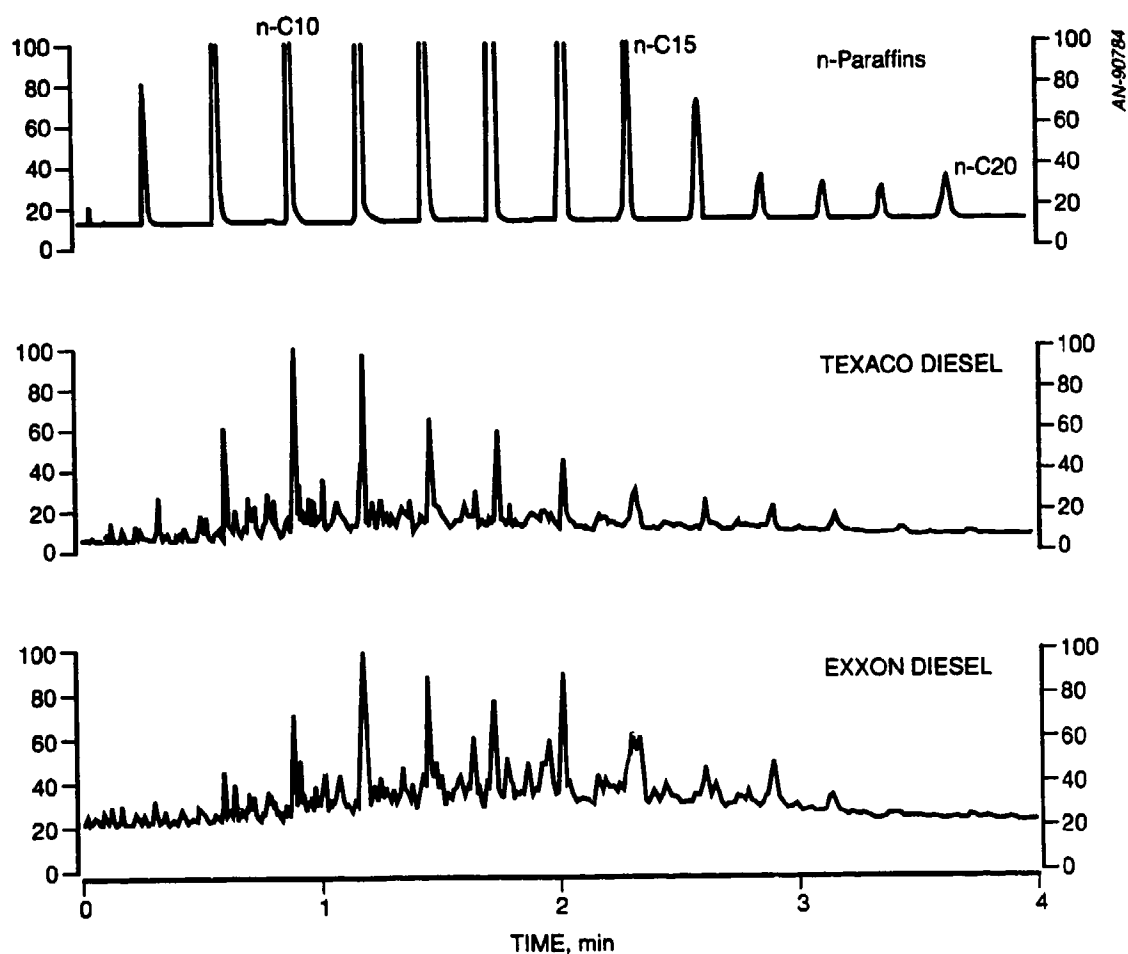
Figure 3-12. Example mini-GC analyses of semivolatiles including paraffin waxes and diesel oils.

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Doubling the temperature ramp rate to a more interesting 2 °C/s results in the chromatograms shown in Figure 3-13 for the same paraffin waxes and the two diesel fuels. Similar resolution is observed with some improvement in the chromatography of the least volatile components. Importantly, the analysis time is approximately halved.
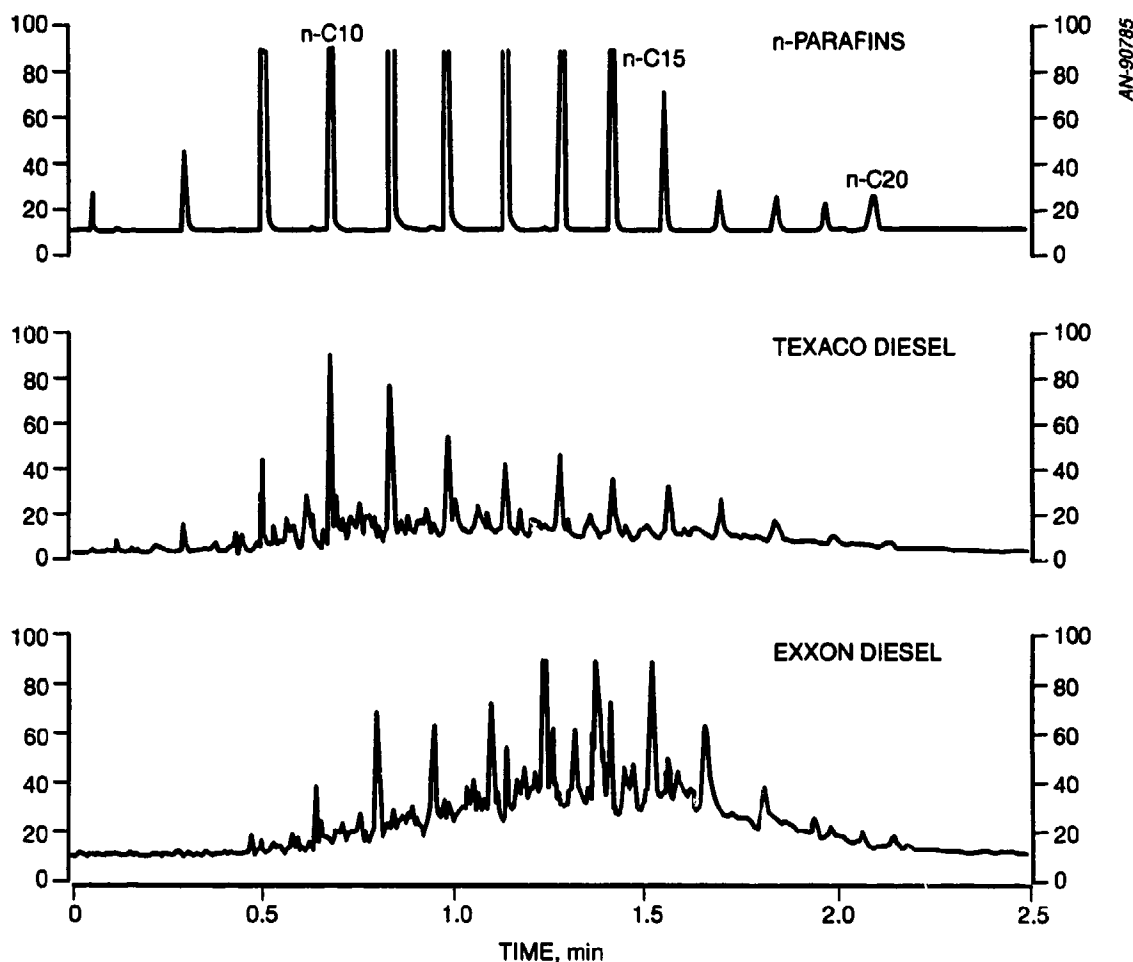
Figure 3-13. Example mini-GC analyses of same mixtures as Figure 3-12 at 2 °C/s ramp rate.

Two examples of very fast temperature ramping of the mini-GC are shown in Figure 3-14. In this test, a test mixture containing carbon disulfide (CS2) and normal alkanes in the range C_7-C_{18} was used. The programming conditions were isothermal analysis at 50 °C for 5 s followed by ramps of 5 °C/s and 8 °C/s. Excellent separations were observed with both of these fast temperature ramps. Analysis times for C_{18} below one minute were obtained with

the 8 °C/s ramp. *These results demonstrate unprecedented analysis speed for the tempera-ture-programmed analysis of semivolatiles by GC using a miniature, low-power approach. The development of this approach for our program fills a crucial technology gap for DNA for the development of fast, handheld GC technology suitable for the detection of the CWC schedule semivolatiles.*
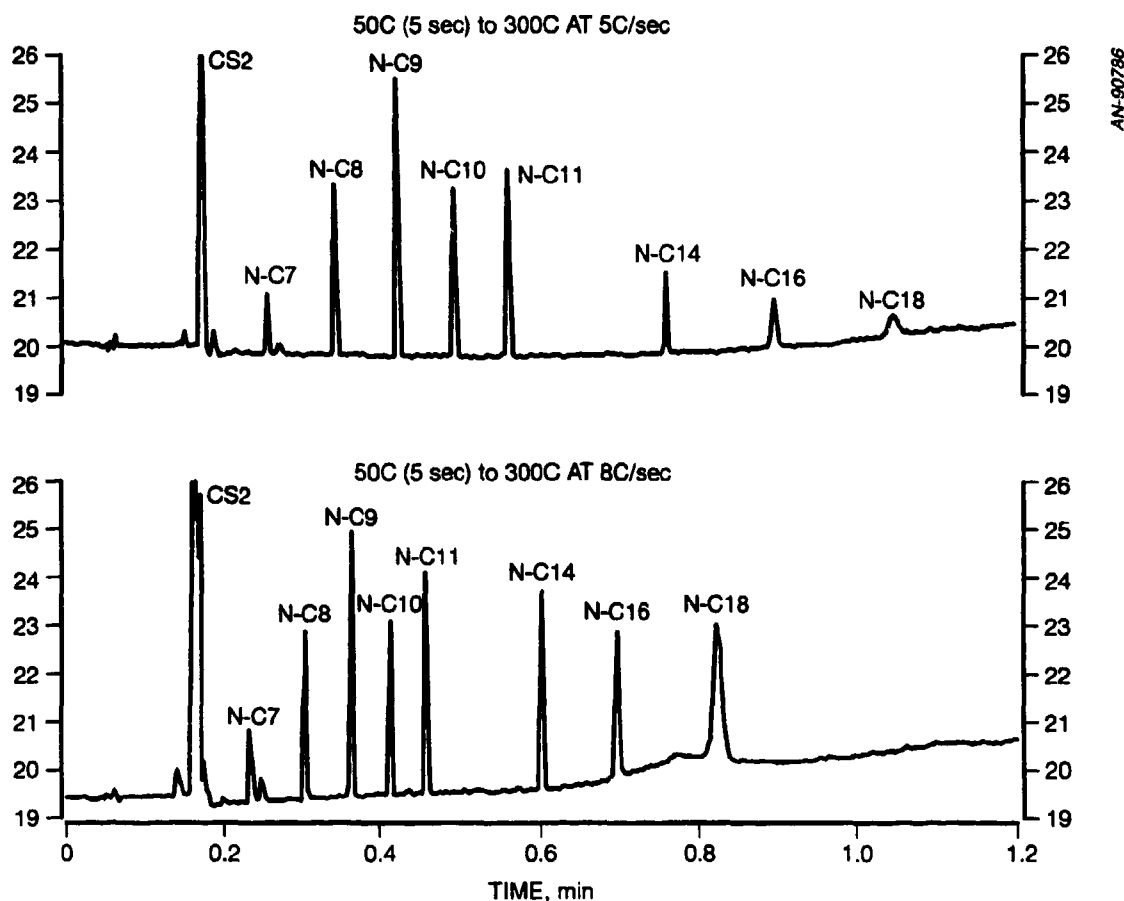
Figure 3-14. Example mini-GC analyses at very fast ramp rates of 5 °C/s and 8 °C/s.

The sensitivity of the mini-GC is determined by the detector used with the mini-GC. CW-selective detectors are of special interest for use with the mini-GC, and this is discussed at length in a later section of this report. The CW-selective detectors of interest are the nitrogen-phosphorus detector (NPD) and the flame photometric detector (FPD). Both of these detectors are capable of detecting 10's of pg or less of target compounds. Coupled with

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preconcentration, these detectors can provide detection levels down to 1-100 ng/m^3 depending upon the specific detector. This corresponds to the low detection limits required for the meeting the TWA levels for the more toxic schedule 1 materials such as VX. Specific sensitivities are discussed for different system configurations in later sections of this report.

3.4 PRECONCENTRATOR PERFORMANCE.

Preconcentration is often the method of choice to enhance the sensitivity of GC analyses. This is especially true in the case of air monitoring of compounds with low vapor pressures, since the low volatility of such compounds reduces their vapor concentration to the point where large samples may be required to ensure detection at required levels. At the same time, however, low vapor pressure enhances the adsorbancy in the preconcentrator. For these reasons, standard air monitoring procedures often include the use of adsorbent tubes which can be used to collect and preconcentrate the samples using portable air sampling pumps.

The key component in this preconcentration approach is the adsorbent bed. In the current program, both Tenax and Carbotrap adsorbents were tested. These two materials are commonly used adsorbents which vary in their surface chemical properties and their adsorption coefficients for different compounds. Surface models for these two compounds are shown in Figure 3-15. Tenax GC has a surface area of approximately 23.5 m^2/g in which the charge density is nonuniform and localized on the oxygen atoms. This gives it increased relative adsorbancy for polar organics. Carbotrap is an activated carbon with a graphite-like surface as shown in Figure 3-15. The surface area is approximately 100 m^2/g and the electronic charge density is uniformly distributed on the surface.

Carbotrap has very high adsorbancy for a wide range of compounds, especially for non-polar organics as shown in Table 6 (Suppelco, 1990). The breakthrough volume is defined as the volume of air required to elute the adsorbed vapors from the trap; i.e., viewing the trap as a chromatographic medium, a sufficient flow of air through the trap will eventually begin to remove the adsorbed vapors. The larger the breakthrough volume, the better

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vapors are retained. This adsorption coefficient describes the distribution of the vapor between the gas phase and the solid surface, and relates the breakthrough volume to the surface area of the adsorbent. Carbotrap's large surface area and adsorption coefficient, together with its tendency to reject water vapor makes it a particularly good adsorbent for preconcentration of non-polar organics.
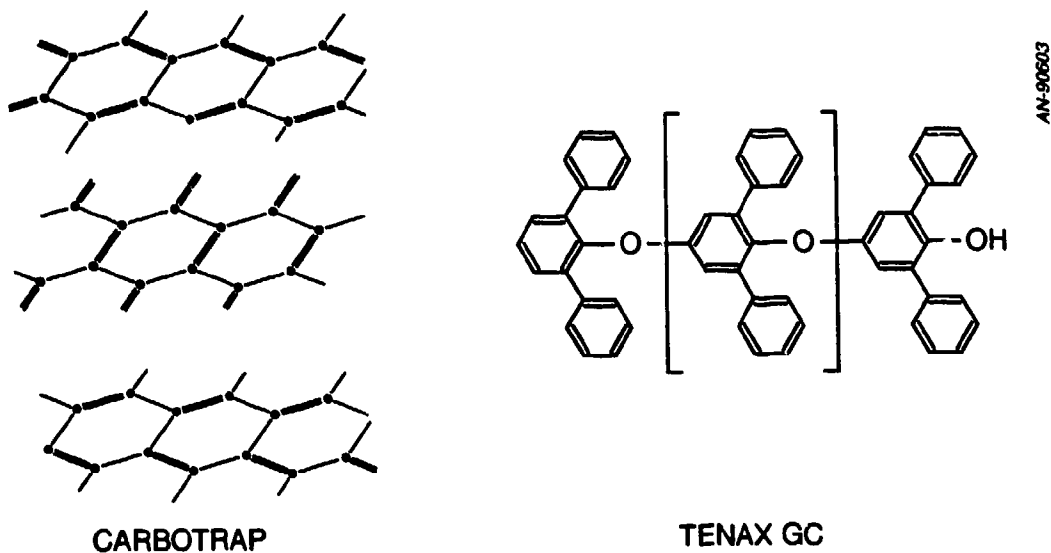
CARBOTRAP   TENAX GC

Figure 3-15. Surface models for Carbotrap and Tenax GC.

Tenax GC, with its smaller surface area and adsorption coefficients, is aromatic in character with ether linkages. This more polar character results in good adsorption of polar organics, and it is the adsorbent that has been most widely used for the preconcentration of chemical warfare agents during air sampling. Various reports in the literature suggest that the CW agents (especially the organophosphorus compounds) are more stable when using Tenax traps for preconcentration (Witkiewicz et al., 1990). At Chemical Research, Development and Engineering Center (CRDEC), now called Edgewood Research, Development and Engineering Center (ERDEC), a comparison of Tenax GC, Porapak-N, and Chromsorb 106 for the preconcentration of two simulants, triethyl phosphate (TEPO) and dimethyl methyl phosphonate (DMMP) found that Tenax GC performed best for both compounds.

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The Army has previously demonstrated that Tenax traps can be used with standard MINICAMS technology to achieve sub-TWA detection of HD, GB and VX. In these tests, air is sampled at 1L/min onto a Tenax adsorbent trap for 3 minutes, followed by thermal desorption into a MINICAMS GC with flame photometric detector. In this application, on desorption the CW agents are re-adsorbed at the head of the (30 °C) thick phase DB-1 capillary column. The column temperature is then ramped from 30 °C to 180 °C in 45 seconds to elute and separate the analytes before detection using the FPD.

In the present program we have examined both Tenax and Carbotrap adsorbents for trapping and thermal desorption of a wide range of materials including hydrocarbons, various polar organics, organophosphorus pesticides, and some CWC schedule 2 and 3 volatiles. These have been investigated using both 0.4 mm I.D. standard sized traps with sampling rates of 0.5 L per minute, and microtraps installed on our M-200 μGC. Except for some of the more chemically reactive materials, both were found to be effective sorbents. Based on the Army's previous experience with Tenax for CW agents, we have identified Tenax GC as the preferred adsorbent for the preconcentration of CWC semi-volatiles. However, a comparison of Tenax with Carbotrap adsorbents may also be examined in developing preconcentrators for the semi-volatiles.

3.5   PERFORMANCE OF CW-SELECTIVE GC DETECTORS.

There are a number of detectors which have been developed for GC which provide varying degrees of detection selectivity with a range of associated detection limits. Of primary interest to this program are detectors which have very high degrees of selectivity for elements which are peculiar to the CWC schedule compounds combined with low detection limits. Detectors which are especially suited to these needs are discussed at length in this section. For general reference to GC detectors, these detectors are summarized and compared in a general survey of GC detectors in Appendix A.

Correlated chromatography has previously been discussed for adding selectivity to the GC detection of CWC schedule compounds. While this approach has been demonstrated to

provide excellent chemical selectivity, additional selectivity *and* sensitivity is possible through the use of specialized detectors which are specific to elements peculiar to CWC schedule compounds. Potential requirements for specialized detection can be developed by reference to the CWC schedules in Table 2-1. This exercise shows the importance of phosphorus (P), nitrogen (N), and sulfur (S). The use of detectors specific to these elements for CWC schedule detection is examined in the following paragraphs.

The CWC schedules shown previously in Table 2-1 can be roughly organized along the capabilities of μGC and mini-GC by sorting the schedules according the volatilities of the compounds. Such a division of the compounds allows the analysis of CW-specific detectors to be coupled with appropriate hardware considerations or requirements by either μGC or mini-GC. Additionally, the present organization of the CWC schedule compounds into categories 1, 2, and 3 is also roughly aligned with the classification of the compounds as semivolatiles and volatiles. The schedule 1 compounds comprise the CW agents, and because these materials must be sufficiently persistent both environmentally and pharmacologically for their toxic effects, they are relatively stable semivolatile compounds. Schedule 3 materials are mostly low molecular weight precursor compounds which are chemically reactive. For this reason they are primarily volatiles which are difficult to preconcentrate using adsorbent trap materials. The schedule 2 materials are mostly semivolatiles. Thus, μGC primarily addresses the need for schedule 3 detection while the mini-GC addresses schedule 1 and 2 detection.

Selective Detectors for CW Schedule Volatiles. A matrix of the applicable detectors on an entry by entry basis for volatile compounds in the three schedules is shown in Table 3-1. While many of the entries are specific compounds, several of the entries are comprised of small groups of compounds. In two cases, the schedule entries correspond to broad classes of compounds. In the cases of these groups or classes of compounds, at least some of the compounds are considered to be volatiles and the entries were included in this table.

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Table 3-1. Selective detectors for CWC schedule volatiles.

Schedule	No.	Small Group of Compounds	Broad Class of Compounds	Applicable Detectors				
				Non Specific	Organic	Phosphorus	Nitrogen	Sulfur
1	1		✓	✓	✓	✓		
	9	✓		✓	✓	✓		
	11			✓	✓	✓		
2	2			✓	✓			
	4		✓	✓	✓	✓		
	7(?)			✓ (?)				
	10	✓		✓	✓		✓	
	11	✓		✓	✓		✓	
	12	✓		✓	✓		✓	✓
	14			✓	✓			
3	1			✓	✓			
	2			✓	✓		✓	
	3			✓	✓		✓	
	4			✓	✓		✓	
	5			✓		✓		
	6			✓		✓		
	7			✓		✓		
	8			✓	✓	✓		
	9			✓	✓	✓		
	10			✓	✓	✓		
	11			✓	✓	✓		
	12			✓				✓
	13			✓				✓
	14			✓				✓
				24	17	11	6	4

The detector categories in Table 3-1 include non-specific, organic, P, N and S detectors. An example of a non-specific detector is the thermal conductivity detector in the µGC which detects inert gases and the vapors of inorganic compounds as well as the vapors of organic compounds. Organic detectors refer to detectors which respond to compounds containing carbon such as a flame ionization detector (FID). Phosphorus detectors include the nitrogen-phosphorus detector (NPD) and the flame photometric detector (FPD). Nitrogen-containing compound detection refers to the NPD. Sensitive detection of sulfur-containing

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compounds refers to the FPD using a different optical filter which is selective for sulfur-related emissions rather than phosphorus-related emissions from the detector flame.

