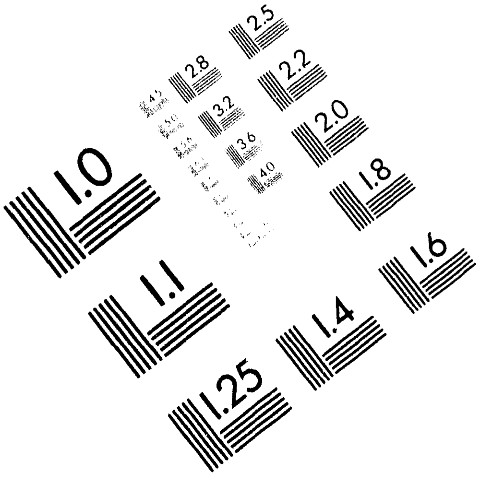

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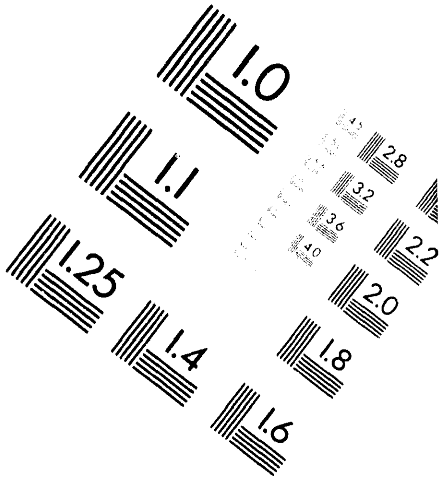

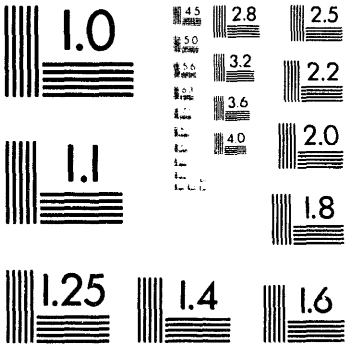

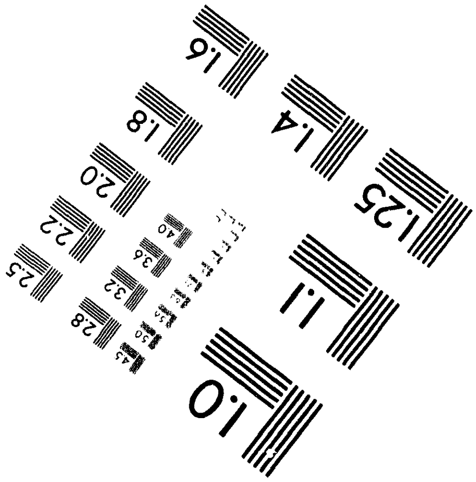

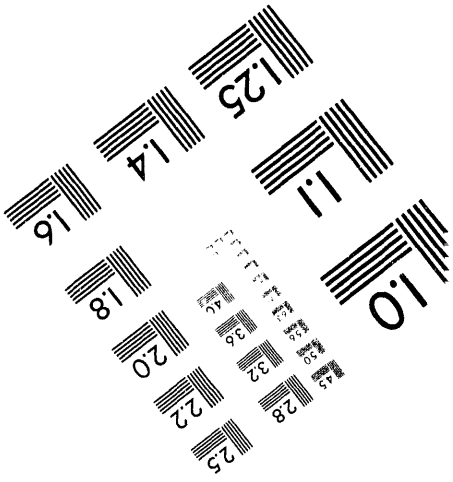

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1 of 1

A Small, Portable Gas Chromatograph–Quadrupole Mass Spectrometer for On-Site Analysis

Introduction

Gas chromatography–mass spectrometry (GC-MS) is the analytical tool of choice for the exact identification of unknown organic chemicals in environmental samples. Capillary gas chromatography, combined with the specific identification capabilities of mass spectrometry, allows the rapid and complete characterization of individual compounds in complex mixtures.

As the technology has developed, many manufacturers have offered bench-top MS systems that provide a variety of analytical capabilities. Many instruments have been promoted as "detectors for gas chromatography." More recently, manufacturers have offered integrated packages that can be transported to the field to provide analytical capabilities previously available only in the laboratory.[1,2] The demonstrated field utility of these field-transportable units has triggered an interest in smaller, lighter weight, and more portable instruments. However, the current weight (>100 lb), large size, and laboratory-based power consumption requirements of these units is viewed as a liability by some potential field instrument users.

Over the past several years, the interest in field-deployable instruments has resulted in research and development into smaller GC-MS systems designed with limited applications.[3] While the development of these instruments is certainly worthwhile, a reliable and robust GC-MS instrument that clearly addresses the field-deployable needs for all environmental sampling and analysis would have considerable utility. Over the past several years, the Lawrence Livermore National Laboratory (LLNL) has been involved in developing portable instruments with analytical performance characteristics similar to those obtained with bench-top instruments. The current instrument, developed at LLNL and described here, was originally designed for use by on-site inspection teams supporting the Chemical Weapons Convention (CWC). The portability and expanded capabilities of this integrated instrument now make it a useful tool for environmental monitoring and on-site analysis studies.

Instrument Analytical Requirements

The CWC has formulated, and now plans to implement, treaties designed to permit on-site inspections of chemical processing facilities to ensure compliance with the treaty goal.[4,5,6] During site inspections, samples from soil, water, and air will be collected, processed, and analyzed to determine if CW agents, precursors, or hydrolysis by-products are present. Swipes, soil, and water extracts will be obtained and they must be analyzed in a timely manner. To accommodate these on-site inspections, a portable GC-MS instrument is needed that can be deployed to identify unknown chemical samples in extraction solvents. Because a wide variety of chemicals may be encountered during these inspections, the GC-MS instrument must possess the sensitivity and specificity of commercial instruments, and the resulting data should approach those of table-top laboratory instruments. Some essential instrument specifications are listed in Table 1.

To accurately identify compounds in the field, the new GC-MS system must also possess certain attributes consistent with laboratory GC injectors, GC columns, and mass spectrometer interfaces.

Injector and GC Column

The set of target chemicals of interest during a CWC inspection range from very volatile, to semi-volatile, to polar compounds. Polar compounds require derivatization to enhance their volatility and chromatographic properties. Derivatization will create semi-volatile compounds with a variety of GC retention times and chromatographic properties. The timely chromatographic separation of volatile and semi-volatile compounds can be accomplished with a heated GC injector, temperature-programmed gas chromatographic column, and

Table 1. Gas Chromatrograph–Mass Spectrometer useful for CW site surveys.

Mass spectrometer	
Mass range	45–650 amu
Resolution m/ m	1000 (±0.5) amu
Mass range programmable	10–650
Sensitivity	<1 ppm
Ionization source	70 eV electron impact
Source temperature	> 175°C
Gas chromatograph	
Temperature software controlled	
Column temperature programmable from RT to 300°C	
Column temperature slew rate linear 10°C/min or better	
Low carrier gas flow rates (typically 0.06 µL/min)	
DP-5 column (100 µm i.d. × 10 m long)	
Injector	
Temperature programmable from RT to 300°C	
Accept liquid injections	
Programmable split ratio	
Carrier gas supply	
Input pressure on the order of 4–5 lb	
Sufficient supply for two weeks of operation	
Vacuum requirements	
Less than 1×10^{-4} Torr during sample analysis	
Able to handle carrier gas load	
Data collection system	
Range 10^5	
Resolution 16 bits	
Scan speed <1 sec	
Operator interface	
Graphics display	
Keyboard and mouse (or track ball) input devices	

heated ionization source, to reduce condensation of GC peaks and lessen background ion signals.

Because most of the samples generated during the CWC on-site inspections will be solvent extracts, the portable GC-MS instrument must have an injector that will accommodate and vaporize liquid sample injections. To provide and maintain the vapor phase necessary for standard GC analysis, an injector temperature up to 300°C is desirable. The injector should also be equipped with split-splitless hardware for complex industrial samples that require high-resolution GC separations.

A gas chromatograph column that can be temperature-programmed from ambient temperature to a sufficiently elevated temperature is highly desirable for field environmental samples. The column temperature slew rate should be programmable with a rate optimized for target chemicals. This temperature ramping will also result in shorter data collection delays when higher boiling unknowns are encountered.

Mass Spectrometer

To reliably identify target chemicals in the field, a portable GC-MS instrument must have the sensitivity and mass range sufficient to detect and display all diagnostic molecular and fragment ions. Auto-calibration requires that the mass resolution and stability of the instrument in the field is sufficient to accurately tune the instrument. The ionization source must produce a stable fragment ion beam; the ion optics and mass analyzer should, therefore, produce a reliable and reproducible mass spectrum that permits computer-assisted comparisons and identification from a reference library.

The minimum mass-range required for most CWC target compounds is from 10 to 350 atomic mass units (amu). To ensure accurate library search results of target compounds, resolution of at least 0.5 amu is desirable. The overall instrument sensitivity must exceed one part per million in the full-scan mode. Most standard mass spectral libraries have been compiled with data obtained from 70-eV spectra. Therefore, a 70-eV electron impact ionization source should be used to generate comparable mass spectral data required for mass calibration and accurate library search routines in the field.

The ion source and GC interface to the source should be held at a stable, elevated temperature to prevent accumulation of contaminates. The heater for the source and interface should maintain the source and inlet at a temperature above that of the upper limits of the GC-program temperature ramp. This will maintain and permit thermal cleaning of the source surfaces prior to injecting new unknown samples.

Portability Requirements

Three major parameters are essential when developing a high-performance, portable GC-MS system. They are weight, size, and power consumption. Quantification of target numbers for these parameters is a partly subjective matter, strongly related to the specific applications. The CWC operational scenario places some upper limits on the weight restraints. The more easily carried, the more convenient the equipment will be to transport from one location to another. The need is to have as lightweight and portable a GC-MS package as possible, which also has all the analytical capabilities of existing laboratory or transportable instruments. The weight and size should minimize the amount of effort to transport the equipment to a target site.