Table 3-1 indicates that all of the compounds are expected to be detectable by thermal conductivity (a non-specific detector). While the detection level without preconcentration is only at the 1 ppm level (as explained in Section 3.1), the commercial μGC hardware includes microfabricated thermal conductivity detectors which can provide detection for compounds which are missed by selective detectors. Furthermore, the thermal conductivity detectors are nondestructive and have good dynamic range to provide high readings when exposed to unusually high vapor concentrations. However, without preconcentration, an additional detector in series is required for achieving the high sensitivities which are generally sought for this detector development.

Flame ionization detection (FID) provides about an order of magnitude more sensitivity in terms of concentrations than thermal conductivity detection and represents a general purpose organic compound detector. However, FID is not particularly selective in that typical environmental backgrounds which are rich in hydrocarbons will be detected. Furthermore, FID would probably need to be used in a correlated chromatography mode to gain sufficient detection selectivity to be useful. Given its modest sensitivity advantage relative to thermal conductivity and its relatively non-selective results, it would only be a marginal addition to the volatiles detection provided by the thermal conductivity detectors present in commercial μGC hardware.

In terms of CW-selectivity which can be used to discriminate against ordinary hydrocarbon background, the remaining detectors represented in Table 3-1 have high selectivity and high sensitivity. The NPD detector is particularly interesting because P and N detection combine for 17 of the 24 entries in the table. This coverage by the NPD is understated, however, because several of the entries are groups and broad classes of chemical compounds. An approximate enumeration of these groups in the table would result in about 99% coverage by P and N detection of the estimated number of volatiles actually represented

by this table. While the primary NPD omissions are sulfur compounds, the overall coverage of the table is excellent.

P detection afforded by an FPD detector also provides excellent coverage of the Table 3-1 volatiles. Again, enumeration of the broad classes of compounds weights the coverage of the table by an FPD. Some of the organonitrogen compounds are missed as well as a few sulfur compounds. FPD can also be used to selectively detect S by a change of optical filters, and dual FPD detectors are commercially available which simultaneously detect both P and S containing compounds in a single flame by the use of dual miniature photomultipliers, one with a filter for P emissions and one with a filter for S emissions. Such a dual detector would detect a few additional compounds in the table. (While this results in a small addition of three compounds in this table, this same approach applied later to the semivolatiles appears to have strong merit.)

Selective Detectors for CW Schedule Semivolatiles. Table 3-2 contains a similar matrix for the semivolatile compounds contained in the CW schedules. This table is complementary to Table 3-1 and contains the CW threat compounds of special interest. Again, the bulk of the compounds contain phosphorus and/or nitrogen, especially if the broad classes and small groups of compounds are enumerated. For this reason, both the NPD and FPD provide excellent coverage of the semivolatile compounds with the notable exception of entry no. 4 in Schedule 1 (mustard). FPD configured as a sulfur detector, or a dual FPD (both P and S detection) will detect mustard, but the NPD will not.

The prominence of mustard as a common CW compound would require either a second detector be used in addition to the NPD, or that the dual FPD be used as a CW-selective detector. With an NPD, possible approaches include the use of a second general purpose detector such as an FID. This is expected to add bulk to the detector since this would require an additional detector, supporting electronics and consumables, and possibly a separate GC column. The dual FPD is an interesting consideration since high sensitivity for both P and S can be obtained from a single GC column with a combination detector. The relative merits of the FPD are discussed in the following section.

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Table 3-2. Selective detectors for CWC schedule semivolatiles.

Schedule	No.	Small Group of Compounds	Broad Class of Compounds	Applicable Detectors				
				Non Specific	Organic	Phosphorus	Nitrogen	Sulfur
1	1		✓	✓	✓	✓		
	2		✓	✓	✓	✓	✓	
	3		✓	✓	✓	✓	✓	
	4	✓		✓	✓			✓
	6	✓		✓	✓		✓	
	9	✓		✓	✓	✓	✓	
	10		✓	✓	✓	✓	✓	
	12			✓	✓	✓	✓	
2	1	✓		✓	✓	✓	✓	✓
	4		✓	✓	✓	✓	✓	
	5	✓		✓	✓	✓	✓	
	6	✓		✓	✓	✓	✓	
	10	✓		✓	✓		✓	
	11	✓		✓	✓		✓	
	12	✓		✓	✓		✓	✓
	13			✓	✓		✓	✓
3	15			✓	✓		✓	
	16			✓	✓		✓	
	17			✓	✓		✓	
				19	19	10	13	4

Survey of Applicable GC Detector Modules for CW-Selective Detection. The detection sensitivities and comparative features of the GC detectors mentioned in the previous sections are shown in Table 3-3. These detectors are shown in combination with either μGC or mini-GC columns since this can influence relative performance and features. The sensitivities are given both at the detector in concentration units and in terms of the amounts which must be presented to the GC columns. While concentrations at the detector are familiar ways of comparing the sensitivities of detectors, the minimum amount of a compound which must be present in the chromatographic column is the realizable sensitivity for the column-detector combination.

Table 3-3. Applicable GC detector modules for CW-selective detection.

GC/Detector Modules	Sensitivity		CW Selective	Detection Gaps	Non-Destructive	CW Volatile				CW Semivolatile			
	Amount	Est. ppb at Detector				HC	P	N	S	HC	P	N	S
µGC/µThermal Conductivity Detector (µTCD)	1 ng	1000			+	+	+	+	+				
µGC/Flame Ionization Detector (FID)	0.1 ng	100				+	+	+	+				
µGC/TCD/Nitrogen-Phosphorus Detector (NPD)	1 ng (HC, S) 0.1 pg/s (P, N)	1000 (HC, S) 0.1 (P, N)	+			+	+	+	+				
µGC/TCD/Dual Flame Photometric Detection (FPD-P&S)	1 ng (HC) ≤10 pg (P) ≤100 pg (S)	1000 (HC) 10 (P) 100 (S)	+			+	+	+	+				
Mini-GC Dual FPD-P&S	≤10 pg (P) ≤100 pg (S)	10 (P) 100 (S)	+	HC, N							+		+
Mini-GC/TCD	100 ng	~100,000			+					+	+	+	+
Mini-GC/FID	0.1 ng	100								+	+	+	+
Mini-GC/NPD	0.1 pg/s	0.1	+	HC, S							+	+	
Mini-GC/Flame Photometric Detector – Phosphorus (FPD-P)	≤10 pg	10	+	HC, N, S							+		
Mini-GC/Flame Photometric Detector – Sulfur (FPD-S)	≤10 pg	100	+	HC, P,N									+
Mini-GC/Photo-Ionization Detector (PID)*	10 pg	10		?	+					?	?	?	?

*Selective for photo-ionizable compounds

For the semivolatiles (mini-GC approach), preconcentration with adsorbent traps can deliver the small quantities required for detection from a large volume of air. This results in low detection limits for these compounds. In particular, the NPD and FPD provide detection for chromatography quantities below 10 pg. A 10 pg quantity captured from a 1 L air sample would correspond to a sensitivity of 10 ng/m^3, the time weighted average/permissible exposure limit for the agent VX, as shown in Table 3-4. This approach provides detection levels which can meet or exceed the lowest levels in Table 3-4 for highly toxic nerve agents. The FPD is an established GC detection method for the monitoring of nerve agents and substantial acceptance testing has been performed with GCs for nerve agent monitoring using FPD detectors. The NPD is capable of an additional 10-100x increase in sensitivity over the FPD detector, but it has not been previously used for nerve agent monitoring applications. It

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is a more complex detector to operate and has previously involved designs in which the detector sensitivity rapidly degraded over time. New NPD developments showing increased stability and sensitivity were of special interest to this program for evaluation.

Table 3-4. TWA/IDLH exposure levels.

Level of Exposure	Agent (mg/m³)				
	GA/GB	GD	VX	H, HD, HT	L
TWA/PEL	.0001	.00003	.00001	.0003	.003
IDLH	.2	.06	.02	.003	.003

IDLH - Immediately dangerous to life or health
TWA/PEL - Time weighted average/permissible exposure limit

NOTE: Time weighted average is based on an 8-hour workday.

As discussed in a previous section, the hypothetical use of an NPD detector in the concept instrument for semivolatiles detection would leave a detection gap for mustard. To cover this detection gap, an additional detector is required. This additional detector could be a non-destructive detector such as a thermal conductivity (TCD) or photoionization detector (PID) in series with the NPD. These non-destructive detectors allow the compounds to pass through the detector unchanged and be analyzed by a second detector. Alternatively, an additional GC column could run a parallel analysis employing a second destructive detector such as an FID or an FPD configured for sulfur detection. The TCD, as shown in Table 3-1, lacks high sensitivity, while the response of the PID is uncertain for unknown sulfur compounds. Additional detectors will have a size and weight impact on the concept instrument. Further, splitting the sample for parallel analyses with additional destructive detectors may not be desirable either. Nonetheless, in a concept design for lowest detection limits and the capability to detect the maximum number of compounds possible, these are possible trade-off considerations.

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The other attractive appealing detector in terms of low detection limits and CW-selective detection is the FPD configured for P detection. While it is projected to be less sensitive that some of the newest NPDs, it does have low detection limits and is the established GC detector technology for the safety monitoring of selected schedule 1 compounds. The P detection configuration of the FPD would still have the S detection gap, and the same complimentary non-destructive and destructive detector options outlined in the previous paragraph apply. An additional option with the FPD which is listed in the bottom of Table 3-1 is the dual FPD option in which a single flame detector is analyzed by a pair of small photomultiplier tubes, one selective for P and one selective for S. This provides low detection limits for both P and S, requires the operation of a single GC column and flame assembly, and can share additional resources of the similar photomultiplier detectors.

The NPD and FPD are the most interesting detectors for the CW-selective detection which is needed for the concept instrument. From the consideration of the compounds to be detected and the capabilities shown in Table 3-1, these two detectors were especially considered in the functional elements evaluation for the added sensitivity and selectivity they could provide. For volatiles detection without preconcentration using a μGC, either detector could conceivably provide the added sensitivity needed for low detection limits using the μGC. Additionally, the μGC includes TCDs which can be utilized for the measurements of high concentrations of volatile compounds. The functional elements evaluation of these two detectors are discussed specifically in the following sections.

NPD Functional Elements Evaluation. The NPD consists of an assembly which is similar to the commonly used FID (flame ionization detector) for the general purpose GC detection of organic compounds. In the FID, a metal jet is constructed so that carrier gas from the GC column is mixed with hydrogen gas and air and is combusted at the tip of the jet. Organic molecules ionize in the flame by losing an electron, and are attracted to an electrode near the flame. The resulting small current is amplified from picoamperes to signals in the millivolt range. For the NPD, the hydrogen gas flow is reduced to a very small flow rate (2-6 mL per minute) and the jet flows onto an electrically heated thermionic surface. Under these conditions, there is insufficient hydrogen to sustain the "flame-like"

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boundary layer when the heating current to the thermionic source is turned off. Under normal operation, this source is heated just to the point that boundary layer of the jet is ignited. Compounds in the jet colliding with the heated thermionic surface which specifically have a nitrogen or a phosphorus group are ionized by a surface chemical reaction. Basically, compounds decomposing in the reaction zone which contain P or N are converted to gas phase negative ions by extraction of electrons from the thermionic surface. The resulting currents are amplified similarly to the FID.

The advantage of the NPD is that it is highly selective. Typically, the response to N- and P-containing compounds is 10^4-10^5x the NPD response to hydrocarbons. The primary difficulty with the NPD detector has been the depletion of the thermionic detector with use. The thermionic detector surface in the NPD consists of a doped ceramic bead, and these beads are depleted with useful lifetimes ranging from 200-2000 hours. Depending upon the depletion rate, the sensitivity gains from the NPD relative to the FPD may be fleeting if the depletion is too rapid. Because NPD from different manufacturers have varied greatly in their performance, we sought an NPD which appeared to present the most stable and sensitive performance. We found this in a new NPD released by DETector Engineering & Technology, Inc. (Walnut Creek, CA).

The DET NPD is illustrated in Figure 3-16. The carrier gas is low flow hydrogen (2-6 ml/min) containing the compounds. This is combined with a flow of air into the source chamber. Alternately, an inert carrier gas can be used and a low hydrogen flame can be introduced at the detector. The source is heated by a constant current supply and is polarized at -5 volts with respect to the collector. During operation, the surface temperature of the source is in the range of 600-800 °C which produces a visible orange glow to the source. In fact, this heated source requirement appears to be one of the biggest drawbacks to the NPD in terms of power considerations. In terms of size, the commercially packaged NPD from DET is generously packaged in a large, multiple compartment housing including the detector, a programmable heater control assembly, an electrometer, and a current source. The basic NPD, however, is quite small and is pictured in Figure 3-17. The fittings are 1/16 inch size and the lengths are quite long in order to center the detector in a large housing.

AN-90750

THERMIONIC SOURCE

HEATING CURRENT

POLARIZATION VOLTAGE

ELECTOMETER

COLLECTOR

REACTIVE GAS BOUNDARY LAYER

AIR

SAMPLE & H₂ (2–6 ml/min)

SAMPLE INLET
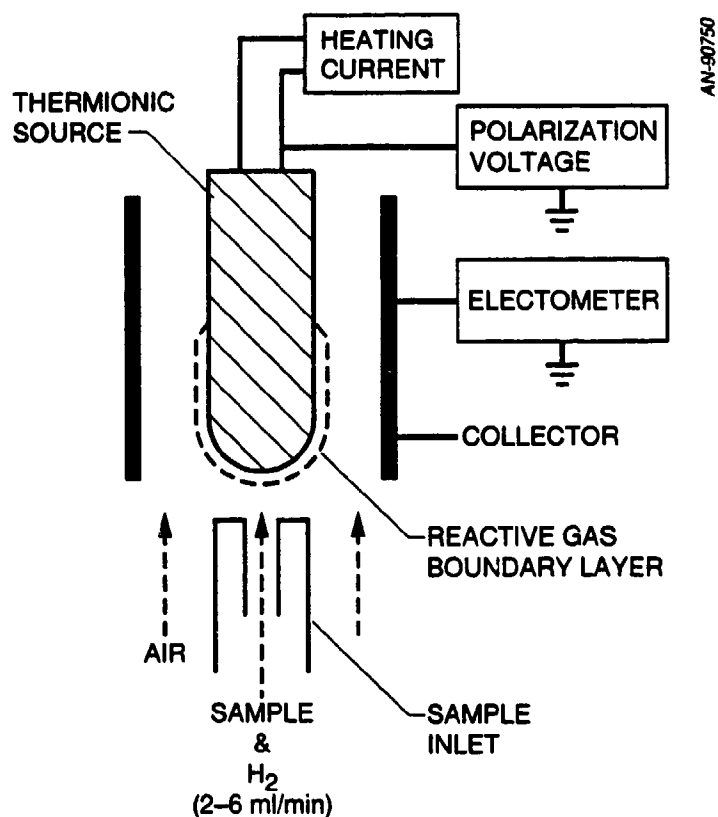
Figure 3-16. Diagram of the NPD manufactured by DETector Engineering & Technology, Inc.
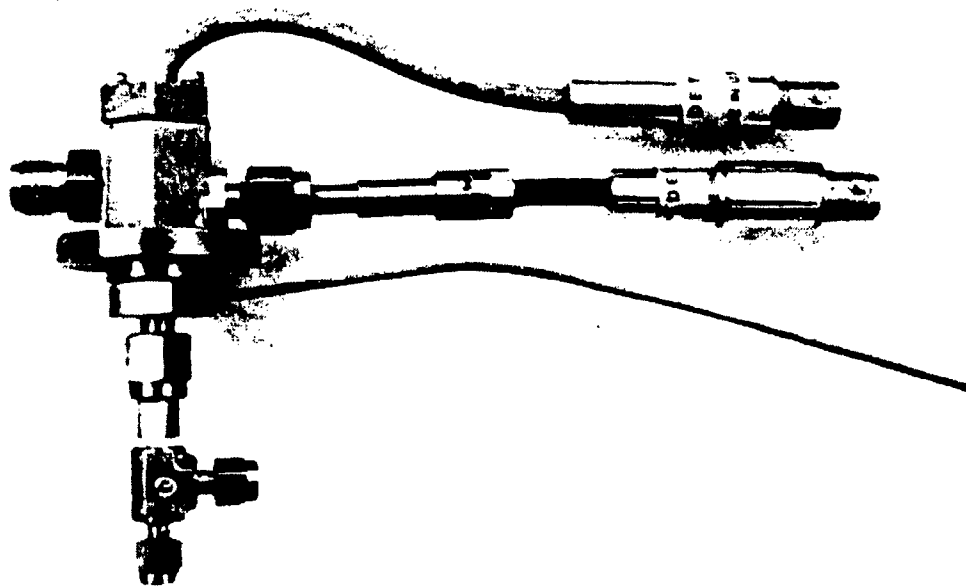
Figure 3-17. Close-up photograph of the DET NPD.

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For testing purposes, the NPD was connected to a 15 m DB-1 capillary column at the opening to a Varian GC oven. Samples could be introduced to the GC via either a thermal desorber or by injection. The GC was temperature programmed to hold constant at 30 °C for 5 minutes followed by a ramping rate of 15 °C/minute up to a final holding temperature of 180 °C. An example analysis of a mix of trimethyl phosphite and triethyl phosphite, compounds number 8 and 9 in Schedule 3 in Table 2-1, respectively, is shown in Figure 3-18 for an injection containing 1 ng. A signal-to-noise ratio of 1,000 was obtained indicating a detection limit below 1 pg. This corresponds to detection levels of less than 1 ng/m3 assuming vapor collection from 1 L of air. These are extraordinarily low detection limits for P-selective detection of CW compounds. A typical background run is shown in Figure 3-19. The peaks are very sharp and there is little background at this high sensitivity because of the normally very low background levels of organophosphorus and organonitrogen compounds.
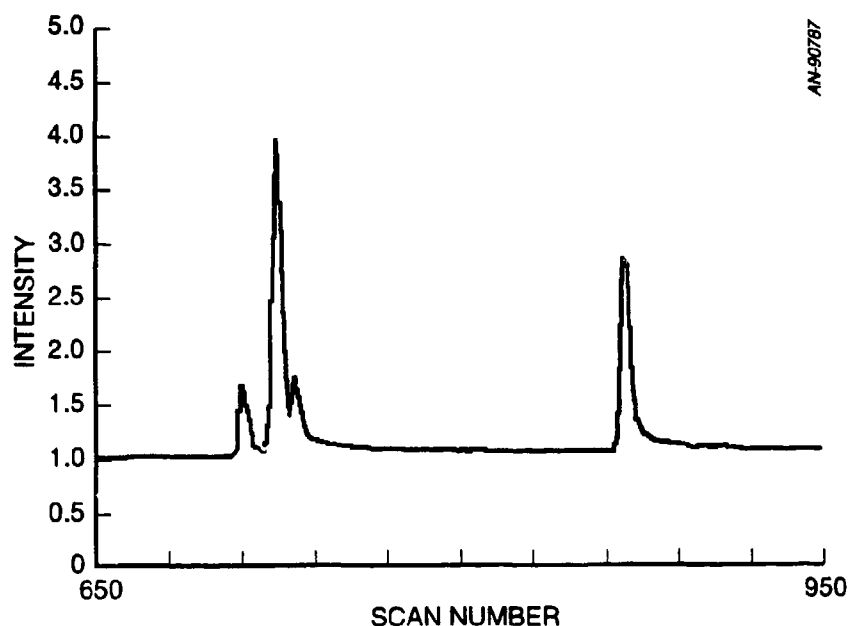
Figure 3-18. GC analysis of a 1 ng phosphite mixture using an NPD.

54
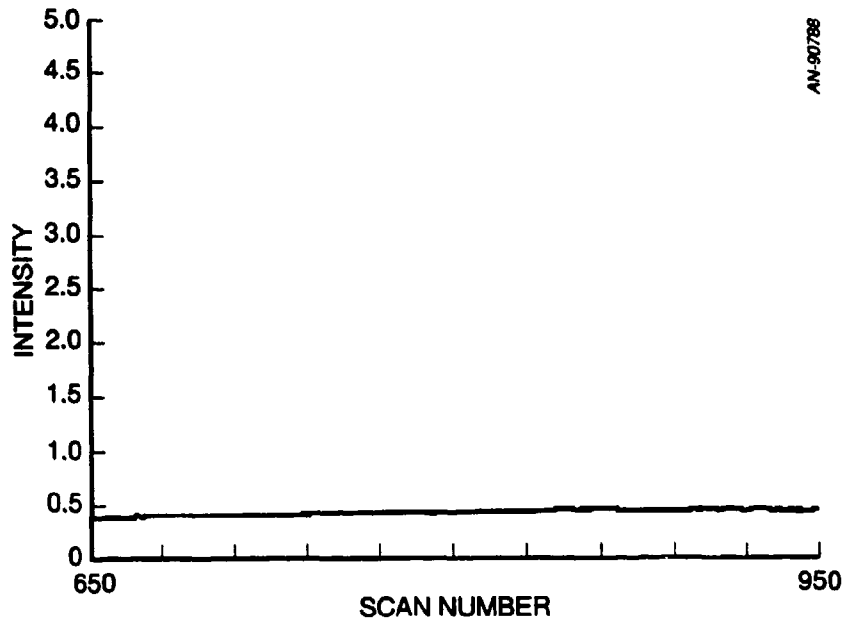
Figure 3-19. GC analysis background run for analysis shown in Figure 3-18.