For adequate environmental sampling and analysis, instrument operational lifetimes should be at least 8 hours. In addition, less reliance on electrical power translates into longer instrument use in the field. The GC-MS instrument will most probably be set up in a temporary field staging area within the site of the industrial facility. This area may be in an open field, within a car or truck, or on a vehicle van-bed. Portable generators or automotive ac/dc power sources will be used.

Using safety criteria established by on-site personnel, a reasonable weight for a one-man-portable GC-MS package would be <50 lb. A 50-lb instrument should permit mobility by an unaided individual, with minimal risk of back strain or injury. This weight would also allow field personnel to carry the instrument easily from place to place without mechanical assistance.

Shipping weight is another important parameter to consider when the GC-MS instrument is to be transported to the inspection site. An overall target size of the GC-MS instrument can be rationalized by considering transportation constraints. In contrast to overland shipment, an alternative might be to check the instrument as airport luggage. Checked luggage suggests a maximum target size of a standard suitcase. If the instrument is to be shipped as checked luggage, the packing material and instrument must weigh <100 pounds. A 50-lb GC-MS instrument would allow for 50 lb of well-protected packaging.

Reduced weight, compact construction, and reduced overall size of the GC-MS instrument will enhance portability. The significant cost of the instrument, the need for immediate deployment under a CWC inspection scenario, and the desire to guarantee instrument performance in the field may require hand carrying the instrument to the survey site or staging area. Therefore, aircraft carry-on of the GC-MS instrument suggests a double-wide briefcase, small enough to fit under a passenger seat.

Finally, with the development of large capacity, very small, lightweight, portable electric generators (1 kW in a 55-lb package), the need for battery-powered CWC instruments has been reduced. Knowing that portable electric generators are available for on-site investigations, GC-MS instrument size and weight reduction considerations are now probably the most important parameters to consider when designing portable GC-MS packages. However, the power consumption of the instrument will directly affect the size and weight of the GC-MS instrument. In general, as instruments require more power, the power supplies will tend to be larger and heavier, adding to the size and weight of the final package. Thus, to minimize size and weight and enhance one-man portability, it is very important to keep the power consumption of the GC-MS instrument as low as possible.

Instrument Description

The latest generation field-portable GC-MS instrument developed at the Lawrence Livermore National Laboratory is shown in Fig. 1. This instrument is contained in a 9.5 x 18 x 27-in. suitcase. This complete GC-MS field instrument includes (1) a conduction-heated and forced-air-cooled, small-bore capillary gas chromatograph, (2) a small gas chromatograph injector assembly, (3) a quadrupole mass spectrometer with electron multiplier detector, (4) a self-contained ion/sorption pump vacuum system, and (5) a dual computer system with software, used to control the hardware and simultaneously acquire, analyze, and identify mass spectral data. A description of each of the instrument's subsystems is presented below.

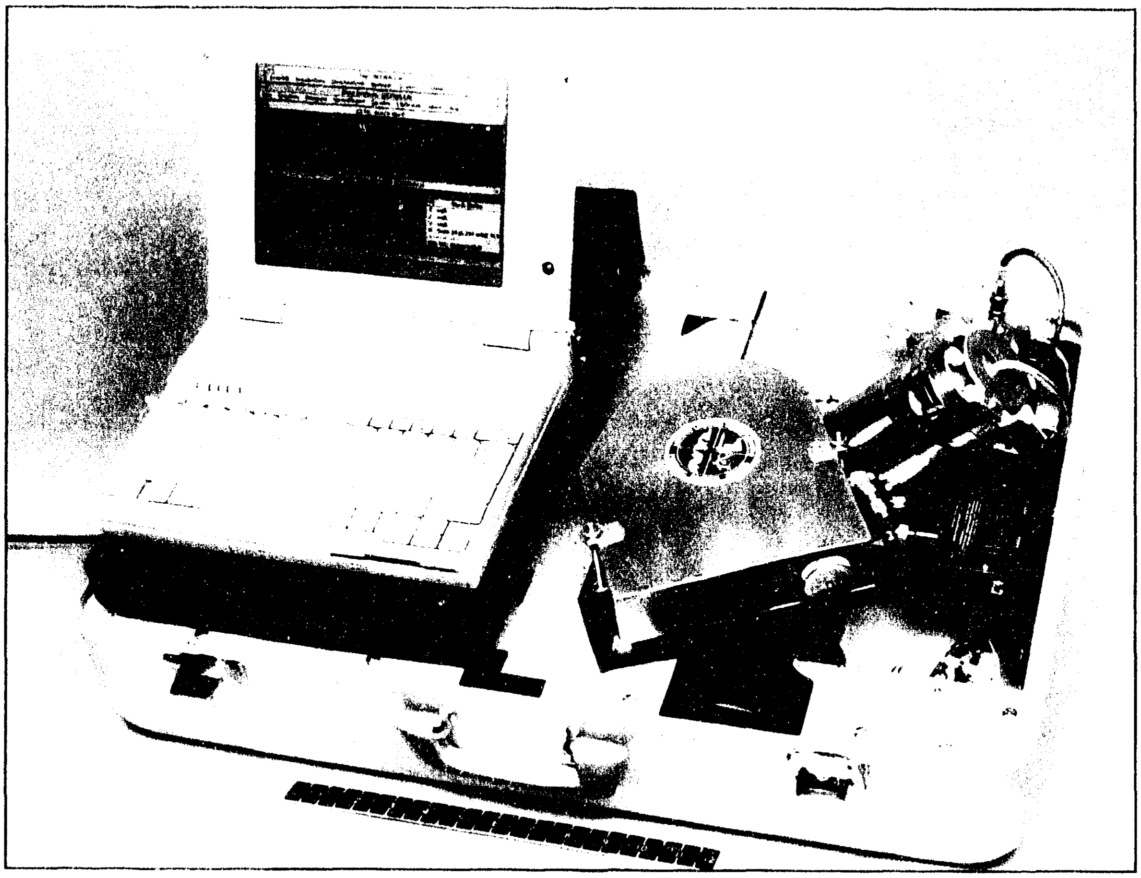

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Figure 1. A small, portable GC-MS instrument contained in a standard 9.5 x 18 x 27-in. suitcase. The package contains a GC, MS, vacuum system, 486 computer, and support electronics. As shown, it weighs 61 lbs.

Gas Chromatograph

The gas chromatograph that has been designed and built for this portable instrument has all the required capabilities of an air-heated commercial gas chromatographic oven. However, it is contained in a 1-in.-high by 6-in.-diameter oven. It can be programmed to an isothermal set point and to any desired temperature between ambient and 300°C. When required, it can also be ramped in temperature from ambient to 300°C . Some design details of the GC oven are shown in Fig. 2.

The capillary column selected for this instrument is a 100 µm i.d. DP-5 column (12 m long). This spiral-wound capillary is heated by a flat pancake heater and cooled with forced air at ambient temperature. The conduction-heated design is incorporated into the GC-MS instrument to maximize heating efficiency and reduce overall power consumption. The small GC capillary is coiled flat and rests on a 10-mil-thick copper plate. The column is held in place and is coiled under an open circular aluminum disk with four internal fingers, which press the capillary column onto the copper disk (see Fig. 2). This column assembly is heated with a pancake disk heater pressed firmly against the copper disk from underneath. The copper disk ensures uniform heating of the whole GC column. The entire disk assembly is held in place by three fiberglass support posts. The supports thermally isolate the GC column and heater assembly from the stainless-steel GC oven housing. The external oven enclosure has a port that allows cooling air from a micro-fan to pass above and below the GC heater assembly.

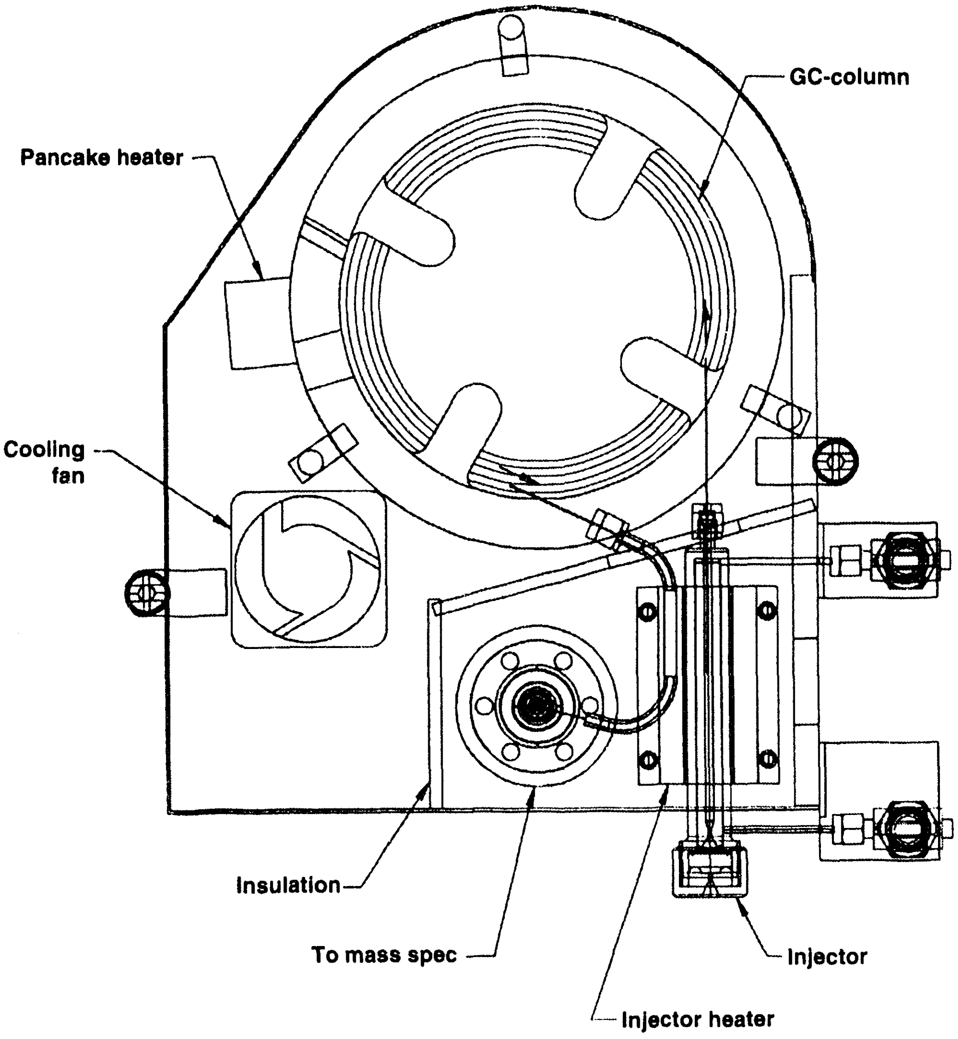

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Figure 2. A very small, conduction-heated, forced-air-cooled gas chromatograph with a heated, high-temperature injector. The GC column can be scanned from anbient temperature to 300°C in less than 15 minutes.