Regarding the sensitivity of the NPD detector, we were not able to perceive significant degradation of its performance over the two week period in which a variety of tests were conducted. The DET NPD is claimed to have a usable lifetime of 2000 hours, but the extent of degradation that would be experienced in this application is undetermined. Our analysis in terms of pros and cons for the potential use of this detector in a handheld instrument are listed in Tables 3-5 and 3-6, respectively. These considerations are based upon our laboratory testing of the commercial DET NPD package and our analysis of the packaged detector.

Table 3-5. DET NPD pros regarding potential use in the concept instrument.

1.	Sensitive (<1 pg detection limit)
2.	Low hydrogen gas consumption (2-6 mL/min)
3.	Lesser gas purity requirements than for other detectors, especially general purposes detectors such as FID
4.	Very high P and N selectivity for CW-selective detection (virtually unresponsive to other compounds such as hydrocarbons)

Table 3-6. DET NPD cons regarding potential use in the concept instrument.

1.	Thermionic source requires high current for operation (2.5 volts into 1 ohm)
2.	Operation is sensitive to vent blockage or disturbance of air flows near vent
3.	Excessive source current or hydrogen flow ignites flame (not autodetectable)
4.	Flow regulators unstable mechanically at low flow rates
5.	Detector baseline "zero" changes with gas flow rates, temperatures, and source current
6.	Higher block temperatures might be needed for keeping the detector clean of the heavier semivolatiles
7.	Detector noise levels vary directly with source current, so noise levels expected to rise as source becomes depleted and source current is increased to compensate for reduced sensitivity
8.	Uncertainty regarding the required programming of the source current for the detector for use in an automated application

While most of the pros in Table 3-5 have already been discussed, the cons in Table 3-6 require discussion. The source and heater currents require significant current for a battery operated instrument. While a 2.5 ampere current can be maintained for several hour periods by some of the more advanced, relatively light weight batteries, this is a power hungry component compared to the other functional elements under consideration for the concept instrument. There may well be cases in which the lower detection limits of the NPD warrant a greater power requirement for the instrument such as safety monitoring applications, for example.

Regarding the current requirement, testing was done to determine if an on-off cycle could be superimposed over the duty cycle presently used to control the NPD in order to save power. The present duty cycle is controlled by the heater control assembly and has a cycle time of about 1-2 seconds. Cooling and heating curves were determined by switching the NPD heater and source current off and on. The temperature recovery times and power requirements were determined for restoration of full operation of the instrument after varying lengths of shut-down; the longer the source current was shut down, the greater the power

saving, but the longer the time to ready the detector for operation. An example curve in Figure 3-20 shows a 15 min shut-down of the heater requiring a 5 min recovery time. Further, the power is not duty-cycled until the desired temperature is regained for detector operation. With a cold detector, the warm-up time is 20 minutes. Because of the greater power required for warm-up, the overall power savings were nominal unless the detector were to be used only infrequently with tolerance for a 20 minute warm-up. For maintenance of a ready-to-test condition, such delays are probably unacceptable. On the other hand, these delays might be acceptable for very intermittent operation.
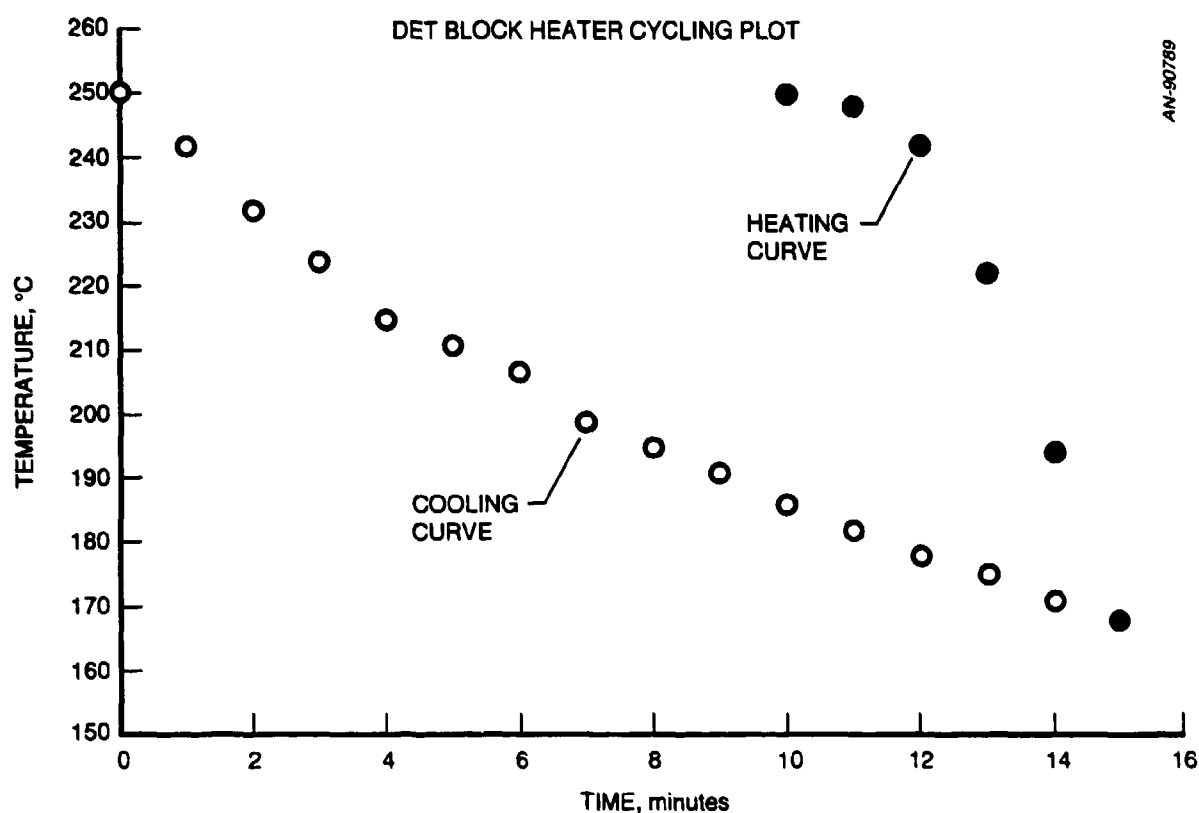
Figure 3-20. Cooling and heating recovery curves for the NPD heater.

Regarding the sensitivity of the detector to vent blockage and air disturbance near the vent, we found the instrument to be very sensitive to any blockage of air flow. Even a momentary blockage will halt the correct operation of the detector. This causes the output of the electrometer/amplifier to reverse sign until proper operation is restored. Return to proper

operation requires about half the time of a cold start. In a handheld instrument design the vent would need to be protected by a screen and possibly involve a larger exit size.

Excessive source current or hydrogen flow was observed to cause the NPD to "ignite" internally. This disrupts the "flame" boundary layer which would otherwise result and be controlled by the thermionic source. We found that this mode of detector malfunction results in a normal appearing baseline but with a complete loss of detection sensitivity. Unlike the vent blockage described in the previous paragraph, the electrometer/amplifier output provides no indication of this malfunction. Other means would have to be developed for detecting this malfunction as its failure to respond could be confused with a negative detection finding.

We found the flow regulators to be somewhat unstable at the low flow rates needed for NPD regulation. These regulators appear to operate by screw valves which control the "leakage" through the regulator by turning the valve. We found these to be very imprecise and difficult to repeat settings. Staged, fixed flow restrictors, for example, would provide more reproducible settings for controlling the flow rates with this detector.

The baseline "zero" was observed to be very sensitive to temperature, flow rates, and source current. We do not believe that this poses a significant difficulty because the proposed detection algorithms are insensitive to GC baselines and baseline drift.

The NPD normally operates with a small heater block on its housing that operates at a fraction of the source current. This was operated at 250 °C for our testing. For preventing the detection carryover of any heavy semivolatile materials, it might be desirable to raise the temperature of the NPD housing. This would require additional current, but may not need to be done on a continuous basis.

The final cons listed in Table 3-6 regard the noise level dependence on the source current and the level of programming and instrument control which may be required for an automated system to monitor the depletion of the thermionic source and adjust the source current accordingly. The DET Inc. product literature suggests periodic, stepwise adjustments

of the source current to compensate for the slow depletion of the thermionic source material. This would required additional experience with these detectors to determine the best way to monitor their performance on a long term basis and make the required source current adjustments on an automated basis. It is possible that such adjustments would only be required very infrequently and could be accomplished by instrument diagnostic software rather than the instrument control software. The noise level will also rise as the source current rises, but this will be part of the expected loss of detection sensitivity as the source becomes depleted. The sources are replaceable in the NPD and DET Inc. has an exchange program for source replacement. Periodic maintenance and replacement of the sources may alleviate these concerns. For example, routine replacement of the sources after every 1000 hours of usage might guarantee a sufficiently fresh thermionic source for reliable detection measurements. A quantitative calibration would be required on a periodic basis to monitor the performance of the NPD. Long term quantitative data would be used with this development, as any other detector development, to determine the required calibrants, procedures, and interval between calibrations.

The steps that would be required to modify the DET NPD for use in a handheld instrument were assessed. We examined the operational and control requirements, the hardware layout and packaging, and potential design issues to arrive at a sequence of steps. The packaged NPD detector consists of 4 housings which are attached as stacked pairs. The sequence of steps for modifying and repackaging the detector for use in a small instrument is listed in Table 3-7. The bulk of the commercial package is replaced by the battery supply for the instrument. The detector head and electrometer need repackaging and the adjustable controls can be hardwired to high sensitivity settings that would be required for the CW detection application.

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Table 3-7. Sequence of steps required to modify and repackage the NPD manufactured by DET, Inc. for use in a small instrument.

1.	Remove electrometer board from the electrometer housing and hardware "zero," gain, and attenuation controls. Supply ± 15 VDC for op amp use.
2.	Don't use the DET Inc. current package at all. Replace with a battery to supply 2.5-4.0 VDC at 2.5-4.0 amps.
3.	Repackage the detector head. Possibly use better insulation (current insulation has a K factor of 0.8 at 1,000 °F). Shorten and redesign vent tube.
4.	Don't use the heater control package at all. Use battery to heat detector and the instrument control system to sense temperature.
5.	Don't use gas shutoff valves in the heater control package either. These are normally closed, use computer control instead.
6.	Supply -5 VDC bias to source from battery rather than from the DET current package.
7.	Provide an enclosure for detector and electrometer.
8.	Use a DC to DC converter for -15 VDC, -5 VDC, +5 VDC at 2.5-4.0 amps.

In summary, the small NPD manufactured by DET, Inc. has the potential to provide 10-100x lower detection limits than the state-of-the-art CW monitoring technology using GC with FPD. This may provide a needed margin of detection sensitivity relative to the very low TWA levels of highly toxic materials such as VX. The gain in sensitivity with this detector has an added power cost, however. This is especially true for battery-powered operation. There are some stability and long term performance issues which would need to be investigated. Overall, the NPD reduction to use in a small instrument appears feasible, but has risk attached in view of the uncertainties expressed above and the extent of the detector modifications which are required to properly field this detector in a small instrument under automated operation. This must be carefully contrasted with the FPD, especially the dual FPD, for consideration in the near term implementation of the concept instrument.

FPD Functional Elements Evaluation. We have not conducted experimental testing of an FPD unit, but can rely on the experience of several manufacturers with this detector and its acceptance by the CW safety monitoring community as a GC detector of past choice for

CW-selective detection. The history of this detector in the CMS Research Corporation products developed over the last decade for the safety monitoring of GD, GB, VX, and HD attest to its utility for CW monitoring application. The detector and the pros and cons of its use in the concept instrument are discussed in the following paragraphs.

The FPD is similar to FID except that the flame emissions generated by P or by S are detectable using a small photomultiplier tube. The detector body is light tight and a secondary flow of hydrogen is usually used to ensure a hydrogen rich flame. In a hydrogen rich flame, P emits yellow (526 nm) light which is selectively detected by the use of a yellow filter before the photomultiplier tube. This phosphorus emission comes from the HPO species and is proportional to the concentration. S emits blue (394 nm) light which is separately detectable using a blue filter before the photomultiplier tube. The sulfur emission is due to the S_2 species and is proportional to the square of the sulfur concentration. The FPD detection sensitivity for P is typically about 10x that for S. Because P detection only with the semivolatiles in the CW schedules leaves a critical S detection gap, a single flame detector having dual photomultipliers, one for P and one for S, provides an interesting option for coverage of the schedule compounds.

The pros and cons of the FPD are listed in Tables 3-8 and 3-9, respectively, and are discussed as follows. Many of the advantages are similar to those listed for the NPD, although the initial NPD sensitivity is expected to be 10-100x greater than the FPD. The operation is expected to be relatively simple compared to the NPD. After ignition and stabilization of the flame, the performance is relatively constant and primarily a function of the flow rates. There are no depleting components such as the thermionic source in the NPD. Because the FPD technology has been available for more than twenty years, it has been utilized in CW-related detectors such as the instruments for stack gas monitoring and safety monitoring made by CMS Research Corporation. These approaches have primarily focused on individual compound detection or the detection of a family of compounds such as G agents. For this development, it is particularly attractive to consider the potential merits of a flame photometric detector having dual photomultiplier tubes for simultaneous detection of P

and S. Such FPDs have recently been developed and are commercially available using miniaturized components.

Table 3-8. FPD pros regarding potential use in the concept instrument.

1.	Very sensitive (≤ 100 pg detection limit for P; ≤ 100 pg detection limit for S)
2.	Lesser gas purity requirements than for other detectors, especially general detectors such as FID
3.	Highly selective detection of P or S for CW-selective detection (approximately 10,000x less sensitive to hydrocarbons
4.	Simple operation comparable to the operation of a standard FID
5.	No depleting components as in the NPD
6.	Modest power requirement relative to the NPD
7.	Accepted GC detector for safety monitoring of selected CW agents
8.	Dual photomultiplier use with a single flame possible for providing simultaneous P and S detection

The disadvantages of the FPD with regard to its use in the concept instrument are summarized in Table 3-9. The FPD has a higher rate of consumables use than does the NPD. This magnitude of hydrogen flow is not supplied by the carrier gas, but is provided directly to the flame. Some FPDs are difficult to light and the flames can blow out. This can be corrected in the design by the inclusion of an electrical starter which can light the flame and ensure that the flame stays lit. This approach is used on some FPD designs. Detector noise is partially the result of noise from the photomultiplier tubes which is temperature sensitive. For this reason, the photomultiplier tube should be placed in a cool location, but as close to the flame as possible for minimizing the optical path (maximizing the light intensity). This trade-off results in a relatively close positioning of the photomultiplier tube with adequate ventilation around the tube. While the photomultipliers and their spacing away from the flame add to the bulk of the FPD, miniature photomultiplier tubes are available in current FPD designs which reduce the detector bulk. Additionally, the miniature FPD components are very light in weight.

Table 3-9. FPD cons regarding potential use in the concept instrument.

1.	Large hydrogen flow rate required (50-150 mL/min) for hydrogen rich flame
2.	Some FPDs are difficult to light or prone to flame-outs
3.	Photomultiplier noise is temperature sensitive.
4.	Repackaged FPD expected to be slightly bulkier than other detectors, although light in weight

The repackaging expected to utilize a commercially available FPD in a handheld instrument is listed in Table 3-10. This table is similar to Table 3-7.

Table 3-10. Sequence of steps expected for modifying and repackaging an FPD for use in a small instrument.

1.	Remove electrometer board and hardware "zero," gain, and attenuation controls. Supply 15 VDC for op amp use.
2.	Repackage the detector head. Possibly use better insulation.
3.	Use single, small high voltage supply for both photomultipliers.
4.	Provide an enclosure for the electrometer and a light-tight enclosure for both photomultiplier tubes.
5.	Use a DC to DC converter for op amps and power supplies where necessary. Connect to the voltage regulated supplies where available in the instrument control hardware.

The FPD appears to be a proven and accepted GC detection technology for the CW-selective detection of certain Schedule 1 materials. While it is less sensitive than the initial NPD sensitivity, it is simpler to operate and involves no depleting components. It also has very modest power requirements compared to the NPD which greatly reduces battery requirements. Further, the ability to utilize new FPD designs using small components which provide simultaneous P and S detection may be especially important to provide the detection coverage needed by inspectors using the concept instrument. *Overall, the FPD is viewed as a much lower risk CW-selective detector option in the short term in view of the uncertainties*

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und issues to be resolved with the NPD. The NPD appears to be an attractive longer term development which has the definite potential to provide an additional 1-2 orders of magnitude reduction in detection limits. This may provide highly desirable detection margins in safety monitoring applications. Further, where external power is available in some of these situations, the higher power requirements of the NPD are not a concern.

3.6 BATTERY TECHNOLOGY FOR HANDHELD CW INSPECTION INSTRUMENT.

The concept instruments which will be described in Section 4 of this report will require battery-provided power for their field operation. (The instruments can easily be designed to also operate from power converters where external power is available and mobility of the instrument is not critical.) Because batteries are anticipated to be a major contributor to the weight and size of an instrument based on the anticipated power requirements, a survey of different commercially available battery technologies was conducted to determine their performance characteristics, weights, sizes, and costs.

All comparisons were made with respect to our anticipated battery performance requirements. Our requirements include the delivery of high currents (several amperes), low battery weight, deep cycle discharge capability, reasonable expense, and moderate-to-fast recharge rates. Based upon our analysis of typical small GC instrument requirements, we set a baseline unit of battery performance for comparison purposes at 10 amperes/hour for 4 hours. This provides a battery performance benchmark projected to be sufficient for a half-day of instrument operation. These relative results can be scaled for higher current requirements or different performance intervals accordingly.

A comparison of commercially available battery technologies is shown in Table 3-11. Battery types in this table include common alkaline, gel cell, nickel cadmium, silver zinc, nickel metal hydride, lithium thionyl chloride, and lithium sulfur dioxide. Large numbers of some of the battery types need to be paralleled to deliver the required current. In many cases, batteries must also be placed in series to provide the required voltage. The relative weights range from heavy to light depending upon the technology. Some of the lightest, the lithium

Table 3-11. Comparison of battery technologies for delivering 10 A/Hr for 4 hours.

Battery Type	Example	No. Cells Reqd	Total Weight	Total Volume
Alkaline "D" Cells	Duracell MN1300	150	20.5 kg (45 lbs)	10.6 L (650 cu. in.)
Pros			Cons	
Very available			Heavy	
No charger needed			Need to be paralleled	
Cells per pack flexible			Can't be recharged (must be disposed)	
Gel cell	Powersonic PS-12500	1	14.1 kg (31 lbs)	7.0 L (425 cu. in.)
Pros			Cons	
No paralleling needed			Won't fast charge	
Sealed, leakproof, use in any orientation			Can't add "another cell" easily (only add another battery	
Low cost				
Nickel Cadmium "D" Cell	SAFT VR4D	100	14.5 kg (32 lbs)	7.8 L (478 cu. in.)
Pros			Cons	
Can fast charge (1 hr)			More expensive than alkaline or gel cells	
Lighter total than alkaline				
Can supply large currents for short times due to low internal resistance				
Cells per pack flexible				
Silver-Zinc	Eagle-Picher	10	4.5 kg (10 lbs)	2.5 L (150 cu. in.)
Pros			Cons	
No paralleling needed			Very expensive ($200 per cell)	
Very light weight			Longer charge time (8-12 hours minimum)	
Very small volume			Faster charge loses electrolyte and shortens cycle life	
25 year proven technology in space/military uses			Low cycle life (4-6 month use)	
Cells per pack flexible				

Table 3-11. Comparison of battery technologies for delivering 10 A/Hr for 4 hours (Continued).

Battery Type	Example	No. Cells Reqd	Total Weight	Total Volume
Nickel Metal Hydride	Eagle-Picher	10	10.1 kg (22.4 lbs)	3.3 L (200 cu. in.)
Pros			Cons	
No paralleling needed			Expensive (more than Nickel cadmium, less than Silver zinc)	
Low volume				
Lower weight				
Can be fast charged (< 3 hrs)				
Cells per pack flexible				
Lithium Thionyl Chloride	SAFT LSH20	20	2.6 kg (5.6 lbs)	1.6 L (100 cu. in.)
Pros			Cons	
Very light weight			Can't recharge	
Long shelf life (10 years)			Hard to find	
No recharge needed			Paralleling needed (should be diode isolated to prevent cells from charging each other	
Emits no toxic substances (dispose of as industrial scrap)			Expensive	
Employ built-in diode isolation and reversible circuit breaker			Passivate after partial heavy use	
Cells per pack flexible				
Lithium Sulfur Dioxide	SAFT LO39SH	20	2.7 kg (6.0 lbs)	1.6 L (100 cu. in.)
Pros			Cons	
Large 3 V cell potential requires fewer cells			Discharge rates above 5 A require monitoring of cell temperatures	
No recharge needed			Probably need 4 packs (5 batteries each) in parallel for 4 hours use	
Very low weight			Paralleling of cells needs diode isolation incorporated to prevent some cells from charging others	
Very low volume			Cells are pressurized and pressure increases with discharge (1-3 atm)	
Cells per pack flexible			Can't recharge	
			Disposal hazard potential	
			Heating or excessive current can cause sulfur dioxide venting hazard and require evacuation	
			Not readily available	
			Passivate after partial heavy usage	

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batteries, are difficult to use in parallel because differences between individual batteries can result in undesirable charging of some of the cells which can cause severe failures including battery ruptures. Intermediate weight technologies which are moderately expensive are the nickel metal hydride and the silver zinc. For example, while the silver zinc battery costs $2,000 for a pack of ten, the cost is $20-25 per use over an expected life of 80-100 charging cycles. In cases where the weight of the instrument needs to be as light as possible for the convenience the inspectors, the use of this more expensive battery technology may be warranted. Further, the nickel metal hydride and silver zinc batteries can be custom packaged in different sizes and their cost would be lower when purchased in quantity.

An example voltage curve for a 40 Amp-Hour silver-zinc battery discharged at a rate of 10 amperes/hour is shown in Figure 3-21 (data provided by Eagle-Picher). The voltage is seen to remain relatively constant for the duration of use. The charging efficiency as a function of charge rate for the same battery is shown in Figure 3-22. A fast charge rate of 4 hours results in only an 83% recharging (overnight charging at a rate of 3 amperes is recommended as it gives high charge efficiency).

An additional test cycle example for the less expensive and intermediate weight nickel metal hydride battery is shown in Figure 3-23. In this example, two different 10 Amp-Hr batteries were discharged at a rate of 5.0 amperes to 0.5 V from its starting potential. The potentials declined slightly over the duration of the discharge with an average potential of about 1.25 V. This demonstrates the high discharge rates which can be reproducibly achieved with these cells.

Given the substantial weight of the batteries which may be required to power the portable inspection instruments, it may be necessary with some instrument configurations to consider off-loading the power source to a belt pack or other external configuration to achieve the low weight required for a handheld instrument. This is standard practice for portable television cameras, for example. One of the concept instrument designs which is presented later in this report, for example, has a weight of 10.5 kg (23.1 lbs) including the battery. This same instrument with the battery removed would weigh 7.4 kg (16.3 lbs). It should be

AN-90764
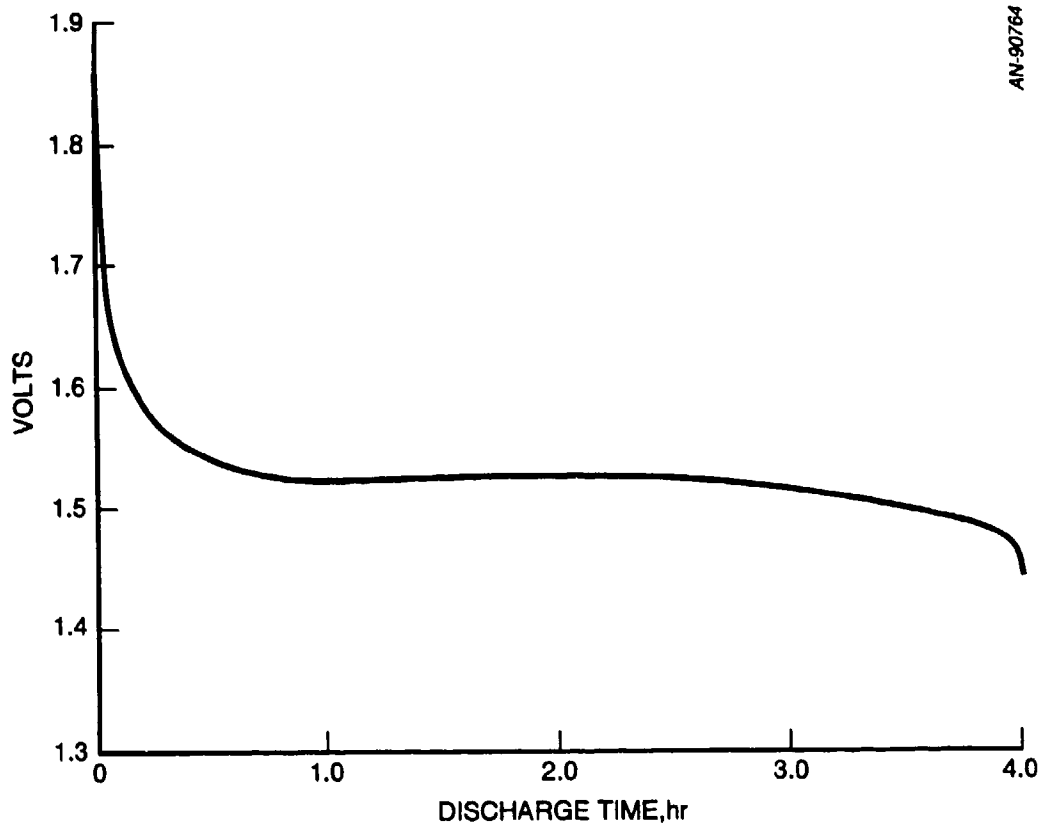
Figure 3-21. Discharge curve for a 40 amp-hour silver-zinc battery discharged at 10 amperes/hour.

AN-90765
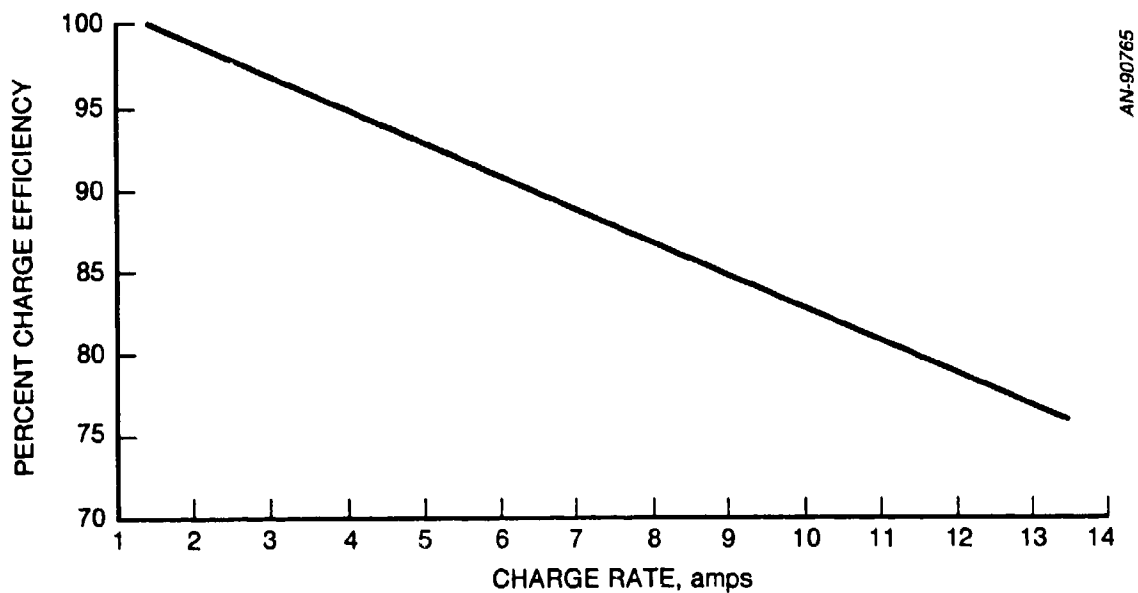
Figure 3-22. Charging efficiency for a 40 amp-hour silver-zinc battery as a function of charge rate.

68
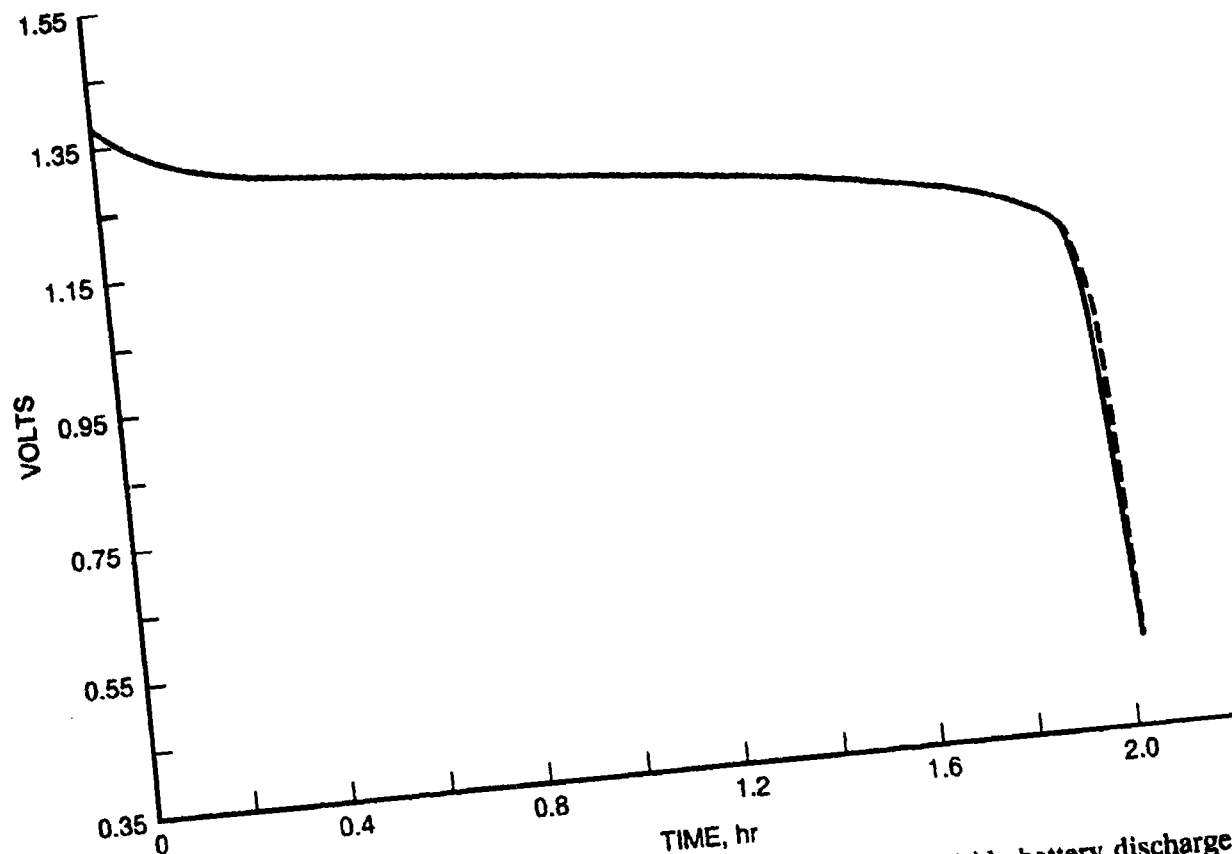
Figure 3-23. Discharge curve for a 10 amp-hour nickel metal hydride battery discharged at 5 amperes/hour.

noted that this instrument weight without battery is for a prototype instrument, with the weight much smaller for a pre-production prototype (3.3 kg or 7.3 lbs). The battery weight itself (3.1 kg or 6.8 lbs) is large relative to the instrument weight, especially with respect to the pre-production instrument. For this reason, it may be desirable to consider a belt pack or other type of battery pack which can be worn or carried along with the instrument.

Considerations regarding battery packs include possible need for parallel operation (to increase power), packaging to protect battery structures from physical impact shock, and individual cell construction. For example, specifications for individual battery cells far exceed pack specifications due the presence of welded connectors, cell movement in the packs, and the pack housing materials. The shock testing of packs is usually left to the user.

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Paralleling of batteries is best avoided because individual cells aren't identical in potential and paralleling leads to charging of some cells by others. This can be avoided by selecting designs which provide single cells of the desired capacity. Batteries having end caps probably should also be avoided. End caps are frequently used in alkaline and nickel cadmium batteries. The end caps are often poorly welded or sometimes only press-fitted to the battery case. Also, individual cells must be packaged so that they do not shift in a pack if it is dropped. Battery manufacturers who make custom packs are familiar with many of these issues in battery pack design and are expected to provide useful advice.

SECTION 4
CONCEPT INSTRUMENT DESIGN SPECIFICATION

The results of the functional elements evaluation provide the basis for developing a Concept Instrument Design Specification for the CWC schedule chemicals. A major part of the concept design process involves a consideration of the trade-offs associated with the physical and chemical properties of the schedule materials, the various functional elements, and treaty inspection operational needs. For example, the vapor pressure and chemical stability of the various schedule materials will drive the choice of the sampling system for concept instrument designs. In this case, a number of the volatile precursor chemicals on schedules 2 and 3 are chemically too reactive for adsorbent trap preconcentrators to be used, whereas preconcentration is needed for the CW agent semivolatiles on schedule 1 due to their low vapor pressure and very low TWAs. As a result, the detection of some schedule 3 volatiles may be difficult using a single GC module with a preconcentrator.

Various approaches to the concept system together with their pertinent characteristics and projected coverage of the CWC schedule compounds are illustrated in Figure 4-1. The first concept system illustrated is a "dual module" system intended to cover virtually the full range of CWC schedule compounds by combining a correlated column µGC module without preconcentrator for the volatiles, with a mini-GC module with preconcentrator for the semivolatiles. The tradeoff for this system is the increased size, weight, and power required to address the full range of schedule materials. The second concept system illustrated is a semivolatiles mini-GC instrument that has been designed to extend coverage to as many of the CWC schedule volatiles as possible. This allows size, weight, and power requirements to be significantly reduced with some loss of coverage of CWC volatiles (especially the lightest and most chemically reactive ones). The final concept system illustrated is a µGC volatiles instrument that has been enhanced to extend coverage somewhat toward the lightest semivolatiles, but without preconcentration. This reduces size, weight, and power requirements, but with significant loss of coverage of the CWC semivolatiles (especially the heavier CW agents with low TWAs).

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INSTRUMENT APPROACH

CW SCHEDULE COVERAGE
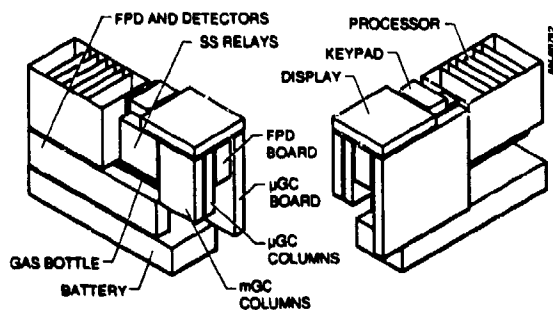
"DUAL MODULE" INSTRUMENT
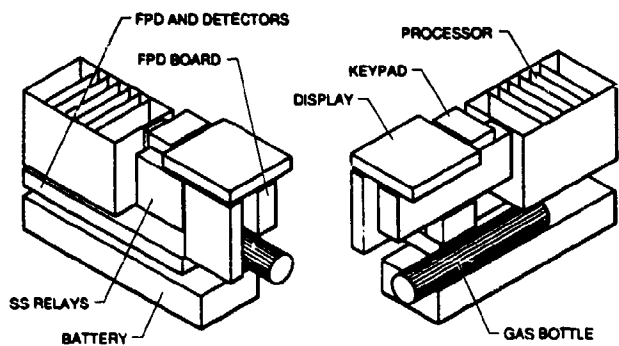
ENHANCED MINI-GC INSTRUMENT
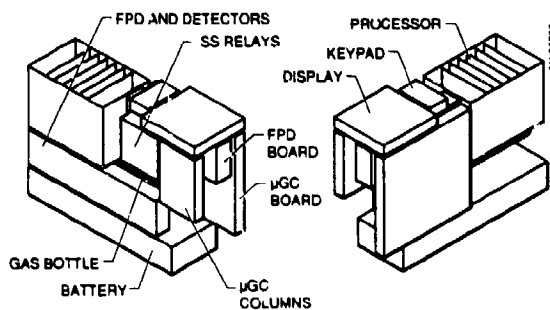
µGC INSTRUMENT

Figure 4-1. Three concept system approaches and their relative CWC schedule coverage.

Operational considerations and projected CWC inspection scenarios are important considerations in the proposed concept instrument design. For example, key inspection scenarios are likely to fall into two distinct types, mainly inspections of existing schedule 1 CW agent storage/distribution sites and inspections of declared schedule 2 facilities. In the first case, pre-screening measurements for schedule 1 CW agents down to TWA levels may be the primary concern. In the second scenario, screening for the presence of schedule 1 materials is a likely subject for detailed investigation at a declared schedule 2 site. As a result, a concept design to cover the full range of CWC schedule compounds may increase the size and weight of the inspection instrument beyond the convenient handheld size that would best meet the key operational needs of the inspectors. Concept designs which recognize the user's need for operational flexibility are also important. For example, an instrument designed to take a variety of different sizes of easily changed battery packs would allow inspectors to select a preferred configuration for a given inspection task.

During the concept instrument design process, system design descriptions of proposed instrument configurations are developed and presented with sketches and flow diagrams of the instrument. Critical design decisions are described including the rationale for concept selections and trade-off decisions. Justifications are given for any major new components which are introduced and different in principle of operation from the components examined in the functional elements evaluation. Finally, a summary of the functional elements and components to be utilized is listed and briefly described.

4.1 DUAL MODULE INSTRUMENT CONCEPT DESIGN.

Based upon the results of the functional elements evaluation with respect to semivolatiles detection by the mini-GC, volatiles detection by the µGC without preconcentration, and the specifics of the NPD and FPD detectors, a Concept Instrument Design Specification can be developed for the handheld CWC inspection instrument. Because our baseline approach was to specify a single design which could cover all of the GC-detectable compounds in the CWC schedules, this design grew to encompass two separate GC detection approaches to address the semivolatiles and the volatiles. The inclusion of two different approaches in a

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single instrument results roughly in a doubling of the concept instrument size and complexity. We believe that operational trade-off arguments can strongly be made in favor of an inspection instrument utilizing a mini-GC enhanced for volatiles by itself. This reduces the concept instrument back to the original concept size which is suitable for a handheld instrument. (This enhanced mini-GC concept instrument is presented in Section 4.2.). However, because of the comprehensive scope of the baseline concept instrument, it is presented first, with smaller concept designs that are more attractive for handheld inspection purposes in the next two sections. These smaller systems consist of enhanced performance subsets of the dual module concept systems of the baseline approach.

4.1.1 Survey of Module and Detector Combinations for Maximum Coverage of the CW Schedule Compounds.

A variety of possible CW-selective detector and GC-module combinations are possible which utilize the NPD and FPD. To arrive at a baseline or multiple baseline concept instruments, it is necessary to consider combinations of modules and detectors for maximizing the coverage of GC-detectable compounds in the CWC schedules. The emphasis from the perspective of the baseline concept instrument is on the broadest possible detection coverage with good sensitivity and selectivity, with size a secondary consideration. Thus, maximum detection capability is sought in the baseline concept instrument. A full consideration of the trade-offs is later introduced to develop alternative concept instrument designs of smaller size which retain the maximum possible detection coverage, sensitivity, and CW-selectivity.

A survey of dual module (mini-GC and µGC) combinations with respect to potential coverage of CWC semivolatiles and volatiles is shown in Table 4-1. Paired µGC modules capable of correlated chromatography are indicated by µGC$^{(2)}$. Included in the commercial µGC modules are thermal conductivity detectors (TCDs) which are small, microfabricated detectors with about a 1 ppm detection sensitivity. Various combinations of NPDs and FPDs with GC columns and µGC modules are shown in the table. FIDs are also included in some cases to show how a sulfur detection gap with the semivolatiles GC module, the mini-GC, can be closed. It is possible to operate a flame detector as an FID and an FPD simultaneously, although a compromise in sensitivity is usually involved. This combination is labeled

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FID-FPD where it occurs in the table. A dual FPD in which a photomultiplier for P detection and a photomultiplier for S detection are used with the same flame is labeled FPD-P&S where it is used in the table. Detectors in addition to the miniature TCDs are also shared wherever possible to reduce the number of these added detectors. A shared NPD with the μGC modules could be utilized by sequentially operating each μGC module, for example. Furthermore, a detector shared with the GC mini-module could first be used to analyze the output of the μGC modules while vapors are being preconcentrated for mini-GC analysis. While this sharing importantly reduces the number of components, it also introduces some risk by comp ...ating the operation of the instrument.

Table 4-1. Survey of dual module combinations for coverage of CW schedule compounds.

Module Combinations	No. GC Columns	No. Detectors	Sensitivity								No. Different Detector Types	Selectivity/Sensitivity
			Volatile				Semivolatile					
			Hc	P	N	S	Hc	P	N	S		
μGC(2)/TCD/FPD-P&S (shared) + GC/FPD-P&S (shared)	3	3	L	H	L	H	—	H	—	H	2	Excellent P and S N Gap
μGC(2)/TCD/NPD (shared) + GC/NPD (shared) + GC/FID	4	4	L	H	H	L	M	H	H	M	3	Excellent P&N Moderate S (not selective)
μGC(2)/TCD + GC/NPD + GC/FID	4	4	L	L	L	L	M	H	H	M	3	Weak on volatiles Moderate S (not selective)
μGC(2)/TCD + GC/NPD	3	3	L	L	L	L	—	H	H	—	2	Weak on volatiles S gap
μGC(2)/TCD/FPD-P (shared) + GC/FID-FPD-P	3	4	L	H	L	L	M	H	M	M	3	Excellent P Moderate S (not selective)
μGC(2)/TCD/NPD (shared) + GC/TCD/NPD (shared)	3	4	L	H	H	L	L	H	H	L	2	Excellent P, N Poor S

H = High (low conc.)   L = Low (high conc.)

The numbers of GC columns and detectors are separately listed in the table, with detection sensitivities for different classes of compounds for both volatiles and semivolatiles also indicated. The results for volatiles refer to the detection used with the μGC, and the results for semivolatiles refer to the detection results with the mini-GC. Hc stands for

hydrocarbons, while P, N, and S refer to the CW-selective detection of these elements. High sensitivity (low detection limits) are indicated by H and refer to ≤10 pg of P or ≤100 pg of S detection capability. At the other extreme, low sensitivity on the order of 1 ng is indicated by an L. Intermediate detection sensitivities are indicated by M, with detection gaps indicated by a dash. The number of different detector types is indicated in a separate column. The detectors should be considered in terms of the potentially different hardware support required for each in the form of consumables, power supply, etc. The final column in the table provides a brief characterization of the relative selectivity and sensitivity of these different module and detector combinations with regard to coverage of the CWC schedule compounds.