A thermocouple is clipped to the copper disk of the GC assembly. This temperature-sensing element is used to monitor and control the column temperature. Temperature control is achieved using a dedicated computer in a power control loop, which regulates the overall heater power.

The pancake heater used in this small GC oven is rated at 105 W; however, not all its capacity is required during normal operation. The column temperature can be ramped (at ~15°C/min) from room temperature to 280°C in about 15 min using <75 W of heater power. The upper limit of 280°C can then be maintained with only 55 W of power. This could be reduced even more with better insulation of the stainless-steel GC oven enclosure.

A single, small-capacity fan is used to cool the column at the end of the GC-MS run. Using this fan at ambient room temperature, the GC column assembly can be cooled from 280°C to 50°C in approximately 10 min. This permits a full-temperature GC-MS ramp-up and cool-down cycle to be completed in <30 min. In order to maintain GC peak resolution, an insulation barrier is placed between the GC column, the mass spectrometer source inlet, and GC injector. This prevents unwanted cooling of these components and helps maintain a uniform GC column temperature between GC-MS runs.

Injector

The stainless-steel GC injector was designed to accommodate commercial sample syringes and injection needles. The injector assembly was designed with split-splitless interface ports and machined from stainless steel. One end connects to the input end of the chromatograph capillary and is sealed with standard swage locks and capillary gas chromatographic ferrules. At the opposite end of the injector assembly, sample injections are made through a Teflon-backed rubber septum held in place with a circular locking nut. A positive GC carrier-gas seal is achieved in the septum with a knife edge machined into the underside surface of the septum locking nut. As the nut is hand tightened, the knife edge cuts into the septum to form a gas-tight seal. The inside of the injector also holds a standard glass sleeve, which can be removed for easy cleaning. The injector is enclosed in the gas chromatographic oven housing; however, the thermal insulation barrier permits independent temperature programming of the injector. A sturdy fiberglass clamp supports the injector for hand injections through the rubber septum.

To heat the injector to 300°C, a tubular metal heating coil is tightly wound over the injector body. This heater coil also contains a thermal sensor, which is used to monitor and control the injector temperature. Using <75 W of power, the injector temperature can be ramped from room temperature to 300°C in <8 min. The power required for normal GC-MS operation (300°C isothermal) is <27 W.

GC Column–Mass Spectrometer Inlet Interface

The output of the capillary column is connected to the mass spectrometer through a heated MS inlet interface. The design utilizes a short length of 1/8-in.-diameter copper tube, which routes the GC capillary column from the GC heater disk directly into the mass spectrometer ion source region. Gas exiting the GC capillary passes directly into the ion source region. There is no membrane used to limit gas loads on the vacuum system. At one end, the copper tube makes a vacuum seal to the mass spectrometer housing. At the other end, the copper tube is fitted with a swage lock and graphic ferrule to form a vacuum-tight seal around the GC column. The copper tube is bent to make thermal contact with the GC injector. This is done so the MS source inlet tube and inner capillary column remain heated at all times. In addition, a 50-W source heater is used to supply additional heat and to maintain the inlet interface at an elevated temperature.

Mass Spectrometer

The basic mass spectrometer selected for our new field-deployable GC-MS instrument was the instrument package utilized in the Hewlett Packard GC-MSD (Mass Selective Detector) instrument, 5971a. This is a quadrupole mass spectrometer with mass range sufficient for identifying all CW-related chemicals. The entire mass detector assembly is self contained, lightweight, robust, and has a demonstrated ability to function in transportable instruments. This mass spectrometer detector was sufficiently small to be incorporated into the required suitcase-size targeted configuration. The 5971a mass spectrometer assembly includes a two-filament, 70-eV electron impact ion source, a pre-aligned quadrupole analyzer, an electron multiplier, and is designed to accept a GC column.

To operate the 5971a MSD requires only two electronics circuit boards, a calibration source, applications software, and a computer with operating software. Certain hardware modification were made to hold the MSD mass spectrometer in an LLNL custom vacuum housing. The source, quadrupole analyzer, and electron multiplier assembly were detached from the commercial support base and mounted on a metal support frame, which fit into the vacuum chamber enclosure. This new design provided us with the ability to rapidly and easily set up the mass spectrometer, optimize its performance, acquire GC-MS data, store runs, display and analyze the calibration data, and finally, to take the instrument into the field to identify unknown compounds.

Vacuum System Considerations

The vacuum system for any GC-MS must be able to maintain a minimum operating pressure within the spectrometer vacuum housing. Maintaining this pressure is complicated by the fact that the GC connected to the mass spectrometer provides a gas load, or "leak," which the vacuum pumping system must accommodate. This gas load will depend on the GC column design, carrier gas, and carrier gas pressure. Other gas loads can come from leaks in the vacuum envelope and outgassing from materials within the vacuum chamber. A good operational mass spectrometer pressure is typically near or below 1×10^{-4} Torr. To provide adequate vacuum with a substantial inlet gas flow requires a significant vacuum pumping system; however, the flow rates for smaller bore capillaries can be less than 0.1 mL/min.

It is germane to calculate the required pumping speed needed to achieve optimum instrument performance under different GC flow conditions. The capillary flow rate and desired operating pressure determine the capacity of the vacuum pumping system. The pumping capacity or speed, S, is related to the desired pressure, P, and the flow rate, Q, by the following equation:

$$Q = S \bullet P \qquad \text{(Eq. 1)}$$

If we assume that 0.1 mL/min is leaked into the GC capillary at one atmosphere, then the flow rate, Q, is

$$Q = 760 \text{ Torr} \bullet 0.1 \times 10^{-3} \text{ L/60 sec.} \qquad \text{(Eq. 2)}$$

Thus, Q equals about 1.27×10^{-3} T-L/sec. Therefore, for a maximum mass spectral pressure, $P = 1 \times 10^{-4}$ Torr, S would be Q/P or:

$$S = 1.27 \times 10^{-3} \text{ T-L/sec} / 1 \times 10^{-4} \text{ T}, \quad \text{or}$$

$$S = 12.7 \text{ L/sec.} \qquad \text{(Eq. 3)}$$

Commercial GC-MS systems operate at pressures of 5×10^{-5} Torr, maintained with pumping systems capable of 50 to 60 L/sec. The above estimate suggests that systems could be built with less pumping capacity. However, these systems would perform marginally because the pressure expected would be higher with larger GC columns, and other gas sources (e.g., outgassing and leaks), which are not considered. Therefore, the above facts lead to a realistic conclusion that self-contained portable systems will require pumping systems with capacities approaching 50 L/second.

Of all vacuum system configurations, only a "getter" pumping system can achieve the above pumping capacity with minimal weight, volume, and power consumption. This fact is graphically displayed in Fig. 3. The bar graphs reveal comparisons of the weight, size, and power expenditures for various vacuum systems that would provide the pumping capacity necessary for GC-MS instruments. These numbers were developed from lists of commercial vacuum pumping systems, most of which are capable of achieving the desired pressures required for MS instruments. The figure also plots the key package parameters for 13 pumps: one diffusion pump system (system 1), four turbo pump systems (systems 2 through 5), two molecular drag systems (systems 6 and 7), two ion pump systems (systems 8 and 9), and four chemical sorption/ion pump systems (systems 10 through 13). The diffusion pumping system is not considered portable, but is listed because it is used with commercial, bench-top GC-MS systems.