The first two entries in the table are the most interesting with respect to the baseline concept instrument designed for maximum capability. As discussed in the Functional Elements Evaluation section of this report, the FPD-P&S unit provides the capability for high sensitivity detection of both organophosphorus compounds and sulfur compounds with a single GC column. By using the FPD-P&S unit with both the GC and the μGC, the detector count is reduced to a total of three, with this including the two miniature detectors already present in the μGC modules. Such a unit, shown as the first entry in the table, would have high sensitivity for the majority of CWC schedule compounds. The gap with regard to semivolatile CWC materials which contain neither P nor S is small and consists of relatively low profile CWC compounds.

The second entry is similar to the first, except that an NPD detector is substituted for the FPD-P&S and an additional mini-GC column and FID detector is included for S detection. Compared to the first entry in Table 4-1, this configuration requires an additional GC column and GC detector. It features highly selective and sensitive P and N detection and moderate sensitivity for sulfur-containing compounds, but no selectivity for sulfur. While this is expected to be a bulkier instrument design than the first entry, it is included in the dual module instrument designs for the baseline concept.

The remaining entries in Table 4-1 have varying combinations of these detectors and modules, but these combinations are either non-selective with regard to sulfur-containing

compounds or have sulfur detection gaps. They do not appear to offer any advantages over the first two entries in the table. Based upon these results, the first two entries in the table are carried forward into the dual module instrument design specification in the next section.

4.1.2 System Design Description.

Block diagrams of the concept instrument designs for the first two entries of Table 4-1 are presented in Figures 4-2 and 4-3. These designs basically consist of two parallel systems, a mini-GC for the CWC schedule semivolatiles and a µGC for the volatiles. High sensitivity is obtained with both by use of the CW-selective detectors, the FPD-P&S and the NPD, respectively. On the top left in both figures, vapor samples are drawn onto the adsorbent trap which is connected to the inlet by a valve. The sampling pump provides the suction required to draw vapors onto the trap when it is activated and the valve to the trap is open. After preconcentrating sample vapors on the trap, the sampling pump is turned off and the valve to the pump is closed. The adsorbent trap is then heated releasing vapors to the capillary column(s) of the mini-GC shown on the left of both figures. A capillary column having a high phase ratio is used to provide a high capacity for the desorbed vapors from the trap. The temperature programming of the mini-GC is operated by the controller which also controls the operation of the preconcentrator. The compounds eluting from the mini-GC column(s) are detected, signal conditioned, and analyzed by the signal processor. The signal processor also controls the display and the data storage, and communicates with the controller of the µGC for control and data acquisition from the µGC shown on the right hand side of both figures.

The µGC portion of the diagrams in both figures is shown on the right hand side. Vapor samples enter the inlet and are injected by the micromachined silicon valves onto the µGC columns. Chemically reactive CWC precursor chemicals are measured by direct sampling of the vapors in this way. By operating both µGC modules at the same temperature, the two µGC modules should be combinable back-to-back in a single temperature control unit. This not only combines two µGC modules into the space of one, but it may be
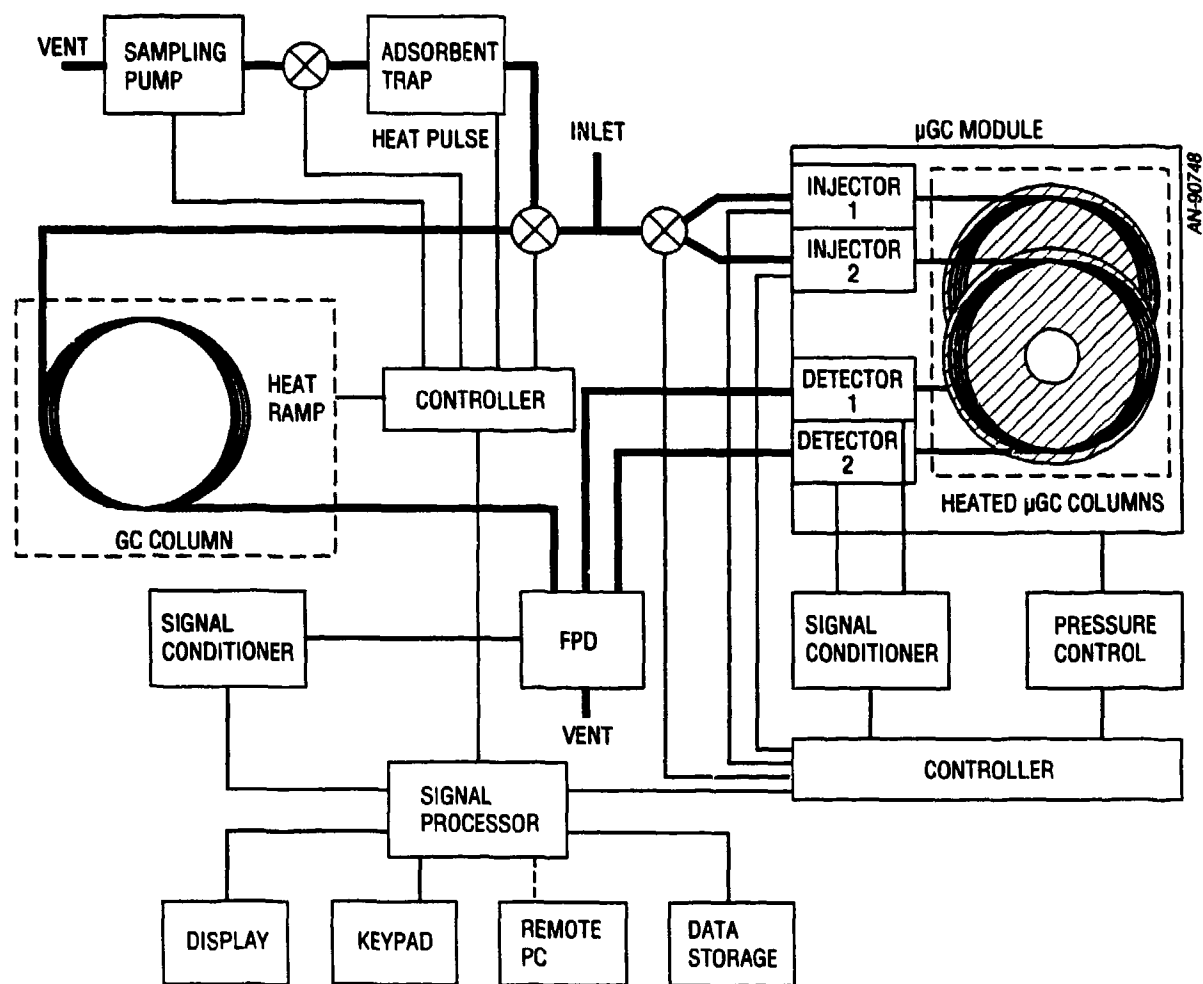
Figure 4-2. Block diagram for a dual module concept instrument equipped with an FPD having simultaneous phosphorous and sulphur detection capability.
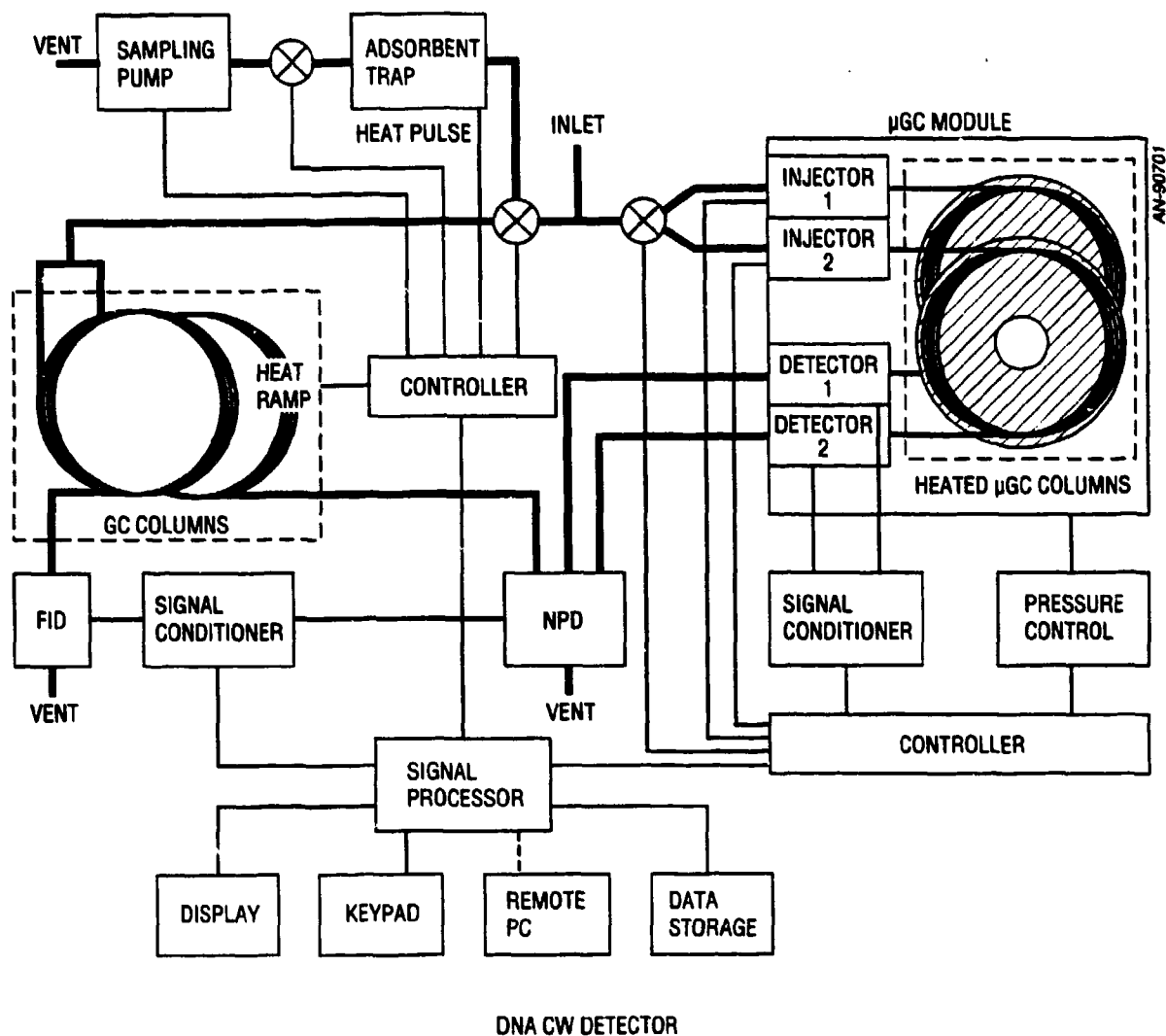
Figure 4-3. Block diagram for a dual module concept instrument equipped with an NPD and a supplementary FID.

possible to use a common pressure manifold and valving assemblies for the combined μGC module.

The μGC hardware and firmware (ROM-based programs in the commercial μGC units) communicate with the signal processor downloading the operation instructions to the μGC controller and receiving μGC data from the controller. The signal processor contains the peak detection and target matching algorithms, and also can be connected with a remote PC for software modifications or diagnostics.

Possible component configurations for the different dual module concept instrument designs are shown in Figures 4-4 and 4-5. The modularity of the designs is emphasized in the sketches. Estimates of the volumes, weights, and power requirements for these components are shown in Tables 4-2 and 4-3. The volumes are in mL, the weights are in g, and the powers are in watts. These estimates are based upon our analysis of the current μGC package, the design for the mini-GC, and our analysis of the detectors and required processing packages. The volumes and weights are approximately 50% of the commercially packaged components. We believe that these values are representative of weight and size reductions that can be readily achieved in prototype instruments in Task 4 of this program.

As discussed earlier, the sizes and weights of these baseline concept designs having dual GC approaches are excessive for a handheld inspection instrument. The dual system using the FPD-P&S, the first system in Table 4-1, has a projected weight of 9.1 kg (20 lbs) without batteries. As discussed earlier in the functional elements evaluation of batteries, the choice of a light-weight battery such as the silver-zinc, for example, would add an additional weight of almost 3.5 kg (7.6 lbs) weight for 4 hr operation. The batteries in Figure 4-4 are shown beneath the instrumentation to allow ready visualization of the instrumentation with and without an attached rechargeable battery package. With an instrument this size, a detached battery may be preferred such as one which could be worn as a belt pack. For longer or shorter durations of continuous operation than 4 hours, adjustments must be accordingly made to the size and weight of the battery pack. The size of this baseline concept instrument with batteries is also shown in Figure 4-4. The approximate dimensions

FPD AND DETECTORS

SS RELAYS

PROCESSOR

KEYPAD

DISPLAY

FPD BOARD

µGC BOARD

µGC COLUMNS

GAS BOTTLE

BATTERY

mGC COLUMNS

AN-90762

50.4 cm

17.8 cm

36.9 cm
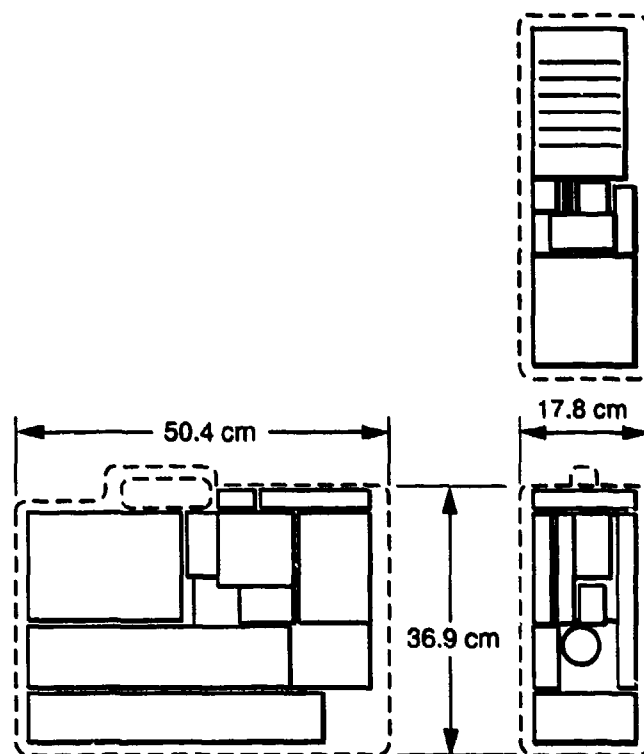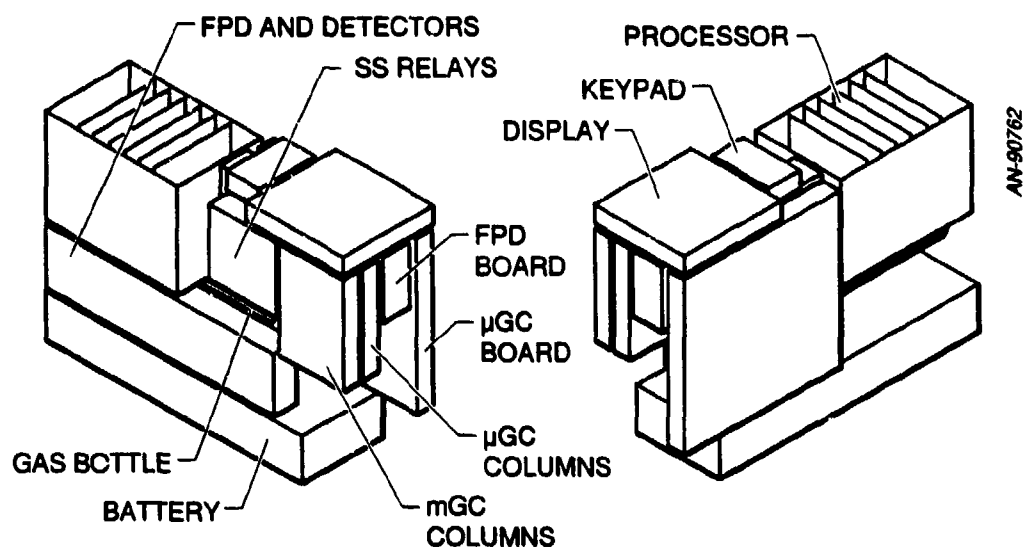
Figure 4-4.   An example component configuration for the dual module concept instrument equipped with a dual FPD.

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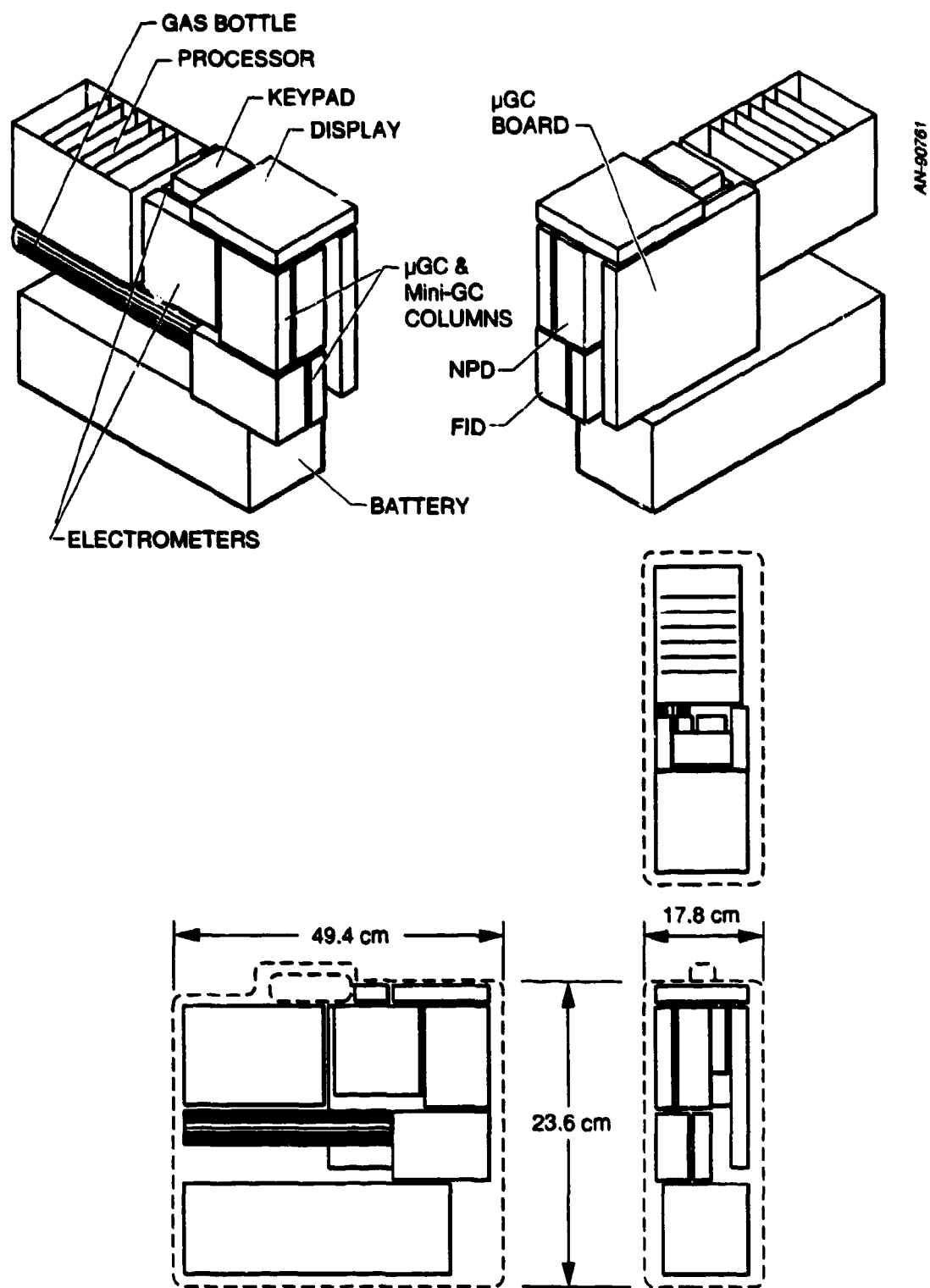
Figure 4-5. An example component configuration for the dual module concept instrument equipped with an NPD and a supplementary FID.

Table 4-2. Estimated volume, weight, and power requirements for the dual module instrument with an FPD.

Component	Volume (mL)	Weight (g)	Power (w)
μGC	2425	1150	8
mGC	1180	500	20
FPD	2275	1254	30
Processor	3975	2200	18
Gas	787	1000	
Connections	4542	0	
Subtotal	15183	6104	76
w/Housing	17949	9156	
Battery	1604	2876	
w/Housing	2784	3451	
Total	20733	12607	76

Table 4-3. Estimated volume, weight, and power requirements for the dual module instrument with an NPD and supplementary FID.

Component	Volume (mL)	Weight (g)	Power (w)
μGC	2425	1150	8
mGC	1180	500	20
NPD	1314	950	35
FID	1314	950	20
Processor	3975	2200	18
Gas	787	1000	
Connections	4711		
Subtotal	15705	6750	116
w/Housing	18574	10175	
Battery	2452	4388	
w/Housing	3968	5266	
Total	22542	15441	101

are a box 50.4 cm (L) x 17.8 cm (W) x 36.9 cm (H). The display is on the top surface of the instrument with thumb control of a pair of buttons which control the menus of the display.

As a result of the higher power requirements of the NPD and the extra volume required for the inclusion of an additional FID detector, the roughly equivalent concept system utilizing the NPD has greater size and weight. The approximate dimensions are a box 49.4 cm (L) x 17.8 cm (W) x 44.7 cm (H). The weight in this case is 10.3 kg (22.6 lbs) without batteries, and 15.5 kg (34.2 lbs) with light-weight batteries adequate to provide continuous operation for a 4 hour period. The impact of the battery volume is seen in Figure 4-5. Besides being larger in size than the baseline concept system shown in Figure 4-4, the NPD-configured concept instrument is viewed as having greater near term development risk than the FPD-configuration as discussed in the Functional Elements Evaluation section.