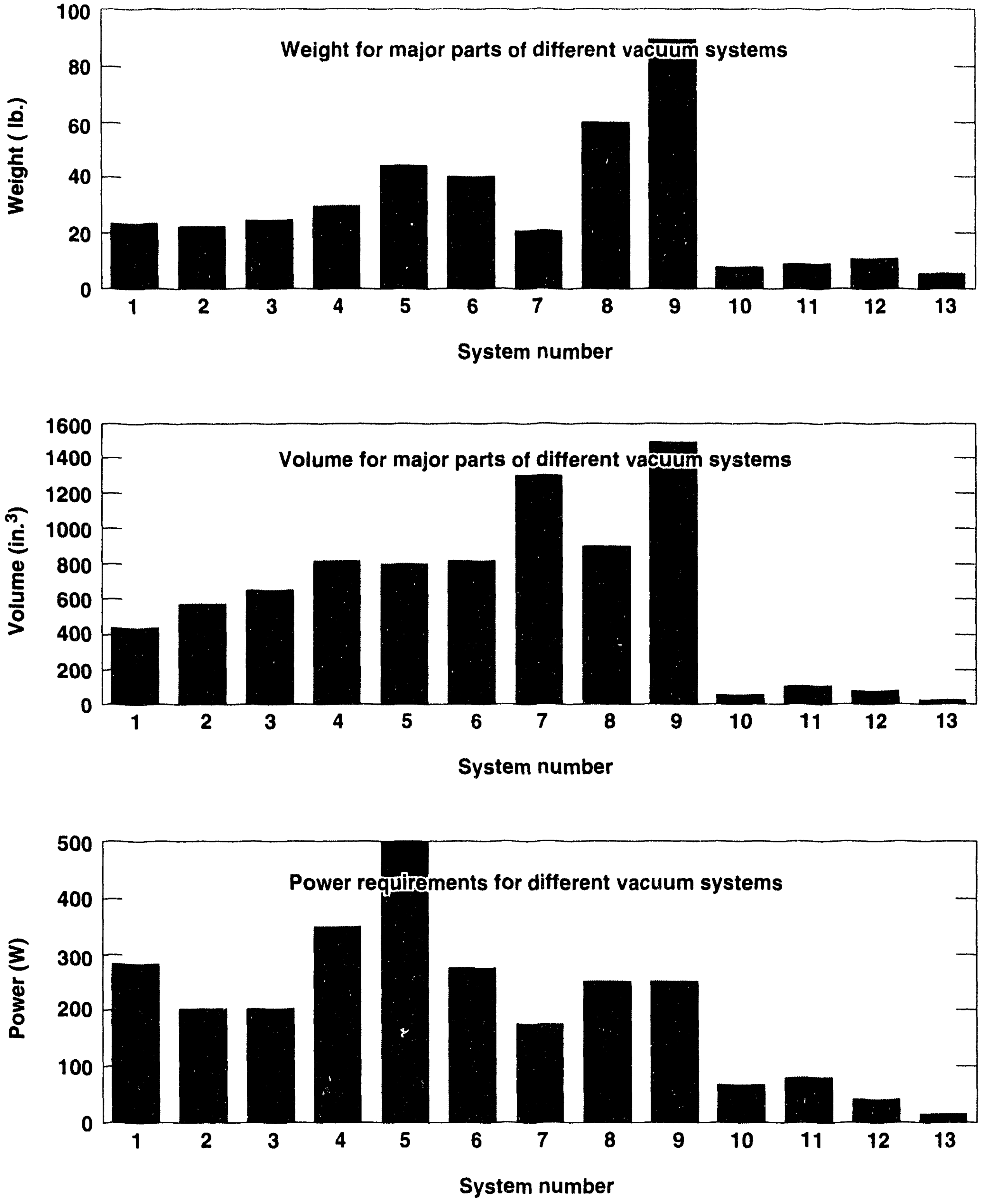

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Figure 3. Bar graph summary of the portability parameters (weight, volume, and power consumption) for 13 vacuum systems. The figure data were developed from a list of commercial vacuum pumping hardware, most of which is capable of achieving the pressure required within the MS system. The figures plot the key pack parameters for one diffusion pump system (system 1), four turbo pump systems (systems 2 through 5), two molecular drag systems, (system 6 and 7), two ion pump systems (systems 8 and 9), and four chemical sorption/ion pump systems (systems 10 through 13).

From the calculated results shown in Fig. 3, it is evident that sorption pumping systems offer significant advantages when a portable vacuum system is needed. Over the past several years, prototype instruments employing this technology have been reported. The availability of this vacuum pumping technology for portable instruments is no longer the issue. The major issue is the operational requirements imposed by this new technology. What technical changes are necessary to enhance the utility of such pumping systems in portable GC-MS systems?

The first issue that surfaces when sorption pumps are used relates to operational lifetimes. Chemical sorption pumps function by reacting chemically with gases, producing compounds that have negligible vapor pressure. When sorption/getter material has been reacted with the chamber gases (and become fully depleted), the system can no longer maintain a vacuum. A new charge will be necessary to replace spent sorption/getter material. Replacing the getter material requires the use of an auxiliary pumping station for initial pump down and material activation. Depending on the system design, this process could take 1-2 hours. A fixed amount of sorption/getter material within a pump will allow for a fixed vacuum pumping capacity. To maximize the instrument operational time, it is important to maximize the getter pumping lifetime. This can be done by increasing the amount of material used in the pump and/or decreasing the gas load.

Current Vacuum System Descriptions

The last two vacuum systems used in our suitcase instruments are shown in Fig. 4. The earlier generation system on the left was constructed around a commercial enclosure, manufactured specifically to house the mass spectrometer. This housing was made of cast aluminum. Attached to this housing was a 6-L/sec ion pump and GC interface port. A sorption pump manifold containing an isolation valve, pump-out valve, and modified commercial sorption pump (Sorbodyne) was attached to the side of the chamber using a rubber vacuum gasket. The pump contained 300 g of getter material (Fe/Zr), which provided a specified hydrogen pumping speed of 250 L/sec. This pumping speed was reduced considerably by the elbow connecting the pump to the mass spectrometer chamber. The vacuum seals used to interface the GC and calibration source were made with Viton o-rings.

To improve the overall vacuum performance, a new stainless-steel chamber (shown on the right in Fig. 4) was developed. The completed system included a 6-L/sec. ion pump and a new pump-out valve with a metal valve seat. All interfaces to the chamber were made with metal vacuum seals. The isolation valve between the pump and mass spectrometer chamber was eliminated. A new sorption pump was designed to be an integral part of the the mass spectrometer enclosure.

Vacuum pumping by the sorption/getter material requires sorption/getter heating to 280°C. Also, prior to pumping, the material must be activated at an elevated temperature (~480°C) for 1 hour to drive off water and allow the surface of the Fe/Zr metal to become chemically active. To provide the heat required, an electric cartridge-heater was installed into the center of a sorption holding cage. The cage was heated with 16 W of electrical power during normal operations. A temperature of 480°C (activation temperature) requires 40 W of power. The temperature to the sorption cage is controlled using a dedicated computer that senses an imbedded thermocouple. A small computer subroutine controls the feedback and heating of the pump.

For simplicity and ease of maintenance, it was decided to make all electrical connections to the MS assembly through a single vacuum flange. To do this required extending the RF quadrupole drive wires. Extending these wires increased circuit capacitance and upset the resonance conditions in the RF circuit. To re-establish resonance, the drive coils were modified to reduce their inductance. This design change permitted easy removal of the spectrometer assembly for cleaning and repair.

Electronic System

The suitcase GC-MS system contains two computer systems used to control the hardware and acquire spectral data. A block diagram of the electronics system is shown in Fig. 5. The first-generation electronic system used a single-board 386 computer for instrument control, data acquisition, and data display. As designed into the instrument package, this computer package included 4 Mbyte of RAM, a 1-Mbyte floppy disk drive, and an 80-Mbyte hard disk drive. A separate liquid crystal display, keyboard, and mouse provide the necessary instrument display and user control interface. In a second-generation electronics package, a 486

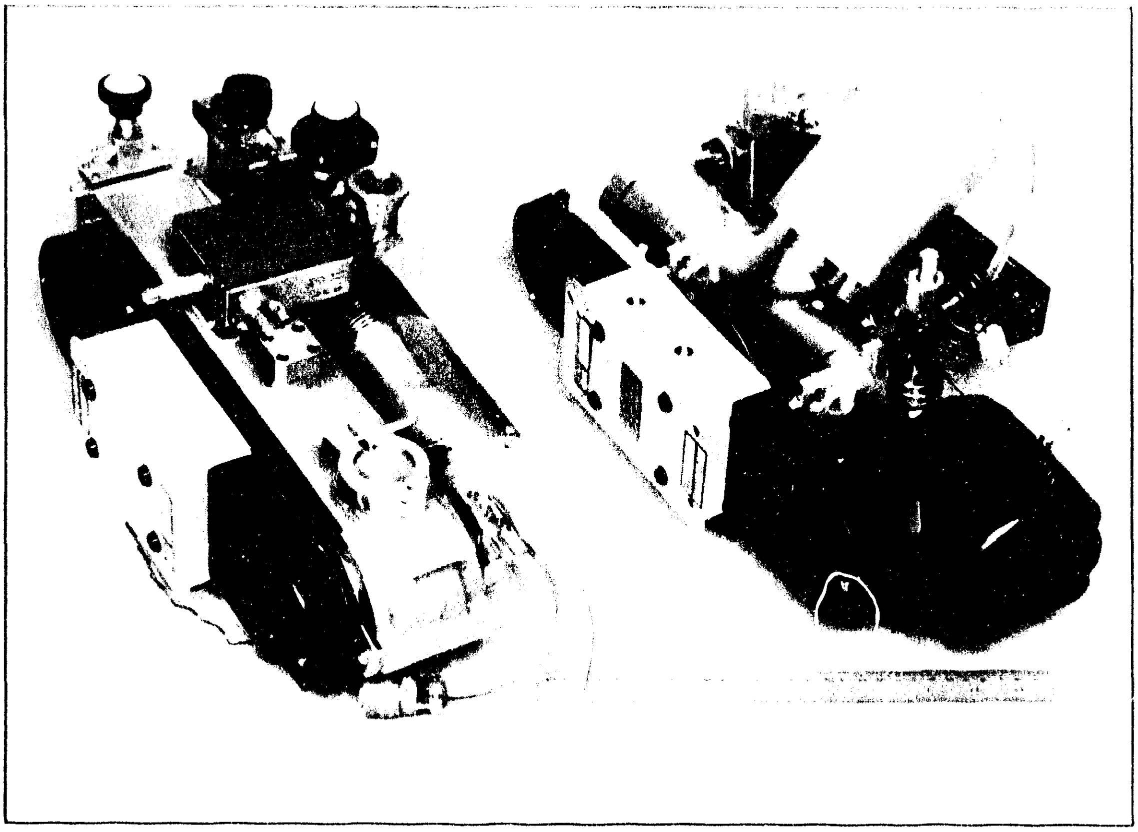

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Figure 4. Two vacuum systems evaluated during the development of the suitcase GC-MS instrument shown in Fig. 1. The system on the left was a modified version of the HP 5971a cast aluminum vacuum enclosure. The unit on the right was designed using stainless-steel and copper-gasket vacuum seals.

lap-top computer was installed in place of the computer assembled from discrete components. The lap-top provided all the features of the discrete component system in a smaller, self-contained package. Control of all MS functions was achieved via an HPIB interface board linking the 486 computer and MS electronics.

A second micropowered computer system is used to control the instrument heater's pumping system and purge valve. This microcomputer is an Onset Computer Corp. model 5. It is built on a 2 × 1.4-in. PC board and contains a Hitachi 6303Y processor. The 6303Y system contains 11 channels of 10-bit A/D input and has 17 digital I/O lines. The digital lines control zero crossing ac circuits, which provide power to the instrument heaters. Temperature monitoring is provided by thermocouples connected to the A/D inputs. All temperature control is accomplished via software control loops. This control computer is interfaced to the 486 unit via an RS232 data link. Setup and control of this computer system is achieved using a terminal emulator running in a Windows environment.

The operational software is both commercial and LLNL-generated. As shown in Fig. 6, it is used to (1) control the pumping system, (2) control the gas chromatograph and injector temperatures, and (3) acquire, display, analyze, and identify mass spectral data. The 486 lap-top computer runs MS/DOS and MS Windows to permit simultaneous running of the mass spectrometer control and acquisition application, and the terminal emulator software. The emulator software is used to load and run the microcomputer software. The software used in the control microcomputer is written in a company version of BASIC provided by the manufacturer.

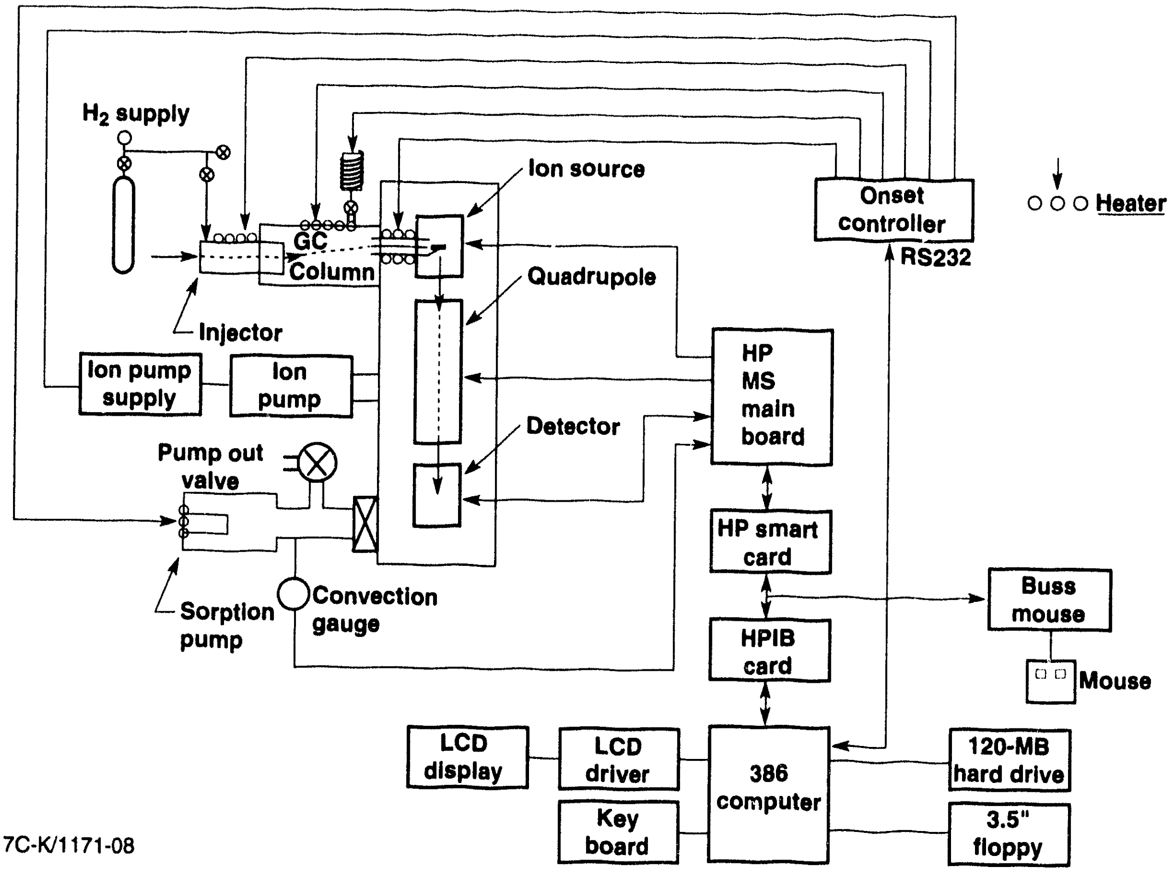

Figure 5. Block diagram of portable GC-MS electronics system. The system uses a 486 lap-top computer package for main control. An onset computer is used to control all the system heaters, ion pump power, and carrier gas flow.

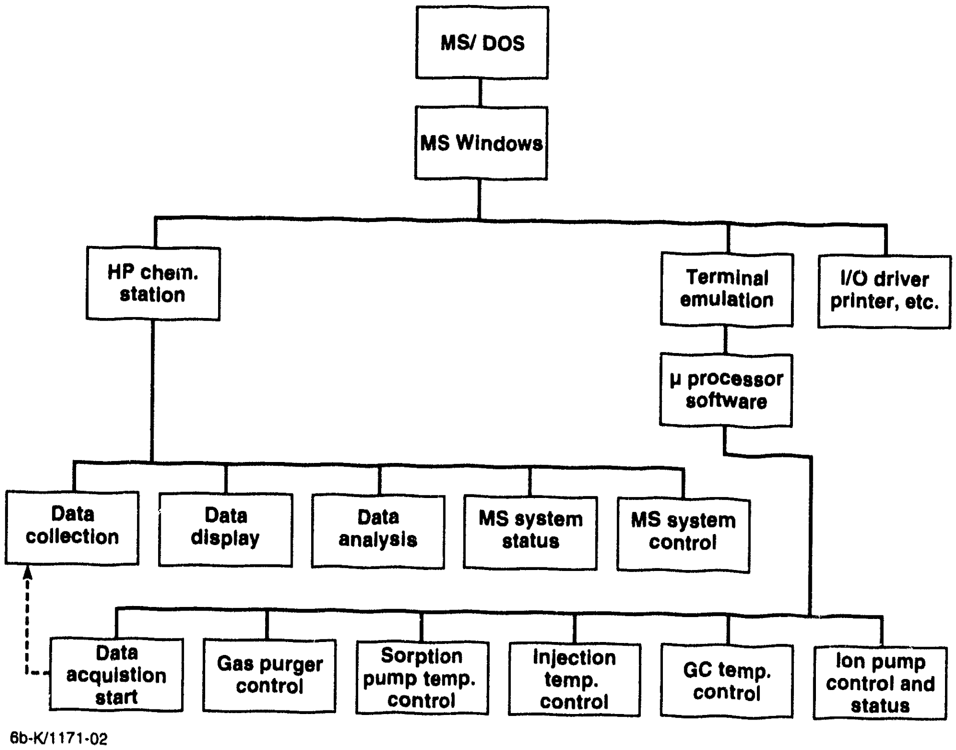

Figure 6. Layout of software used in suitcase GC-MS instrument. All software used in the microprocessor was developed for specific control of the instrument.

Instrument Performance

Analytical Performance

Initial evaluation of the very small gas chromatograph (VSGC) was performed using a narrow-bore GC column (0.10 mm i.d. × 10 m long) and nitrogen as the carrier gas. These laboratory tests were run with the instrument connected to an external turbo pumping system. The main objective was to evaluate GC performance apart from other instrument performance issues. Figure 7 is a total ion chromatogram (TIC) of an Alltech standard test mixture (QC Test Mix 1, cat. no. 41700). This mixture is used by the GC column manufacturers as a quality control test mix. The TIC peak width of under 12 sec, for most species, permitted a good separation of all seven peaks. An industry test mixture "Grob Mix" was also used to evaluate the VSGC system performance for heavier volatiles. The chromatographic data shown in Fig. 8 are more than adequate for separations of the heavier, less volatile compounds.

The overall performance of the suitcase instrument can be demonstrated when analyzing three sample types. Figure 9 (a and b) shows the TIC and a mass spectrum of one component from an injection of 1 µL of an LLNL test standard. When comparing these chromatogram data with an identical injection into a 5988 Hewlett Packard GC-MS instrument, Fig. 10, the results are similar. The relative peak areas and heights agree within a factor of two. Because of the different GC temperature slew rates, the absolute retention times differ by about 8 min. However, the TICs for the four compounds are comparable between the two runs. The residual solvent (CH_2Cl_2) background on the GC total ion plot was not a problem in operating the mass spectrometer and identifying the individual component compounds. Using standard spectral background subtraction techniques, the ions solvent can be subtracted from the compound fragment peaks. This subtraction process significantly reduces any mass spectra distortions associated with multiple compound spectra.

To test the sensitivity of the portable instrument, a 100-ng injection of methyl stearate, in hexane, was injected into the portable GC-MS instrument. The resultant data are shown in Fig. 11. Given the S/N level and the displayed noise level for the 100-ng sample, the estimated sensitivity of the portable instrument is better than 1 ng/µL. No effort was made to optimize the instrument parameters prior to this injection.

After obtaining this initial performance data, an effort was made to improve the portable vacuum system and evaluate extended operational lifetimes for field use.

Vacuum System Performance

Laboratory experience and field testing showed the cast aluminum vacuum housing used in earlier prototypes (see the left side of Fig. 4) was most difficult to work with, and the vacuum integrity became unreliable. Because of the many rubber o-ring parts, maintaining a good vacuum seal was difficult. In addition, outgassing characteristics of the cast aluminum vacuum enclosure and o-ring parts required a significant pump-down time. After pump-down and getter activation, operational records revealed that the system's vacuum could be maintained for a maximum of only about 13 days. Given the gas loads and amount of getter material expended, this is consistent with only 5- to 7-day lifetimes reported elsewhere in the literature for a similar package.[3]

In contrast, our new vacuum enclosure (shown on the right in Fig. 4) dramatically improved the vacuum performance of the instrument. The system's outgassing was significantly reduced and base pressures approaching 1×10^{-7} Torr were obtainable. A lifetime test with continuous carrier gas flow showed that the new getter pump could maintain a very low operational pressure for longer than 31 days. These data are plotted in Fig. 12. When compared with the empirical predictions of pumping capacity, total vacuum pumping capacity exceeding 60 days appears possible.