4.2   ENHANCED MINI-GC INSTRUMENT CONCEPT DESIGN.

An attractive alternative to the dual module instrument concept, which offers reduced size, weight, and complexity, is a concept design based on a enhanced mini-GC module only. In this design, the innovative low thermal mass mini-GC column with integral heater used for semi-volatiles is enhanced to extend the range of operation to CWC volatiles. The previous functional elements evaluation of the mini-GC demonstrated that under the proper operating conditions, coverage of many of the most important CWC schedule volatiles could be achieved. This makes a stand alone mini-GC concept instrument design which covers most of the CWC schedule materials feasible, while significantly reducing the complexity, size, weight and power requirements compared to a dual module instrument.

4.2.1   Hardware Options.

The low thermal mass and integrated heater of the mini-GC approach provides an excellent basis for developing a compact handheld instrument. For GC analyses directed at CWC schedule materials, and especially the semi-volatile CW agents, selective detectors provide important capability. Details of the NPD and dual FPD detectors have been com-

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pared and discussed at length in previous sections. As noted earlier, the dual FPD detector has some important advantages over the NPD in terms of detector stability, power consumption, coverage of HD (with sulfur detection), and widespread user acceptance for safety monitoring at TWA levels. Based on these considerations, a dual FPD detector has been selected for the present concept design.

The selection of the highly selective dual FPD detector (phosphorus and sulfur) greatly enhances selectivity for CWC schedule materials, and obviates the need for correlated column GC to achieve good selectivity. This allows one dual FPD detector and a single GC column to be used in the concept design, thus substantially reducing power requirements and weight, making handheld operation feasible.

4.2.2 Concept Design Description.

A block diagram of the concept design for an enhanced stand alone mini-GC instrument is shown in Figure 4-6. The key elements of the design basically consist of the innovative low thermal mass mini-GC column with integral heater, a sampling "front end" with absorbent trap and Peltier-boosted cooling for the head of the GC column, the dual FPD detector for phosphorus and sulfur, and signal processing and control functions. High sensitivity for CW related materials is achieved by the use of a trap preconcentrator with sample "refocusing" at the head of the GC column, and selective detection of phosphorus- and sulfur-containing compounds by FPD.

In this design, a sampling pump draws an air sample onto an adsorbent trap when it is activated and the valve to the trap is opened. After sample vapors have been preconcentrated on the trap, the sampling pump is turned off and the valve is closed. The adsorbent trap is then heated, thermally desorbing preconcentrated sample into the high capacity capillary column. Here, semivolatile and many volatile components are adsorbed into the high capacity stationary phase at the head of the GC column, with atmospheric gases and the lightest volatiles passing through. Thus the head of the column itself serves as a secondary preconcentrator for most of the CWC schedule components. The temperature programming of the

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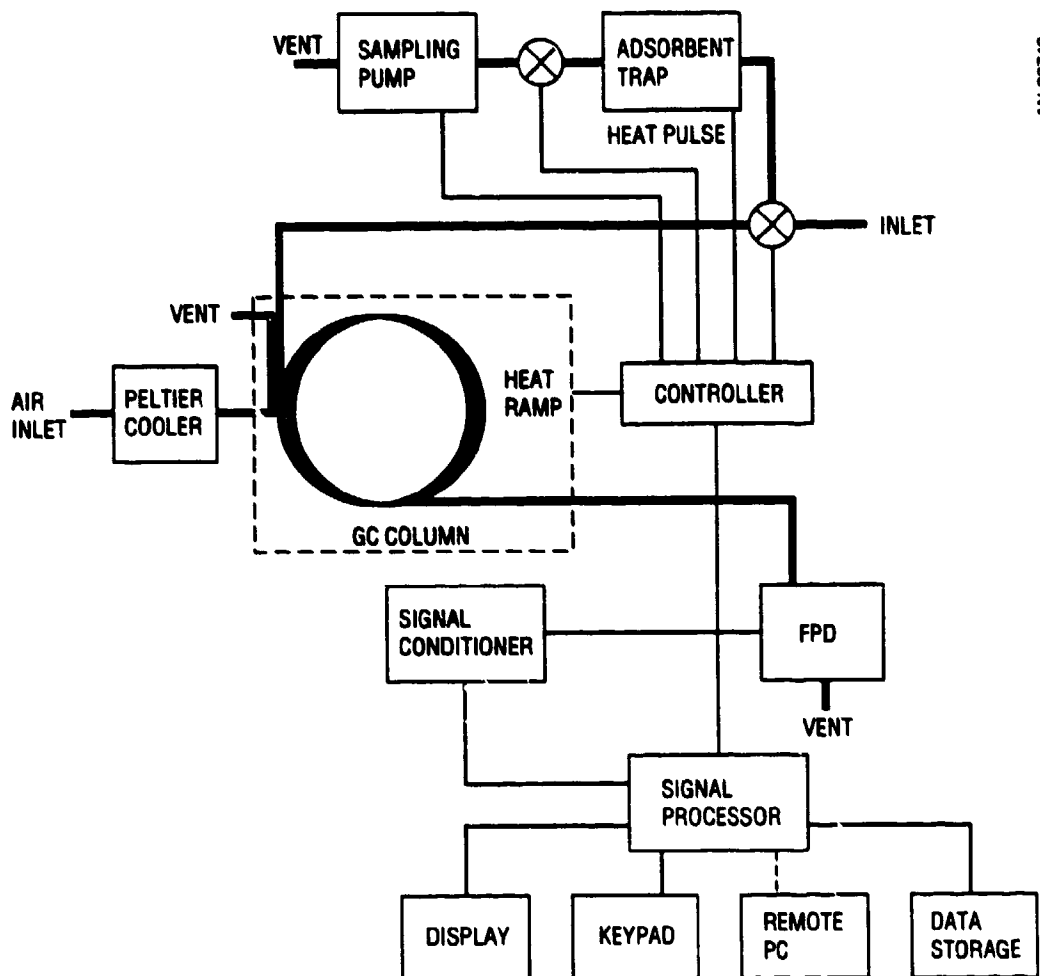
Figure 4-6. Block diagram for an enhanced mini-GC concept instrument equipped with a dual FPD.

mini-GC is then activated. This releases the mixture of volatile and semivolatile components for elution on the column, generating the chromatogram. The components eluted from the column are detected, with signal conditioning and analysis performed by the signal processor. The signal processor also controls the user display and data storage.

The range of volatiles that can be analyzed by this enhanced mini-GC concept design depends on the initial temperature at the head of the GC column before the run. Generally, the lower the temperature at the head of the column, the more effective the trapping becomes for progressively lighter volatiles. During the functional elements evaluation, we found that trimethyl phosphite could be preconcentrated at the head of a thick phase DB-1 column at 30°C. Further reducing this temperature by a few 10s of degrees and using Peltier boosted cooling at the head of the column (see Figure 4-6), could substantially enhance the collection of light volatiles. This would allow an enhanced mini-GC design to cover all but the lightest or most chemically reactive CWC volatiles. An optional bypassing of the adsorbent trap could be used to analyze the most chemically reactive compounds.

The enhanced mini-GC concept design allows a handheld inspection instrument to be fabricated which potentially covers nearly all of the CWC schedule materials (down to TWA levels), while significantly reducing complexity, size, weight and power requirements compared to a dual module instrument. This approach can provide a good match to the operational needs of CWC inspectors, enhancing operational flexibility in a variety of inspection scenarios.

A possible component configuration for the mini-GC instrument is shown in Figure 4-7. The modularity of the design is emphasized in the sketch. Estimates of the volumes, weights, and power requirements for these components are shown in Table 4-4. The volumes are in mL, the weights are in g, and the power is in watts. These estimates are based upon our analysis of the design for the enhanced mini-GC, our analysis of the detectors and required processing packages. The projected weight for the prototype is approximately 60% of the commercially packaged components. We believe that these values are representative of

FPD AND DETECTORS

FPD BOARD

PROCESSOR

KEYPAD

DISPLAY

SS RELAYS

BATTERY

GAS BOTTLE

AN-90760

46.6 cm

14.0 cm

23.6 cm

30.7 cm
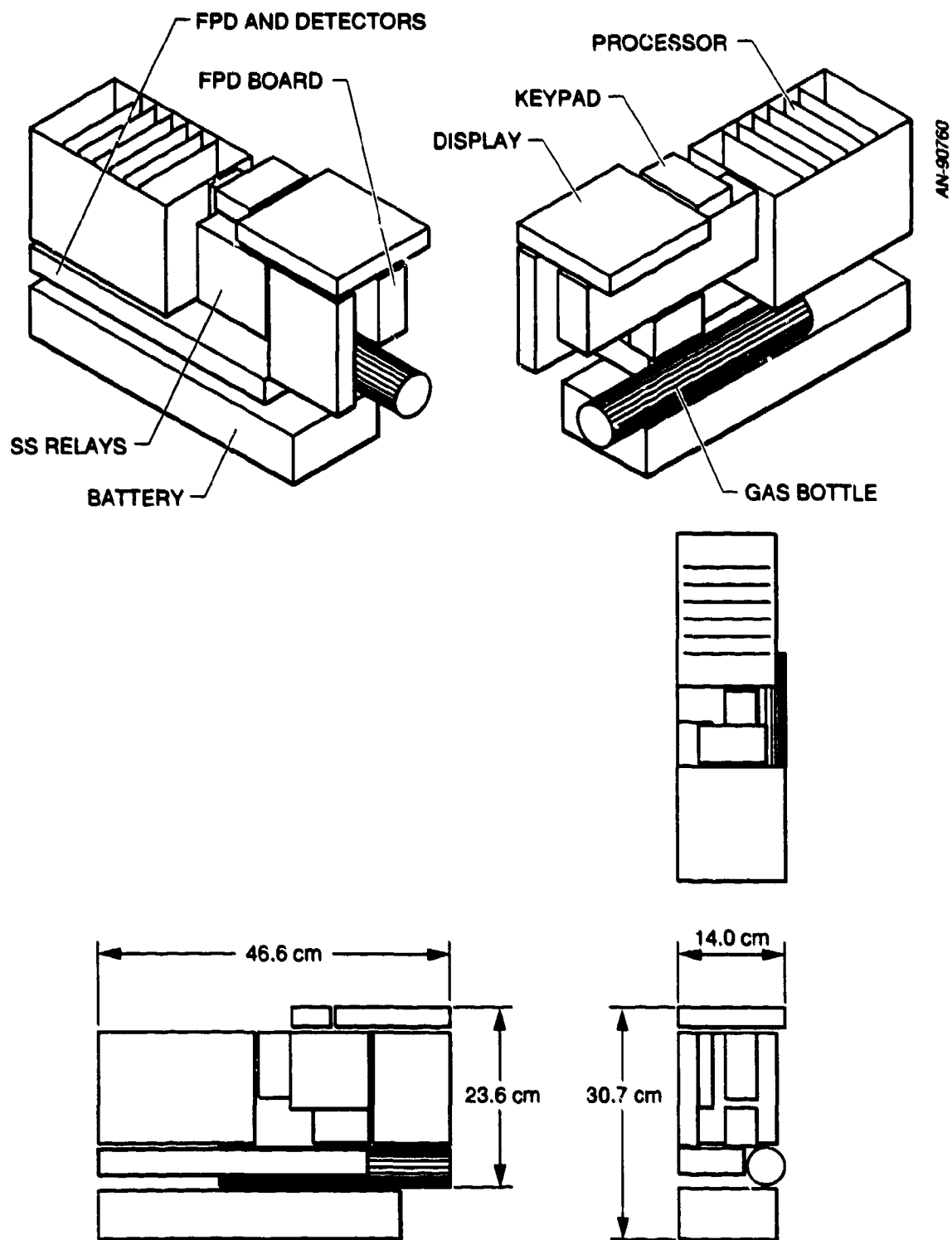
Figure 4-7.   An example component configuration for the mini-GC concept instrument equipped with a dual FPD.

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the weight and size reductions that can be readily achieved in the prototype instrument in Task 4 of this program.

Table 4-4.   Estimated volume, weight, and power requirements for the enhanced mini-GC instrument.

Component	Volume (mL)	Weight (g)	Power (w)
mGC	1180	500	20
FPD	2275	1254	30
Processor	3975	2200	18
Gas	787	1000	
Connections	3433	0	
Subtotal	11649	4954	68
w/Housing	13994	7431	
Battery	1436	2572	
w/Housing	2540	3086	
Total	16534	10517	68

With this approach the projected weight of the enhanced mini-GC instrument package (in its housing) for the initial prototype is 7.4 kg (16.3 lbs.) without batteries. The addition of silver-zinc batteries for 4 hr operation would add another 3.1 kg (6.8 lbs.) for a total weight of 10.5 kg (23.1 lbs.). This results in a weight reduction compared to the lightest of the dual module designs of 1.7 kg (3.8 lbs.) without batteries, and 2.1 kg (4.6 lbs.) with batteries, making handheld inspection more feasible. Further evolution of the enhanced mini-GC design to a pre-production prototype is projected to cut the weight and volume by more than 50% to achieve true handheld operability. This is discussed in Section 4.4. The component configuration for the enhanced mini-GC instrument design in Figure 4-7 shows the rechargeable battery pack underneath. Depending on operational needs and user preference, a variety of other battery pack sizes and configurations can be used with the instrument to increase operational flexibility and ease of use. This would include the use of detached battery belt packs, such as those routinely used with portable television cameras.

4.3 ENHANCED μGC INSTRUMENT CONCEPT DESIGN.

Another alternative to the dual module instrument concept is a design based on an enhanced μGC module only. In this design, the correlated column μGC module used for volatiles in the dual module instrument concept design (Section 4.1), is enhanced to extend its range of operation to include CWC semi-volatiles. This is close to our original proposed concept for a handheld instrument for CWC inspections. The primary advantage of this design approach is a reduction in complexity, size, power requirements, and weight compared to the dual module instrument concept design. The primary drawback is that the extent to which operation can be extended to semi-volatile compounds is limited by existing components. Thus it is likely that the initial concept instrument would need to be supplemented by an additional instrument to analyze for the heavier CWC schedule semi-volatiles. If improved higher temperature components become available, this design approach might be extended to cover the full range of CWC semi-volatiles.

4.3.1 Hardware Options.

Existing μGC instrumentation provides an excellent basis for developing a handheld instrument. The analyses of CWC schedule volatiles have been demonstrated, with extension to semi-volatile analyses being the primary challenge. For this, it will be necessary to increase the operational temperature of the μGC and heat sample inlet lines. While, this has been shown to be effective at extending analyses into the range of semi-volatiles, the existing operational temperature limits of the silicon micromachined injector valve and micro-TCD will restrict operation to the lighter semi-volatiles (see discussion in Section 2 for further details). The temperature limits of currently available μGC components indicate that performance can be extended from the current limit of about C_{10}-C_{11} to the C_{12}-C_{14} range. This would probably be sufficient to detect the lighter semivolatiles ranging from GB (about C_4) to HD (about C_{12}), but would not be adequate for heavier schedule 1 semivolatiles such as VX (above C_{17}).

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The use of selective detectors provides important capability for GC analyses of CWC schedule materials, especially the semi-volatiles. Comparisons of NPD and dual FPD detectors have been given in previous sections. Among the advantages of the dual FPD detector are good detector stability, low power consumption, coverage of HD (with sulfur detection), and widespread user acceptance for safety monitoring at TWA levels. Based on these considerations, a dual FPD detector is selected for use in the enhanced μGC instrument concept design.

4.3.2 Concept Design Description.

The concept design for the enhanced μGC instrument is shown in the block diagram in Figure 4-8. The key elements in the design are the correlated column μGC (combined into a single module), a sampling "front end" with absorbent trap and bypass valving, a dual FPD detector for phosphorus and sulfur (connected to the outlet of both columns), and signal processing and control functions. Very high selectivity for CWC schedule compounds is achieved by the combination of correlated chromatography and selective detection. The correlated columns are run simultaneously with nondestructive detection by TCD, with the outlet of one of the columns also analyzed by the dual FPD detector. This results in a correlated chromatogram for each run, as well as selective detection for both phosphorus- and sulfur-containing compounds.

Using the preconcentration mode, a sampling pump draws an air sample onto the adsorbent trap when the valve to the trap is opened. After sample vapors have been preconcentrated on the trap, the sampling pump is turned off and the valve is closed. The adsorbent trap is then heated, thermally desorbing a preconcentrated sample into the μGC injection valves for the two columns. A correlated chromatogram of the eluting components is then observed using TCD, with signal conditioning and analysis performed by the signal processor. A dual FPD is also used to monitor for both phosphorus and sulfur compounds, with the signal processor controlling the user display and data storage. An optional bypassing of the adsorbent trap could be used for analysis of the most chemically reactive compounds.
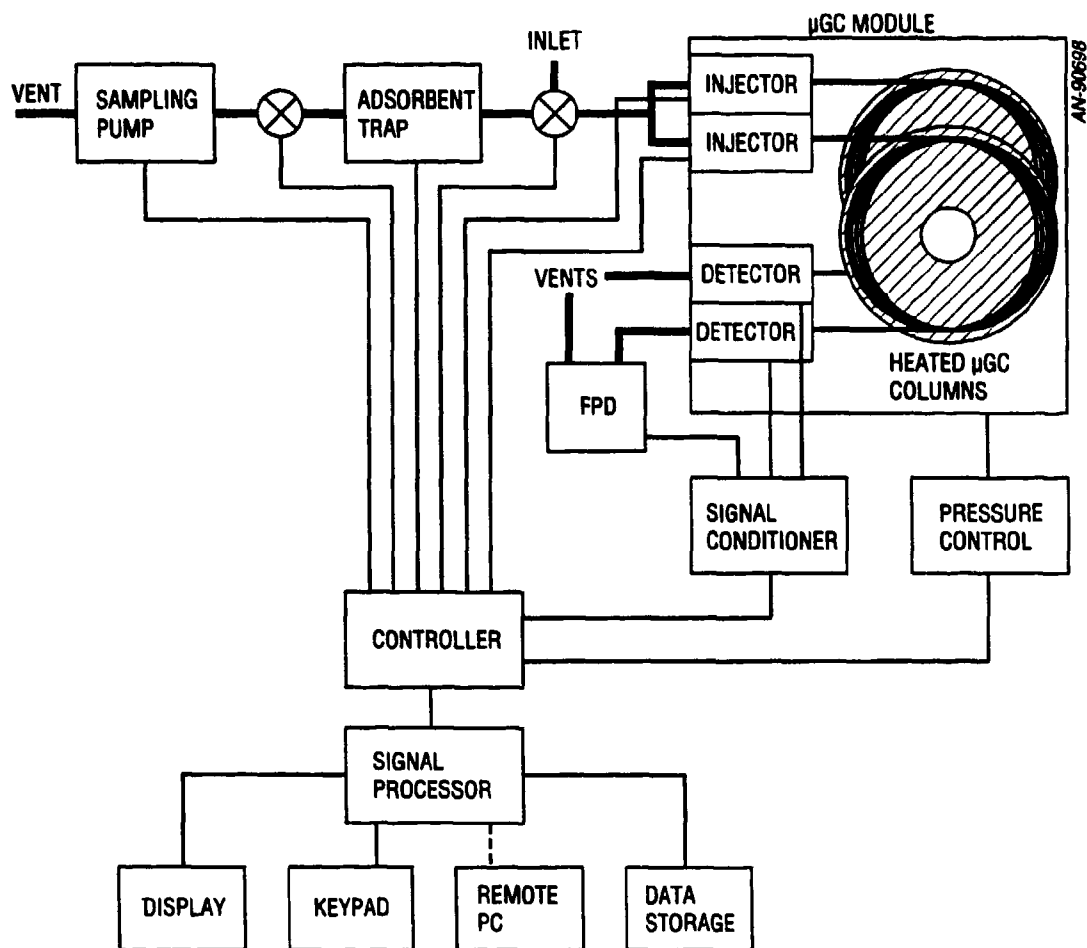
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Figure 4-8. Block diagram for an enhanced μGC concept instrument equipped with a dual FPD.

Figure 4-9 shows a possible component configuration for the μGC instrument, with the modularity of the design emphasized in the sketch. Table 4-5 shows estimates of the volumes, weights, and power requirements for these components. These are based upon our analysis of the design for the μGC, our analysis of the detectors and required processing packages. The projected weight for the prototype is approximately 60% of the commercially packaged components. We believe that these values are representative of the weight and size reductions that can be readily achieved in the prototype instrument in Task 4 of this program.

The projected weight of the μGC instrument package (in its housing) for the initial prototype is 8.4 kg (18.5 lbs.) without batteries. The addition of silver-zinc batteries for 4 hr operation would add another 2.5 kg (5.5 lbs.) for a total weight of 11 kg (24.2 lbs.). Compared to the lightest of the dual module designs, this reduces the weight by 0.7 kg (1.5 lbs.) without batteries, and 1.7 kg (3.7 lbs.) with batteries, making handheld inspection more feasible. Figure 4-9 shows a possible component configuration with the attached recharge-able battery pack underneath. Again, depending on operational needs and user preference, a variety of battery pack sizes and configurations would be available to increase operational flexibility and ease of use.