Practical Considerations

The number and type of samples and solvents injected into the instrument will have some effect on the length of time the GC-MS instrument may be field deployable. Mass balance calculation estimates suggest that one pumping charge (235 g) should allow 10^4 to 10^5 sample injections, depending on the solvent and

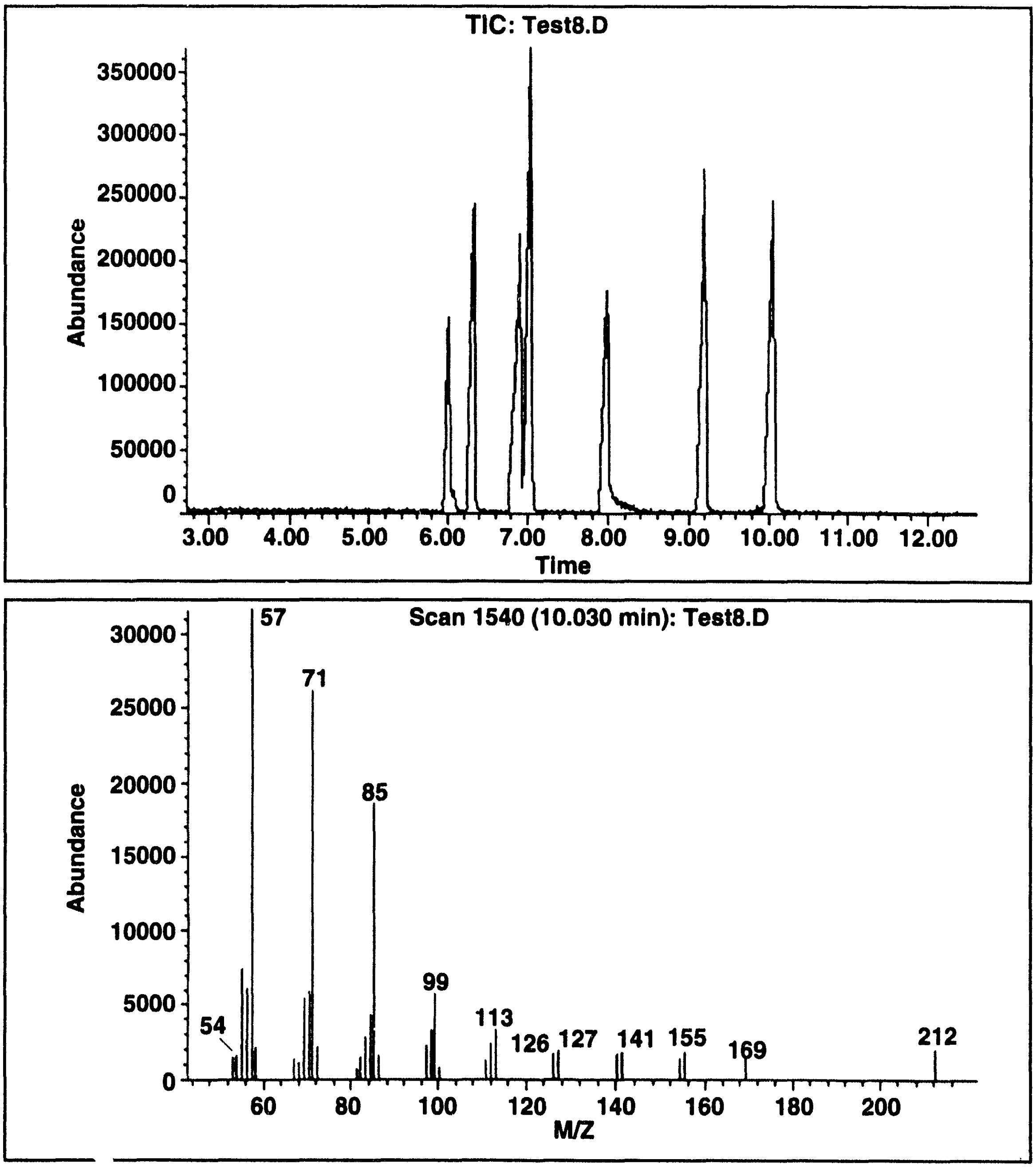

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Figure 7. Total ion chromatogram (TIC) of a standard hydrocarbon mix of seven chemicals. The 12-sec base peak widths permit very good separation of all seven compounds. The carrier gas for this sample was nitrogen with a back pressure of 2.5 lb. The GC column was scanned from 60° to 250°C.

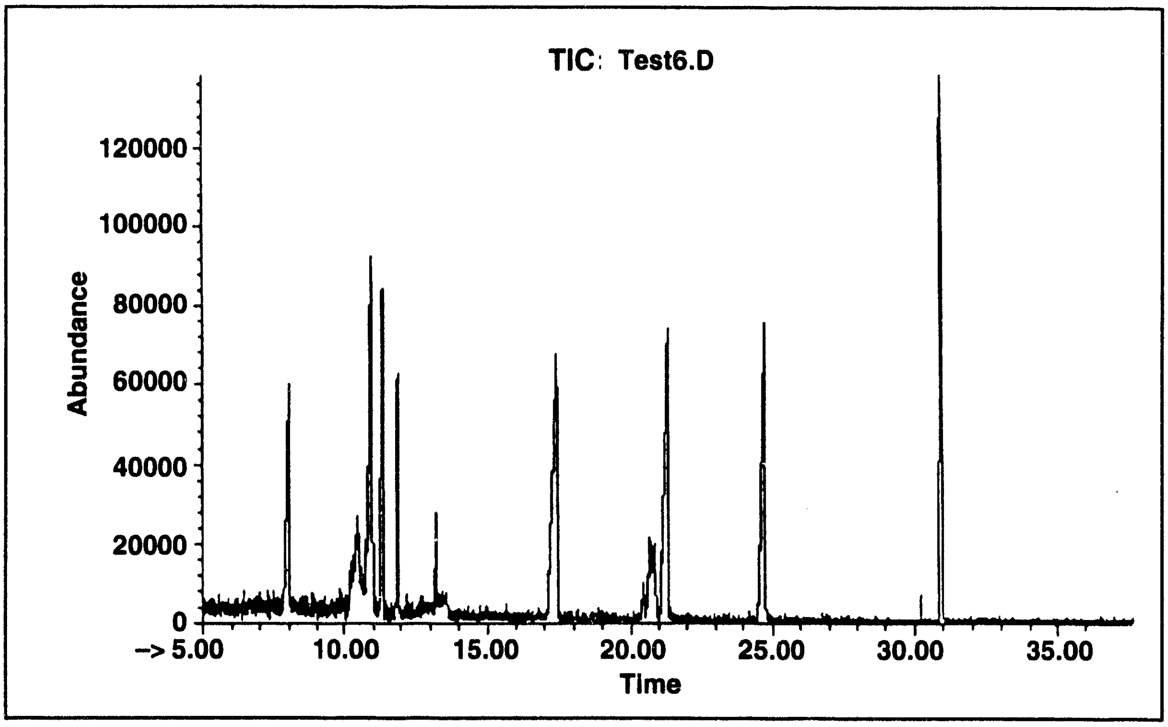

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Figure 8. Total ion chromatogram of an industry test mixture "Grob Mix" containing heavier volatile compounds. The carrier gas for this sample was nitrogen with a back pressure of 2.5 lb. The GC column was scanned from 40° to 260°C.

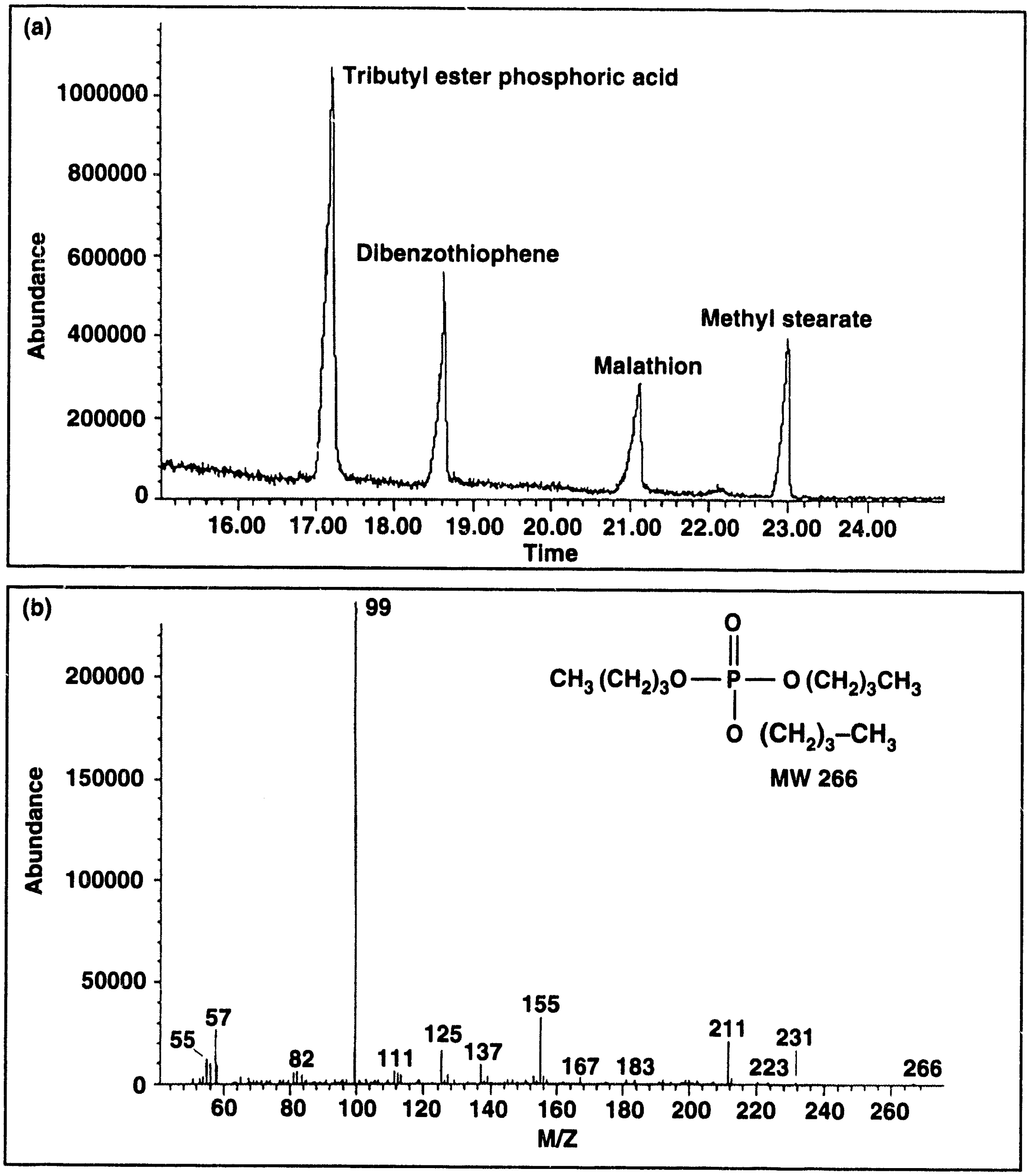

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Figure 9. Total ion chromatogram and selected mass spectrum of a pesticide standard mix of four chemical components. The selected mass spectrum is of the first compound, tributyl ester phosphoric acid. The carrier gas for this sample was hydrogen with a back pressure of 4 lb. A full 1-μL solvent sample and standard compounds were injected into the suitcase GC-MS instrument.