4.4   CONCEPT INSTRUMENT DESIGN SPECIFICATION.

The selection process for the recommended concept instrument design presented here has involved a number of considerations. These include results of the functional elements evaluations, our analysis of a various concept instrument configurations, and how they could best meet the operational needs for CWC inspections. Here, key scenarios are likely to be inspections of existing schedule 1 CW agent storage/destruction sites and inspections of declared schedule 2 facilities, where detection of schedule 1 CW agents down to TWA levels may be the primary concern and focus for a handheld instrument. A final consideration is the projected tradeoff in ultimate size/weight versus cost/risk/development time that could be achieved in a pre-production prototype after some further engineering development.
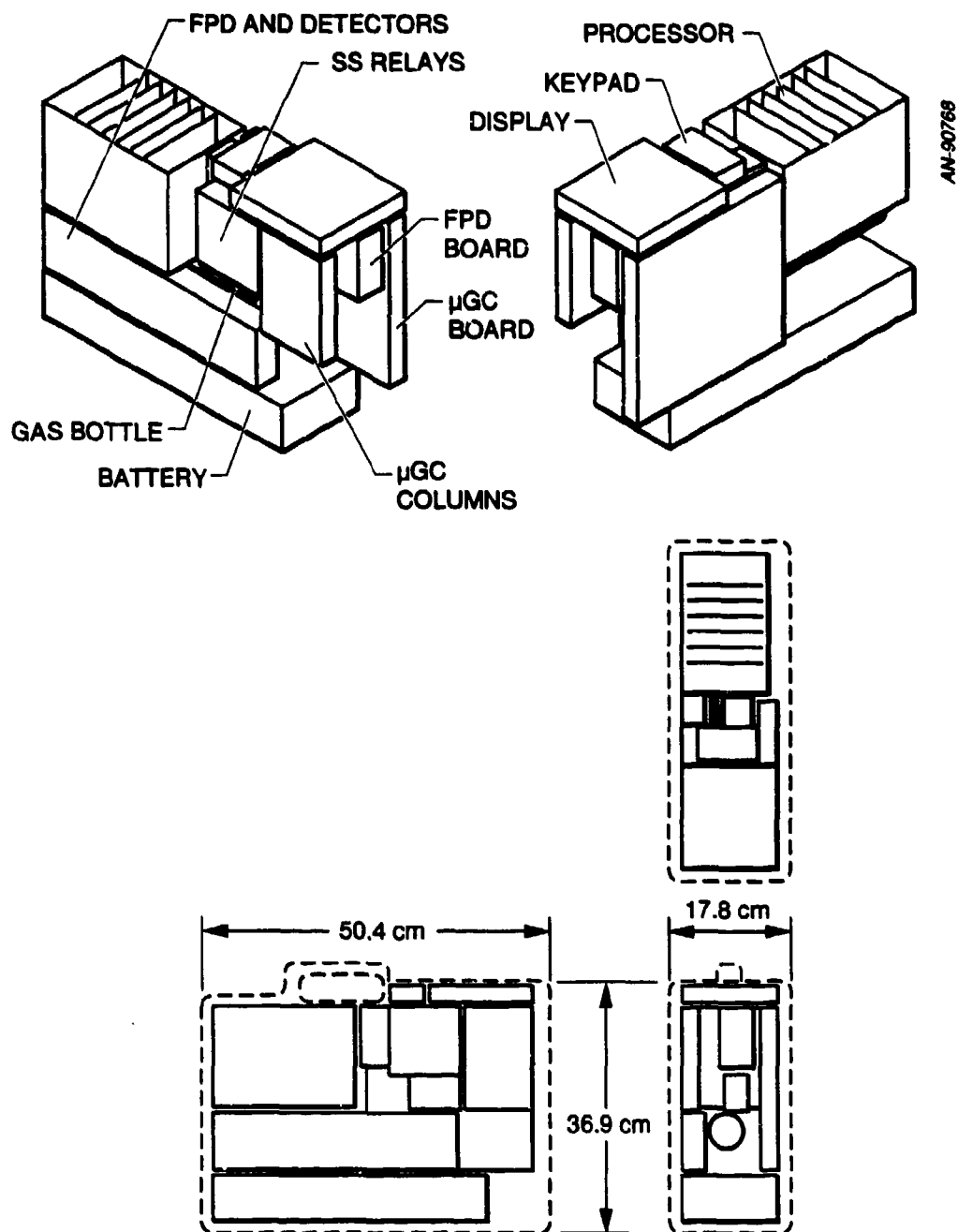
Figure 4-9.   An example component configuration for an enhanced μGC concept instrument equipped with a dual FPD.

Table 4-5. Estimated volume, weight, and power requirements for µGC instrument.

Component	Volume (mL)	Weight (g)	Power (w)
µGC	2425	1150	8
FPD	2275	1254	30
Processor	3975	2200	18
Gas	787	1000	
Connections	3787	0	
Subtotal	13249	5604	56
w/Housing	15790	8406	
Battery	1184	2120	
w/Housing	2164	2544	
Total	17954	10950	56

Our final selection process came down to two concept designs, the dual module concept instrument with FPD detector, and the enhanced mini-GC concept instrument. Of these, the projected weight of a prototype dual module design is heavier by about 20%. This is significant, but not a deciding factor in itself. While the dual module design is somewhat more capable, it is also significantly more complex than the enhanced mini-GC, with the FPD detector shared by three GC columns in a somewhat elaborate timing sequence. This potentially poses detection reliability risks due to potential cross talk of late eluting contaminants and column pressure surges, which could affect the chromatograms. From an operational point of view, the enhanced mini-GC concept instrument more directly addresses the detection needs of the schedule 1 compounds, and offers an innovative low thermal mass mini-GC column with integral heater which can be used to replicate the function of existing CW detection technology in a miniaturized handheld instrument format. Engineering development to further reduce the size and weight of the enhanced mini-GC instrument for true handheld operability is also considered to be more straightforward and less costly than for the dual module design. In particular, advanced engineering development to further reduce the size of the commercial MTI µGC board for the dual module design is projected to

require a significant new effort. Taken together, the operational requirements for focus on Schedule 1 detection capability and the advanced development considerations lead us to favor the enhanced mini-GC design.

Our recommendation of the enhanced mini-GC concept instrument design is based upon the results of the functional elements evaluations, our analysis of various concept instrument configurations, operational needs and reliability factors, and considerations of the cost/development times to reach a final pre-production prototype. The Concept Instrument Design Specification includes: a system design description of the proposed instrument containing sketches and flow diagrams of the instrument; a description of critical design decisions, including the rationale for concept selections and any trade-off decisions; justifications are given for any major new components which are introduced and different in principle of operation from the components examined in the functional elements evaluation; and the selected functional elements and components are listed and briefly described.

4.4.1 System Design Description.

A block diagram of the selected concept instrument design is presented in Figure 4-10. The key elements of this enhanced mini-GC instrument design are an innovative low thermal mass mini-GC column with integral heater, a sampling "front end" with adsorbent trap and Peltier-boosted cooling for the head of the GC column, the dual FPD detector for phosphorus and sulfur, and signal processing and control functions. High sensitivity for CW related materials is achieved by the used of a trap preconcentrator with sample "refocusing" at the head of the GC column (aided by Peltier thermoelectric cooling), and selective detection of phosphorus and sulfur containing compounds by FPD. An on-board computer and data system is accessed from a user interface consisting of a menu driven display and two button keypad.

In this design, when the CWC inspector indicates on the keypad that a sample be taken, the sampling pump is turned on and used to draw an air sample onto an adsorbent trap. The sample inlet is positioned on the GC column side of the trap so that the vapors can be
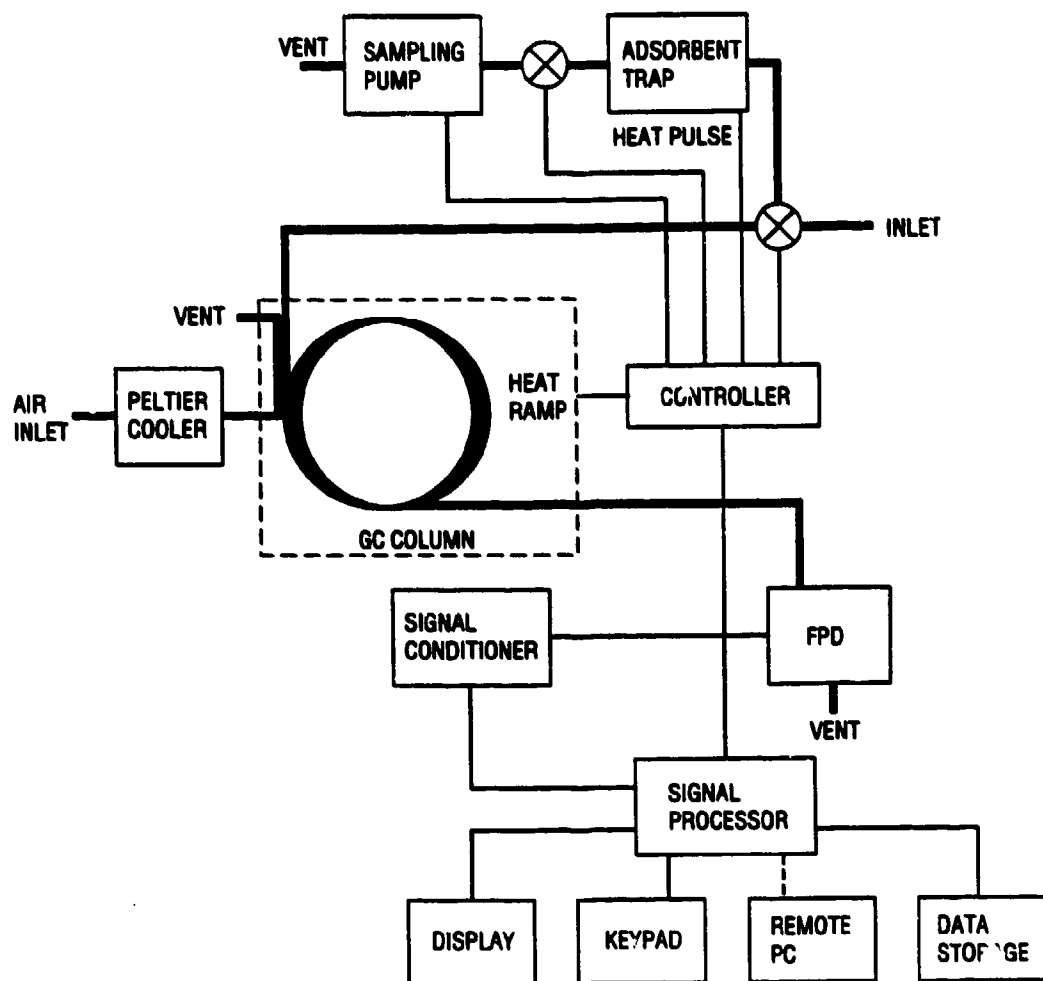
Figure 4-10. Block diagram of the recommended concept instrument featuring a mini-GC and a dual FPD.

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desorbed in the reverse direction that the trap was loaded. With the pump off, the adsorbent trap is then heated, thermally desorbing the preconcentrated sample into the capillary column. Here, the semivolatile and most of the volatile components are adsorbed onto the high capacity stationary phase at the head of the GC column, with atmospheric gases and a few of the lightest volatiles passing through. The head of the column itself thus serves as a secondary preconcentrator for nearly all of the CWC schedule compounds. The use of a Peltier cooler to provide cold air flow to a short length of low thermal mass jacket around the column head during this process substantially enhances on column focusing of the lighter volatiles.

The temperature programming of the enhanced mini-GC is then activated with the Peltier cooling turned off. This begins a rapid (several degrees per second) temperature ramp on the low thermal mass mini-GC column with its integral heater. Here, the controller monitors the temperature of the column by a sensor wire within the low thermal mass jacket which contains both the column and a heating element. With increasing temperature the mixture of volatile and semivolatile components are released for elution on the column.

As the components are eluted from the column they are detected by the dual FPD, simultaneously generating chromatograms for phosphorus- and sulfur-containing compounds. Signal conditioning and analysis is performed by the signal processor which consists of a microprocessor the size of a half-card add-on board. This includes peak detection and target matching algorithms. The signal processor also controls the user display and data storage.

A possible component configuration for the enhanced mini-GC instrument is shown in Figure 4-11, with the modularity of the design emphasized in the sketch. The largest items are the computer card cage and the battery. It is projected that the size and weight of the signal processing module can be reduced substantially during further engineering development. Table 4-6 shows estimates of the volumes, weights, and power requirements for the various components for the commercially packaged components, the prototype, and a pre-production prototype after further engineering development. The volumes are in mL, the weights are in g, and the power is in watts. These estimates are based upon our analysis of
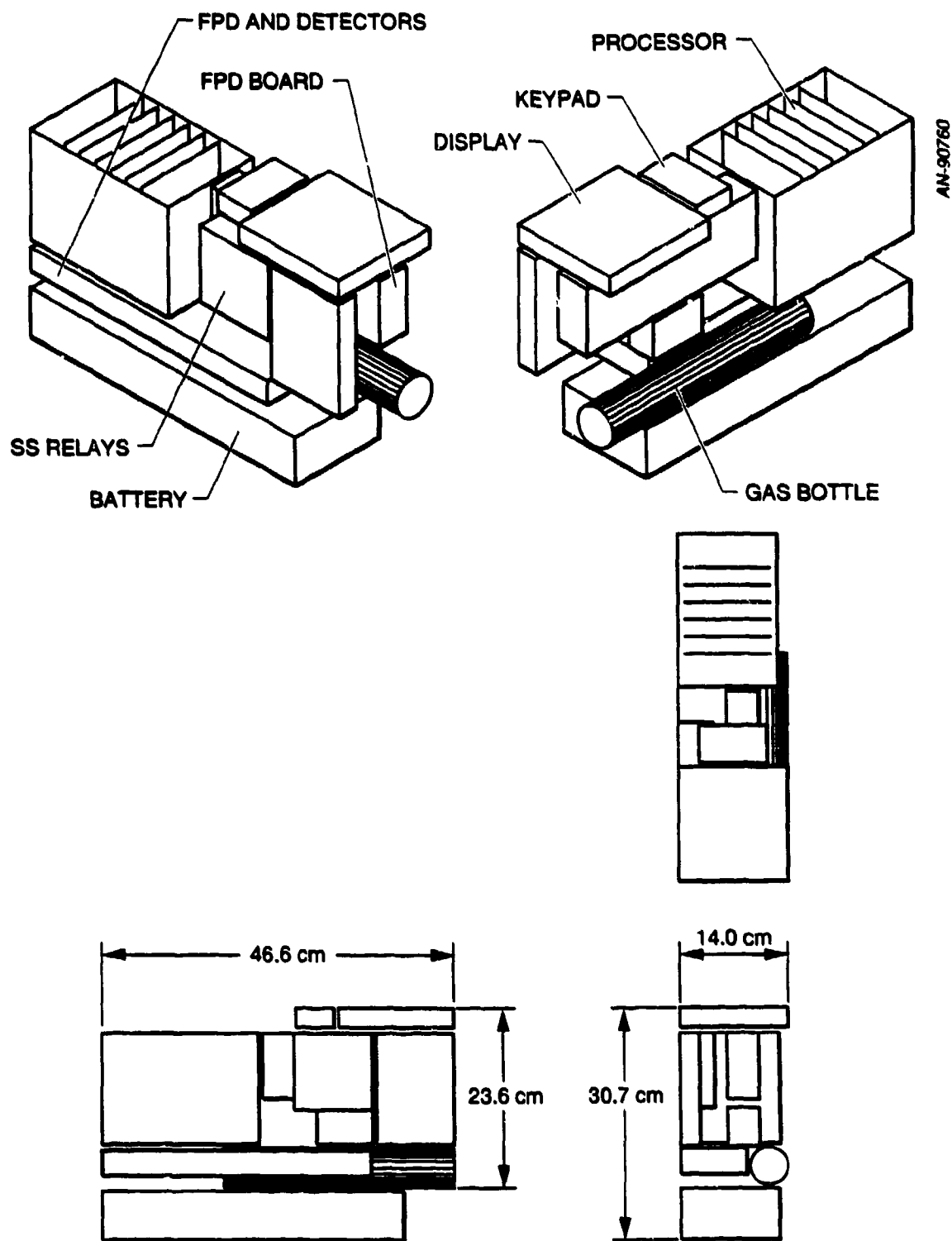
Figure 4-11.   An example component configuration for the recommended concept instrument with mini-GC and dual FPD technology.

Table 4-6. Estimates of volumes, weights, and power requirements for various components for commercially packaged components, the prototype, and a pre-production prototype.

Components	Commercially Packaged Components			Prototype (This Program)			Pre-production Prototype		
	Volume (cm³)	Weight (g)	Power (W)	Volume (cm³)	Weight (g)	Power (W)	Volume (cm³)	Weight (g)	Power (W)
mGC	3146	900	20	1180	500	20	492	250	10
FPD	3307	3870	100	2275	1254	30	1149	677	20
Processor	3975	2200	18	3975	2200	18	1320	600	10
Gas	787	1000		787	1000		393	700	
Connectors	5537	0		3433	0		1463	0	
Subtotal	16752	7970	138	11649	4954	68	4817	2227	40
w Housing	19693	11955		13994	7431		6170	3341	
Battery	2327	7305		1436	2572		844	1512	
w Housing	3187	8766		2540	3086		1652	1816	
Total	19939	16736	138	16534	10517	68	7822	5157	40

the design for the mini-GC, our analysis of the detectors, and required processing packages. The projected weight for the initial prototype is approximately 60% of the commercially packaged components, with a re-engineered pre-production prototype another factor of two below that. We believe that these values are representative of the weight and size reductions that can be achieved using this technology.

The projected weight of the initial enhanced mini-GC instrument prototype is 7.4 kg (16.3 lbs.) without batteries. The addition of silver-zinc batteries for 4 hr operation adds another 3.1 kg (6.8 lbs.) for a total weight of 10.5 kg (23.1 lbs.). Depending on operational needs and user preference, a variety of battery pack sizes and configurations can be used with the instrument to improve operational flexibility and ease of use. This could include the use of battery belt packs, such as those routinely used on portable television cameras to off load

weight from the instrument body. The weight and size of the more advanced pre-production prototype, is projected to decrease substantially, to 5.1 kg (11.2 lbs.) with 4 hr battery, and only 3.3 kg (7.3 lbs.) without. This will offer CWC inspectors excellent flexibility and the potential for true handheld operation.

4.4.2 Summary of Critical Design Decisions.

While the design utilizes commercially-available technology to the fullest extent possible, gaps in the available technology have forced the development of some new technologies to meet the CWC inspection needs. While this introduces new risks, we have sought to minimize these risks by pursuing the simplest and most practical designs possible. Critical design decisions have largely been discussed in the earlier sections of this report, but are summarized in the following paragraphs:

Choice of mini-GC as the baseline technology. μGC was our initially proposed concept technology for a handheld detector. Commercially-available small GC technology is not amenable to handheld instrument development because of the size and power requirements for temperature ramping GC ovens. While the ovens have been reduced in size, they are still relatively large and have high thermal masses requiring large heat flows for fast temperature programming. We proposed and evaluated μGC technology for filling this need and found that μGC could cover the CWC volatiles, but it was limited with respect to many of the semivolatile compounds of primary concern in the CWC schedules. These shortcomings were due to temperature limitations specific to the design of critical micromachined components in the μGC hardware. Microsensor Technology Inc., the manufacturer, informed us that redesigning these components to perform at higher temperatures would require a major development on their part. We determined that μGC performance could probably be extended to include many of the lighter semivolatiles, but cannot be extended to the heavier semivolatile compounds such as VX.

To fill this technology gap, new technology was developed specifically for this program. This technology consisted of an innovative design for an ultra-low thermal mass

GC which could be very rapidly temperature programmed with very low power consumption.
To differentiate this technology from the µGC technology, we have termed it "mini-GC"
technology, but the mini-GC technology is actually the same size or smaller than the µGC
technology. LSU has developed this technology on subcontract to GRC and has demonstrated
unprecedented speed and small size for temperature programmed GC. The data in Section 3
of this report shows fast analyses extending to heavy semivolatiles such as C_{20}. This is
beyond the range of VX (near C_{17}), for example. In our testing of the mini-GC columns and
representative temperature programs, many of the volatiles are also easily measured. In our
discussions in Section 4 of this report, we have included methods which will enhance the
mini-GC to cover more of the CWC schedule volatiles. Taken together, these demonstrations
show that the mini-GC is a viable technical approach to the fabrication of a handheld detector
with a sufficiently wide range of performance to detect the semivolatiles and most volatiles in
the schedules.

Sufficient selectivity through the use of CW-selective detectors. Standard one-
dimensional GC is not a very selective method for the field identification of target compounds
in situations where high and variable backgrounds are encountered. The majority of peaks in
sensitive GC analyses of environmental samples are typically multicomponent and this greatly
complicates the analysis of the results. Our initially proposed approach was to use two or
higher-dimensional chromatography to expand the detection space and greatly increase the
selectivity of detection (i.e., reduction in false alarms). However, the peculiar composition of
the CWC schedules dominated by organophosphorus compounds also allows a highly
selective detector for phosphorus to discriminate against common environmental background
such as hydrocarbons. While multidimensional chromatography and selective detectors can
both be used for selectivity (as shown in the dual module concept instrument in Figure 4-2 in
Section 4.1.2), our decision to select the enhanced mini-GC as the baseline technology has led
to a deemphasis of multidimensional chromatography since it may not add sufficient
additional selectivity. In fact, a detector specifically selective for the range of CWC schedule
compounds can operate with a single GC column greatly minimizing the complexity of a
mini-GC-based instrument.

Our evaluation of CW-selective detectors favors the use of a dual FPD in the concept instrument. Such a detector is actually a double detector which can operate with a single column. The detector provides simultaneous detection of phosphorus- and sulfur-containing compounds with low detection limits (<10 pg for phosphorus and <100 pg for sulfur). The detector is stable and has no depleting components as does the NPD (thermionic nitrogen-phosphorus detector). While the NPD demonstrated a low detection limit (<1 pg) for phosphorus, it does not detect sulfur. This sulfur detection gap requires an additional detector and column which increases the size, weight, complexity, and power requirements of the instrument. Further, the NPD itself consumes much more power and had several stability issues which require further development before its use in a handheld detector. For these reasons, the dual FPD presents the CW-selective detector of choice for near term application in a handheld instrument.

Sufficient detection sensitivity through vapor preconcentration. Vapor preconcentration through the use of adsorbent tube traps is a standard approach to achieving TWA level detection limits for CW compounds. Our experimental testing of preconcentrators is consistent with our expectations of the preconcentration factors which can be gained by preconcentration. The ability to detect 10 pg of phosphorus at the detector resulting from 1 L of sampled air results in a detection limit of approximately 10 ng/m^3. This is on the order of the TWA for VX shown in Table 3-4. This is an established technical approach to maximizing detection sensitivity for detection of vapors in air which should provide the needed detection limits for the handheld instrument.

4.4.3 Summary of Functional Elements.

A brief summary discussion about each of the functional elements of the concept design instrument is given in the following paragraphs.

Air Sampling Pump. This assembly is responsible for providing the large air flow rates needed for a standard size adsorbent tube preconcentrator. It is projected that sampling rates on the order of 1 L/min for one to several minutes may be required. Various small

pump assemblies which can meet this requirement are available, and we have tested one of these in the collection of representative background air samples during Task 1. This assembly is only about 3 cm x 3 cm x 8 cm in size and can operate continuously for more than 24 hours on a small battery pack.

Vapor Preconcentrator. An adsorbent trap consisting of Tenax GC capable of handling flow rates on the order of 1 L/minute appears to the most attractive approach for preconcentrating the vapors of CWC schedule compounds from air samples. We have previously done extensive trace measurements of organic compounds in air using activated carbon-based adsorbents. However, some CWC schedule materials were determined to be too chemically reactive or non-recoverable from these traps. Tenax GC has a history of preferred use for the preconcentration of CW vapors from air and is recommended in the concept instrument design. Small sampling pumps can easily draw 1 L/minute an flow through small Tenax traps having internal diameters of about 4 mm. After thermal desorption, the vapors from the adsorbent trap enter the cool GC column and are adsorbed onto the walls. This is especially effective in the case of the semivolatile compounds, and results in additional preconcentration or "focusing" of the analytes prior to the start of the temperature-programmed GC analysis.

GC. An enhanced mini-GC featuring a low thermal mass column with integral heater is recommended for the concept instrument. The enhanced mini-GC provides detection capability for the semivolatile compounds and many of the volatiles. While we believe that the operational focus for inspections is the CWC Schedule 1 compounds which are mostly semivolatiles, the enhanced mini-GC's performance can be extended to include many of the volatiles. The use of temperature-programmed small GCs is well established for CW agent analysis in instances where low cost technology and low detection limits are required. An example os the small MINICAMS GC made by CMS Research Inc. for the safety monitoring of selected CW agents. GC also does not present an industrial security or espionage threat like mass spectrometry since the GC-based detection algorithms only indicate compounds that the GC instrument has been trained to recognize.

The size and power requirements for conventional temperature programmed small GC ovens are too large for handheld instrumentation. Since we were not able to get the needed performance from µGC, low thermal mass mini-GC technology was developed by this program to fill the technology gap. An innovative approach to fabricating these high performance, ultra-low thermal mass GCs was demonstrated, and has been shown to provide a very wide range of semivolatiles and volatiles analysis. The size of many of these mini-GC components is actually smaller than their µGC counterparts.

CW-Selective Detector. Because of the prevalence and peculiarity of organophosphorus compounds in the CWC schedules, the use of a GC detection technology which specifically and sensitively detects organophosphorus compounds is recommended. Both the thermionic nitrogen-phosphorus detector (NPD) and the flame photometric detector (FPD) were evaluated. The FPD is recommended for use in the concept instrument for several reasons: low detection limits (≤10 pg of phosphorus); selective for phosphorus or separately for sulfur; a modification of the FPD detector can provide simultaneous detection of both phosphorus- and sulfur-containing compounds (this allows a single detector to provide coverage of key CWC schedule chemicals); stable, long-term operation; and no depleting components to impact detection limits. The dual FPD proposed for the concept system consists of a small hydrogen flame assembly with two miniature photomultipliers, one optimized for phosphorus detection and one optimized for sulfur detection. While the NPD demonstrated very low detection limits (<1 pg), its use posed a high level of development risk and its power requirements proved to be excessive. An NPD could potentially be developed for an instrument during advanced development for applications which require lower detection limits and can tolerate higher power requirements.

Enhanced mini-GC Control Electronics. The control electronics consist of an electronics board which provides programmable relay connections to the mini-GC's heater wire, thermal desorber heater, sampling pump, sampling valve, inlet valve, and transfer line heaters. The control electronics monitors the temperature sensors in the mini-GC including the temperature-programming sensor, the desorber, and the temperature control. This board is

connected to the microprocessor board by a serial port for programming control of the mini-GC timing and temperatures.

Signal Conditioning Electronics. The signal conditioning electronics for the dual FPD consists of a board containing two electrometers, amplifiers, and analog-to-digital converters. The conditioned outputs from the two detectors are communicated to the signal processor directly through the bus of the microprocessor.

Signal Processing Electronics/Software. The automated algorithms for GC analysis are run on an onboard microprocessor which receives the conditioned FPD signals. The microprocessor analyzes the signature content of the chromatographic results using algorithms we described in the Task 2 report. The microprocessor drives a display showing results and directing the operator's use of the instrument. A PC-compatible microprocessor is recommended for the concept instrument as this will allow software development on a PC platform which can then be easily ported to the onboard processor.

Display/Alarm Generation/Instrument Controls. A small LCD screen is recommended for the display of the prototype instrument. Such a screen can contain instrument status information, test results, and operator instructions. The instrument controls are expected to be minimal and a two button design which is interactive with display menus is recommended. Through a simple menu design, all possible choices of operation are visible to the operator at all stages of instrument operation. This greatly simplifies the instrument operation to the point that no special technical background is required for instrument operation. An audio alarm that can be turned off is also recommended.

Data Storage. Data storage in the form of PCMCIA cards is recommended for data storage for the instrument. These so-called "flash memory" cards provide non-volatile electronic storage in the form of small cards which have been developed for the laptop PC market. In CWC inspections, the requirement for removable data storage media which are compatible with standard computer formats is deemed crucial.

Off-line Diagnostic/Retraining Software. We recommend the prototype inspection instrument have an interface for communication with a PC for the purposes of diagnostics and software retraining. This can greatly reduce the software burden on the handheld instrument and provides maximum flexibility in the design of the software and the ability to modify it.

Rechargeable Batteries. Rechargeable batteries in a range of weights and costs are available. Basically, the cost climbs rapidly as the weight is decreased. Our projections for 4 hour operation suggest that the battery weight constitutes about 30% of the total instrument weight using light but relatively expensive battery technology such as the silver-zinc batteries. For the enhanced mini-GC design the battery would weigh approximately 3.1 kg (6.8 lbs), including packaging. Configurations could include a battery module which attaches to the bottom of the instrument, a separate battery pack, or a battery belt which could be worn by the inspector. Wearing the 3.1 kg battery as a belt pack reduces the projected instrument weight to 7.4 kg (16.3 lbs). Advanced engineering of a pre-production instrument is expected to reduce weight by an additional 50% for the instrument excluding the battery. Since considerable development of advanced, lighter batteries has already occurred, major weight reductions are not expected for the battery portion of the instrument over the near term, except for reductions of the power requirements of the instrument. While the silver-zinc batteries are expensive ($2000 for small quantities of the 4 hour battery described above), the cost per cycle is projected to be about $20-25 with an expected life of 80-100 charging cycles. Lower cost batteries could be substituted at the tradeoff of increasing weight as described in Section 3.6 of this report.

Rechargeable Gas Supply. Two small bottles of gas are required for the concept instrument, one for GC carrier and one for the FPD detector. The carrier gas utilization by the mini-GC is small. An inert gas such as nitrogen or helium is recommended for compatibility with the thermal desorber. Flows on the order of a few mL/min are expected for the mini-GC. An example bottle provided by MTI for their μGC instrument provides the needed pressure for a sufficient duration of operation and weights about 1 kg. The FPD detector will separately require a substantial flow of hydrogen gas on the order of 50-150 mL/min. A similar bottle of hydrogen gas can provide this flow for the FPD detector. Unlike the μGC,

neither bottle is used for operating pneumatic controls and can function down to low pressures.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

The results of the studies presented in this report have been used to develop a Concept Instrument Design Specification for a portable, handheld inspection instrument for CWC schedule chemicals. Important considerations and tradeoffs in the selection process included an assessment of operational needs, suitability for handheld operation, analytical sensitivity down to schedule 1 TWAs, and good selectivity. Three basic concept design approaches were considered in detail.

• **µGC performance range cannot be sufficiently extended into CWC schedule semivolatiles.** Operation of the µGC at the higher temperatures required to elute the full range of CWC semi-volatile compounds is beyond the temperature limits of the existing components. While it is likely that the operational range can be extended into the semi-volatile range somewhat by heating the inlet lines and injector, this will not be sufficient to analyze for VX, a key CWC schedule compound. This situation has lead us to explore the development of a miniaturized low thermal mass GC.

• **Innovative low thermal mass mini-GC technology developed for this program fills a critical technology gap for handheld instrumentation; a very wide range of performance, small size, and unprecedented speed have been demonstrated.** This approach is based on the development of a low thermal mass column with an integral heater and was designed to cover the full range of CWC semivolatiles using a rapid GC temperature ramp. Functional elements evaluation of this technology has demonstrated that under the proper operating conditions **most of the important CWC schedule volatiles can also be** covered by this technology. This makes a handheld mini-GC concept instrument design which covers nearly all of the CWC schedule materials feasible.

• **Selective detectors offer high selectivity and sensitivity for CWC schedule compounds; they also simplify the mini-GC concept instrument.** The multidimensional chromatography approaches considered for selectivity with µGC can be combined with CW-

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selective detectors for added selectivity, but the risk due to increased instrument complexity appears to outweigh any advantage in selectivity gain. The detailed analyses of several instrument configurations confirm the rising operational complexity, size, weight, and power requirements which arise with more complex configurations. The CWC schedule coverage provided by selective detectors combined with the recently demonstrated wide performance range of the mini-GC indicate that this combination should provide a robust approach for detecting the CWC schedule compounds.

• **Dual flame photometric detector (FPD) provides simultaneous selective detection of phosphorus- and sulfur-containing compounds with a single GC column.** We compared FPD extensively with alternative detectors such as the thermionic nitrogen-phosphorus detector (NPD) and determined that the FPD offered the least development risk over the near term for a highly selective and sensitive instrument. This risk reduction was in terms of the performance of the detector as well as reduced complexity of the instrument. We believe that the latest NPD technology offers a bright long-term prospect for the development of ultrasensitive organophosphorus detectors which can lower detection limits 10-100x over the already low FPD.

• **Concept design specification features the enhanced low thermal mass mini-GC with a dual FPD in a very small instrument configuration.** The detailed analysis of several instrument configurations including mini-GC, μGC, and combined mini-GC with μGC instruments show that a single mini-GC combined with a dual FPD provides very wide CWC schedule coverage with emphasis on the schedule 1 and 2 compounds. We believe that this instrument best fits the expected operational emphasis on schedule 1 and 2 compounds and offers the simplest and most elegant solution combining the miniature technologies required for a handheld instrument. The estimated weight of the prototype is 7.4 kg (16.3 lbs) excluding batteries. An estimated 3.1 kg (6.8 lb) battery belt pack is needed for 4 hour continuous operation of the instrument. Further weight and size reductions that are expected in the fabrication of a pre-production prototype result in a projected 56% reduction in size and a 55% reduction in weight to 3.3 kg (7.3 lbs), excluding the battery pack. This instrument would be capable of unprecedented GC analysis speed and low power requirements for

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the thermal analysis of semivolatile compounds. Further, the detector would provide selective detection of phosphorus- and sulfur-containing compounds at levels which meet or exceed schedule 1 TWAs. Also, detector options such as advanced development of the thermionic nitrogen-phosphorus detector (NPD) could further reduce organophosphorus detection limits by 10-100x.

The selection of the enhanced mini-GC concept design allows a handheld inspection instrument to be fabricated which covers nearly all of the CWC schedule materials (down to TWA levels), while meeting the operational needs of CWC inspectors and enhancing operational flexibility for a wide range of inspection scenarios.

SECTION 6

REFERENCES

Ellzy, M. W., F.E. Ferguson, L.G. Janes and D.A. Paterno, "Solid Adsorbent Trace Analysis of DMMP and TEPO," CRDEC technical report CRDEC-TR-027, January 1989. (UNCLASSIFIED)

Scott, S.A., T.J. McGauley, R.D. Hoffman and R.W. Wise, "Multiagent MINICAMS Performance and Dependability Evaluation," Pine Bluff Arsenal, report PBA-TR-QAL-91-1, May 1991. (UNCLASSIFIED)

Suppelco, "Carbotrap--An Excellent Adsorbent for Sampling Many Airborne Contaminants," The Suppelco Reporter, Suppelco Inc., Bellefonte, PA, Vol. V. No. 1, March 1986. (UNCLASSIFIED)

Witkiewicz, Z., Mazurek, and J. Szulc, "Chromatographic analysis of chemical warfare agents," J. Chromatographic Sci., Vol. 145, 1990, pp. 293-357. (UNCLASSIFIED)

APPENDIX

GENERAL SURVEY OF GC DETECTORS

A summary of detectors is shown in Table A-1 which includes selective detectors believed to have potential application to CW detection. Table A-1 also includes some common detectors such flame ionization and thermal conductivity for reference purposes. Representative detector sensitivities are given both in terms of concentrations at the detector as well as minimum detectable quantities. Whether a detector is selective regarding CWC schedule materials is indicated along with the elemental selectivity of the detector. Detection gaps commonly occur as a function of selectivity and these are similarly indicated. Detectors which are non-destructive are also indicated because these detectors can be used in series with other detectors.

Table A-1. Summary of detectors.

Detectors	Sensitivity		CW Selective	Detection Gaps	Non-Destructive	Comments
	Amount	Est. ppb at Detector				
μGC Injector-μ Thermal Conductivity Detector (μTCD) Combination	1 ng	1000			+	Injector's volume reduces sensitivity
μTCD	1 pg	1000				
Flame Ionization Detector (FID)	0.1 ng	100				Hydrogen required
Nitrogen-Phosphorus Detector (NPD)	1 ng (HC, S) 0.1 pg/s (P, N)	1000 (HC, S) 0.1 (P, N)	+ (N, P)	S, HC		Hydrogen required
Flame Photometric Detection (FPD)	≤10 pg (P) ≤10 pg (S)	10 (P) 10 (S)	+ (P, S)	N, HC		Hydrogen required
Thermal Conductivity Detection (TCD)	100 ng	~100,000			+	Large volume reduces sensitivity
Photo-Ionization Dectector (PID)	<10 pg	10		?	+	Selective for photo-ionizable compounds
Electron Capture Detector (ECD)	<0.1 pg	<0.1	+ (Halogens)	P, S, many HC		Radioactive Ni-63 source selective for electronegative compounds (e.g., halogenated organics)
Electrolytic Conductivity Detector (ELCD)	0.1 ng	100	+ (Halogens, N)	P, S, HC		Complex reaction furnace required; selective for halogens, nitrogen compounds

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The NPD and FPD stand out because of their elemental specificity for the organo-phosphorus compounds in the CWC schedules. These detectors were considered for use in the concept design and they are discussed at length in the functional elements evaluation sections of this report.

The photoionization detector was not discussed at any length in the report because it is selective for photoionizable compounds. These compounds tend to be aromatic organic compounds which have strong ultraviolet (UV) absorption. Typically, UV light having a wavelength of about 121 nanometers is used to ionize aromatic organic compounds such as benzene, toluene, xylene, etc. Some aliphatic compounds are ionized, but many halogenated compounds are not. The primary advantage of this detector is its non-destructive flow-through capability which allows ad itional detectors to be used.

The electron capture detector (ECD) is primarily selective for halogenated and oxygenated compounds which are easily ionized by beta particles. The ECD typically consists of a stainless steel cylinder containing radio-active Nickel-63, a beta emitter. When electronegative molecules such as chlorinated or fluorinated organics enter the beta radiation they are ionized and detected. The sensitivity is compound dependent, but for the compounds which are well ionized, the detection limits can be in the range of 10-100 fg. The dynamic range of the ECD is only about 10-100, but this is increased by pulsing the detection electronics to measure the number of electrons remaining in the cell. The ECD typically requires nitrogen or a special argon-methane carrier gas. Most of the compounds in the CWC schedules contain either halogens or oxygen making them candidates for ECD detection. Some classes of compounds such as VX and Tabun, for example, contain no halogens, but they do contain oxygen. We did not consider ECD because of its limited dynamic range and use of radioactivity. The use of ECD in the U.S. requires licensing (filing with the appropriate state department of health) and bi-annual wipe testing.

The electrolytic conductivity detector is inappropriate for a handheld instrument because it requires a high temperature reaction furnace which heats the column effluent to nearly 2000°C in the presence of hydrogen or air to convert halogenated organics to hydro-

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chloric acid. The hydrochloric acid is microextracted into an aerosol consisting of n-propanol. The transient change in the conductivity of the aerosol is used to determine the acid concentration. This is a relatively complex detector which is often run in series with the photoionization detector.

Regarding the safety of the flame- or ionization-based detectors, the flame photometric and ionization detectors can be made intrinsically safe by the removal of the flame from the environment by a long, small bore exhaust tube which carries water vapor from the flame. The flame is otherwise completely sealed from the environment. With all of the detectors used with GC-based separations of semivolatile organic compounds, potential explosion hazard concerns are also present due to heated transfer lines and thermal desorption vapor traps. The desorbers must heat rapidly to temperatures near 200°C to effectively desorb semivolatile organic compounds. Similarly GC transfer lines (i.e., connections between the analytical column and the thermal desorber as well as the detector) must be continually heated to prevent condensation (i.e., "wall losses") of the semivolatiles. These explosion hazards can be addressed by insulating and isolating these heated parts from the operating environment.

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OTHER GOVERNMENT

ARMS CONTROL & DISARMAMENT AGENCY
2 CY ATTN: DR SEIDERS
ATTN: MR STAPLES
2 CY ATTN: OFFICE OF GENERAL COUNSEL

CENTRAL INTELLIGENCE AGENCY
ATTN: DCI/ACIS/TMC MR SPALDING

DEPARTMENT OF DEFENSE CONTRACTORS

BATTELLE EDGEWOOD OPERATIONS
ATTN: CBIAC
ATTN: MS BRLETICH

GENERAL RESEARCH CORP
2 CY ATTN: R MUSTACICH
2 CY ATTN: P HOLLAND

JAYCOR
ATTN: CYRUS P KNOWLES

KAMAN SCIENCES CORP
ATTN: DASIAC

KAMAN SCIENCES CORPORATION
ATTN: DASIAC

SCIENCE APPLICATIONS INTL CORP
12 CY ATTN: CVR MR FARGO

DIRECTORY OF OTHER

DIVISION OF CONTINUING EDUCATION
ATTN: DR JOHN REDICK

Defense Threat Reduction Agency

8725 John J Kingman Road MS 6201
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TDANP-TRC   August 1, 2001

MEMORANDUM TO DEFENSE TECHNICAL INFORMATION CENTER
       ATTN: OCQ/MR LARRY DOWNING

SUBJECT: DOCUMENT CHANGES

       The Defense Threat Reduction Agency Security Office reviewed the following documents in accordance with the Deputy Secretary of Defense Memorandum entitled, "Department of Defense Initiatives on Persian Gulf War Veterans' Illnesses" dated 22 March 1995, and determined that the documents were unclassified and cleared for public release:

DNA-TR-93-84, AD-B244408, Acoustic Resonance Spectroscopy in CW Verification Tooele Field Trial (August 1992).
DNA-TR-93-129-V1, AD-B192045, Global Proliferation – Dynamics, Acquisition Strategies and Responses, Volume 1 – Overview.
DNA-TR-93-129-V2, AD-B192046, Global Proliferation – Dynamics, Acquisition Strategies and Responses, Volume 2 – Nuclear Proliferation.
DNA-TR-91-216, AD-B163637, Harmonizing the Chemical Weapons Convention with the United States Constitution.
DNA-TR-92-180, AD-B175230, Evaluation of the Concept of a List for the BWC.
DNA-TR-92-61, AD-B167663, Basic State Party Functions and Skills Under CWC.
DNA-TR-92-66, AD-B167357, Domestic Reporting Requirements for Chemical Industry.
DNA-TR-91-213, AD-B163260, Analysis of the Interactions Between Treaties.
DNA-TR-93-70, AD-B177262, Chemical Weapons Convention Inspections of Private Facilities Application of United States Environmental and Safety Laws.
DNA-TR-92-182, AD-B173450, Commercial Products from Demilitarization Operations.
DNA-TR-91-217-V3, AD-B169350, Chemical Weapons Process Parameters, Volume 3 – Users' Guide.
DNA-TR-92-116-SUP, AD-B175292, Technical Ramifications of Inclusion of Toxins in the Chemical Weapons Convention (CWC), Supplement.
DNA-TR-92-128, AD-B175452, Task 1 Report Target Vapor Identification and Database Development.
DNA-TR-92-196, AD-B174940, Task 2 Report Algorithm Development and Performance Analysis.
DNA-TR-93-68, AD-B178109, CW Detection Instrument R&D Design Evaluation.

       Enclosed is a copy of the referenced memorandum. If you have any questions, please call me at 703-325-1034.

ARDITH JARRETT
Chief, Technical Resource Center