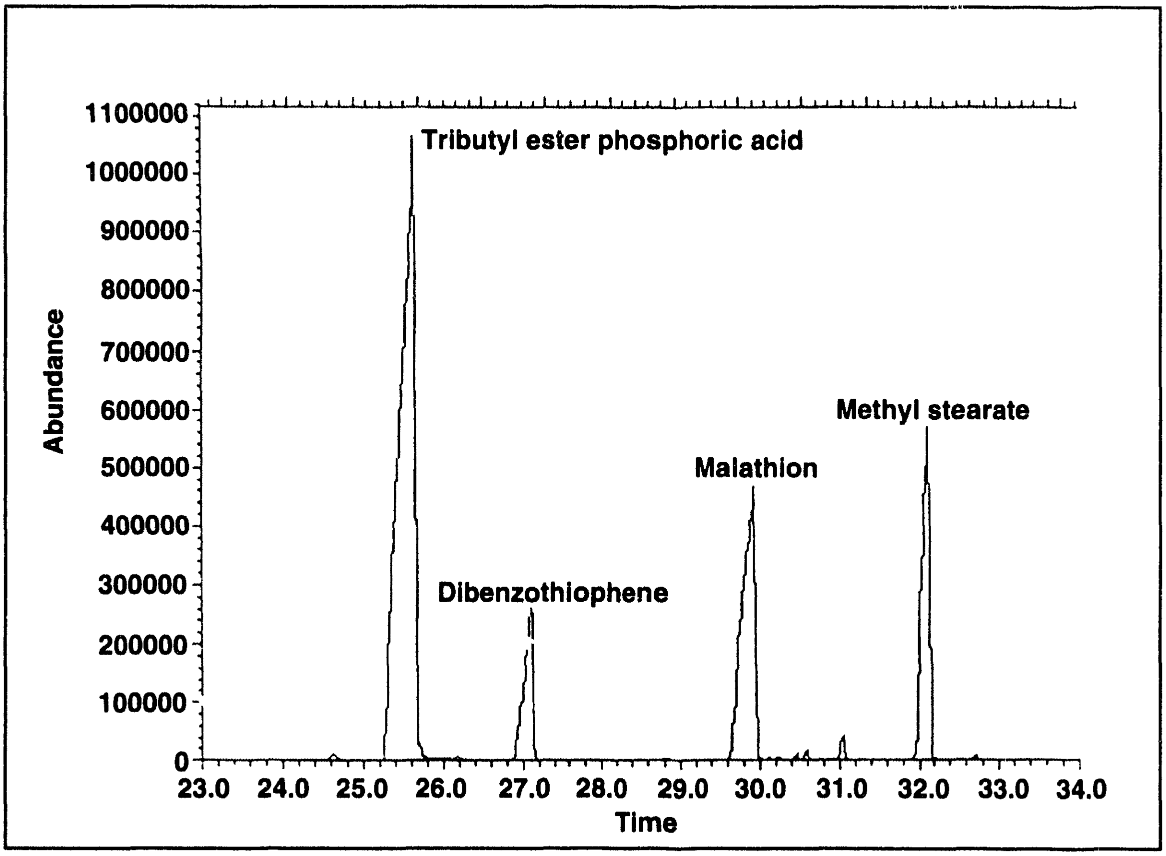

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Figure 10. Total ion chromatogram of the same pesticide standard used to generate the results in Fig. 9. To obtain these data, a full 1-μL injection was made into a Hewlett Packard 5988 GC-MS table-top instrument. Note the similarities and peak shapes seen with the suitcase GC-MS results shown in Fig. 9.

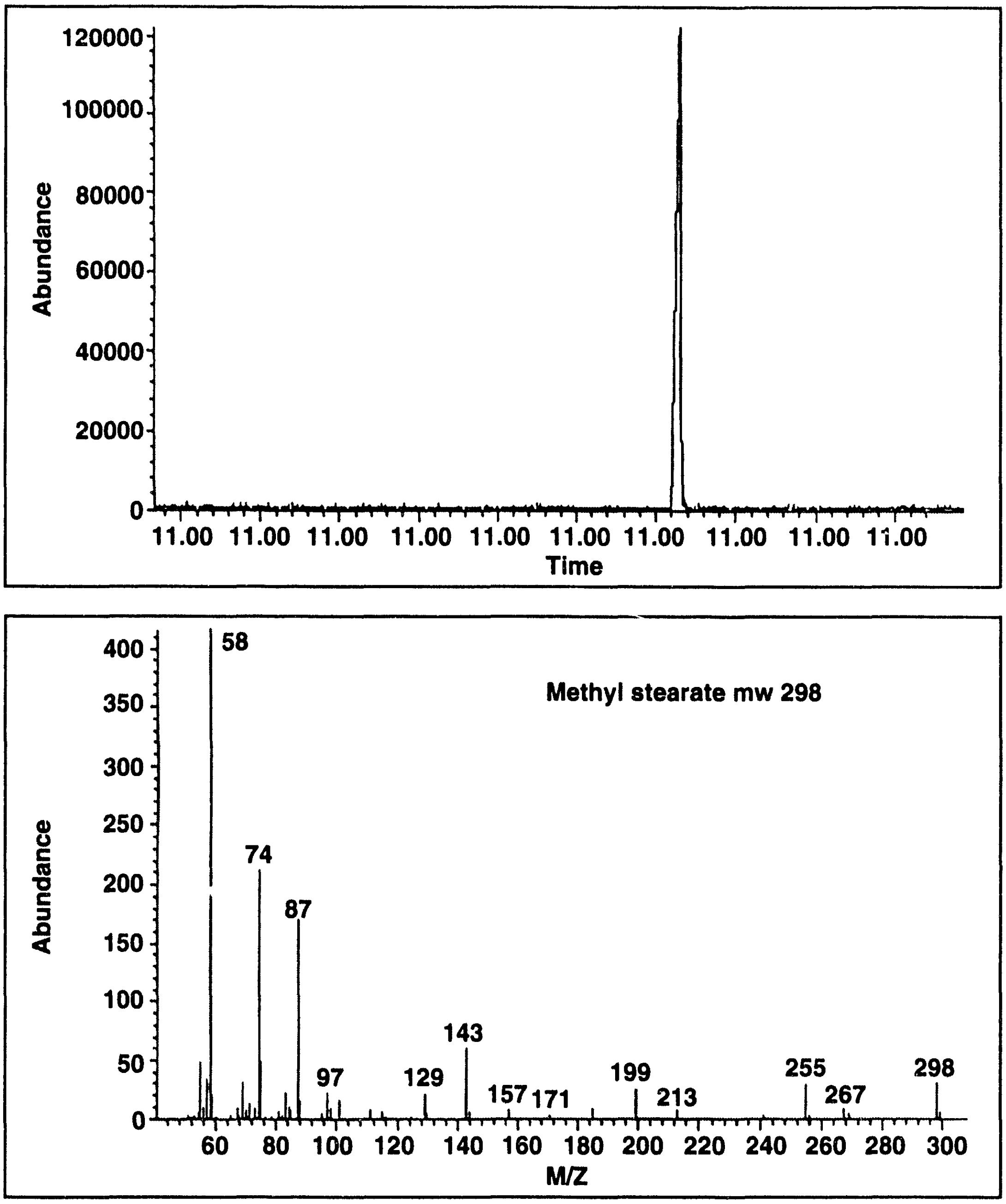

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Figure 11. Total ion chromatogram and selected ion plot of methyl stearate in hexane, 100 ng/μL. The total ion plot, peak height, and baseline noise clearly suggest a sensitivity limit better than 1 ppm.

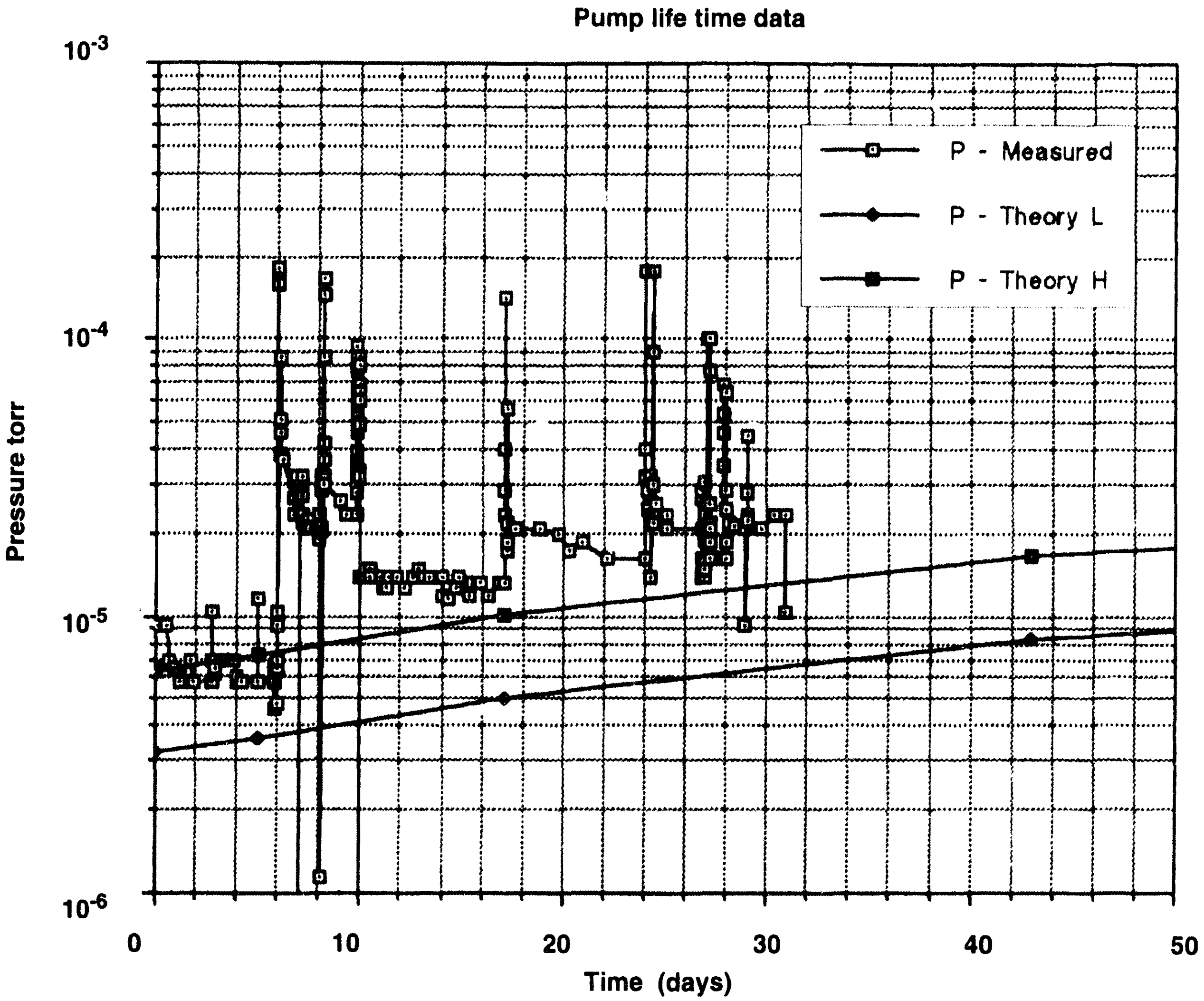

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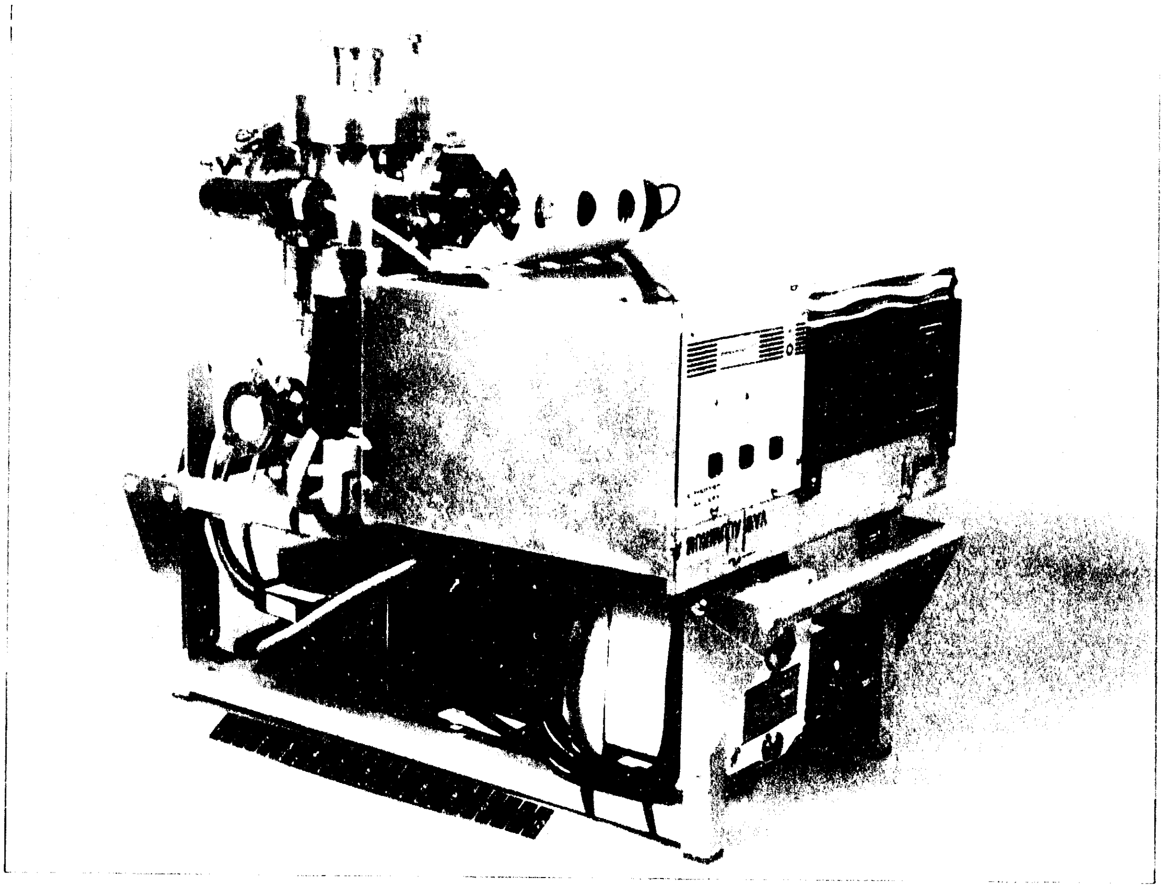
Figure 12. Vacuum system pump life time performance data for the stainless-steel system shown on the right in Fig. 4. As shown in the plot, the pressure was kept below 5 x 10^{-5} Torr with a continuous flow of hydrogen carrier gas. Even after large μL injections of solvent (CH_2CL_2), the pressure returned to a level more than adequate for operating the mass spectrometer (see peaks above). The theoretical empirical calculations of expected pump performance suggest that a useful continuously running GC-MS lifetime of <50 days is possible.

sample split ratios. During this lifetime study, a total solvent load equivalent to over 500 equivalent injections was successfully pumped by the new "getter" system. Solvent injection studies performed during this lifetime test indicated that that this new vacuum system configuration could handle injections that were 100 times the normal solvent loads expected (typical split/splitless 90%) injections.

Because of the tight vacuum design of the new MS housing, tests revealed that, with the carrier gas turned off, the ion pump alone could maintain vacuum pressures below 1 x 10^{-6} Torr for extended periods (months). Following a complete system shutdown, when the sorption and ion pump had been turned off for three days, the vacuum pumping system could be restarted without an auxiliary pumping station and the GC-MS made operational within minutes. Under these conditions, the sorption pump was able to bring the mass spectrometer from the milli-Torr range to the 1 x 10^{-6} Torr range in a few minutes.

Initial activation of the getter pellets requires that the pump and vacuum enclosure be pumped down to 1 x 10^{-4} Torr or better. To accomplish this, initial pump-down and activation of an auxiliary pumping station are required. The pumping station must be able to evacuate the portable chamber and maintain 1 x 10^{-4} Torr during getter pump activation. The pumping station we assembled to accomplish this is shown in Fig. 13. The station shown in the figure contains a 50 L/sec turbo and small backing pump. An added convection gauge



7C-K/1171-10

Figure 13. Experimental auxiliary pumping station used to prepare the suitcase GC-MS instrument for field use. For instrument evaluation, this pumping station was constructed with a convection gauge and ion gauge.

and ion gauge helped evaluate the instrument pump-down status. The convection gauge and ion pump on the instrument could be used to provide this information. Thus, only a simple pumping system without gauges is sufficient for initial pump-down and getter material activation.

During getter material activation, the getter pump temperature is raised to 480°C and held there for up to 1 hour. During the activation time, the mass spectrometer heater (and possibly the injector and GC column) should be raised to operational temperature. This will help expedite surface outgassing and eliminate some surface trapped water. Heating the internal mass spectrometer elements during this high-temperature activation cycle will permit a lower base starting pressure for the sorption pump material and reduce outgassing gas loads.

Summary

The development, evaluation, and field use of the suitcase instrument have demonstrated that a small, light-weight GC-MS instrument can be made that can analyze samples extracted from soil and water using appropriate chemical solvents. The demonstrated operational lifetime, along with the reduced weight and size, should make the portable GC-MS instrument a useful tool for emergency-response personnel trying to identify an unknown chemical spill. Also, the instrument would be of significant utility for firefighters in identifying potentially hazardous emissions from warehouse fires. Having a unit that can be carried by a single individual opens additional application possibilities. A study of the instrument hardware packing density has suggested that a unit about one-half the size of the existing suitcase unit is possible.

References

1. Brian Eckenrode and Russel Drew, "Indoor Air Analysis with a Spectratrak 620 Portable GC/MS Integrated System," *Proceedings of the International Symposium on Field Screening Methods for Hazardous Waste Site Investigations*, Las Vegas, NV, Feb. 1993, pp. 933-936.
2. G. Weiss, G. Baykut, H. P. Vetters, A. Brenkenfield, J. Loffelholz, G. Heinen, and J. Franzen, "Miniaturized GC Module for a Mobile GC/MS," *Proceedings of the International Symposium on Field Screening Methods for Hazardous Waste Site Investigations*, Las Vegas, NV, Feb. 1993, pp. 939-945.
3. N. S. Arnold, P. A. Cole, D. W. Hu, B. Watteyne, D. T. Urban, and H. L. C. Meuzelaar, "The Next Horizon in Portable GC/MS for Field Air Monitoring Applications," *Proceedings of the International Symposium on Field Screening Methods for Hazardous Waste & Toxic Chemicals*, Las Vegas, NV, Feb. 1993, Vol. 2, pp. 915-933.
4. "Report of the *Ad Hoc* Committee on Chemical Weapons to the Conference on Disarmament," *Conference on Disarmament*, CD/1108, Aug. 27, 1991.
5. "Draft Convention on the Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and on their Destruction," *Conference on Disarmament*, CD/CW/WP.400/Rev. 1, June 22, 1992.
6. E. A. Tanzman, B. Kellman, and R. Stockton, "Harmonizing the Chemical Weapons Convention with the United States Constitution," Defense Nuclear Agency Technical Report DNA-TR-91-216, Nov. 1, 1991.

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