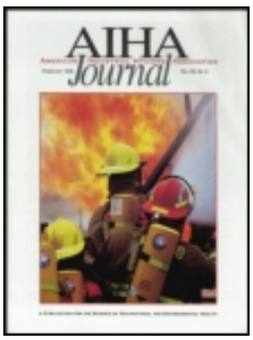

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A Field Deployable Gas Chromatograph/Mass Spectrometer for Industrial Hygiene Applications

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To study the feasibility and efficacy of field gas chromatograph/mass spectrometers (GC/MS), the National Institute for Occupational Safety and Health (NIOSH) conducted laboratory and field testing of a commercial transportable GC/MS. That unit was reengineered and reconstructed by NIOSH as a more portable GC/MS (can be moved, set up, and operated by one person), incorporating novel weight and size-reducing vacuum technology. Further laboratory and field tests were then accomplished. This NIOSH-developed vacuum technology has proven important in reducing the size and weight of the GC/MS by up to 50%, making it much more suitable for field use. Experience has shown that for a large class of survey situations involving monitoring of components of complex mixtures of vapors and gases field use of GC/MS can be very useful.

Keywords: GC/MS, gas chromatography, mass spectrometer, portable

The National Institute for Occupational Safety and Health (NIOSH) has had a continuing interest in the possibilities of constructing portable mass spectrometers for industrial hygiene applications.

The needs for bringing such laboratory instrumentation to the field include an ability to rapidly determine the chemical constituents of complex mixtures of vapors and gases; to measure concentrations of specific vapors in complex mixtures as a function of time and location, when simpler instruments are inadequate. It could also enable conducting real-time surveys for selected components of complex mixtures using single ion monitoring and direct atmospheric sampling (this is dependent on an initial GC/MS study of the sample matrix to identify ions uniquely associated with specific components.) Sample tube "problems" for certain chemicals may also be avoided by the use of direct injection techniques. The availability of field GC/MS data could be important to the selection of instruments and survey techniques used to complete a field study. It may also allow modifications to survey procedures in reaction to short-term survey results, not normally allowed by alternative laboratory analysis of sampling tubes.

Early NIOSH efforts included the commissioning of two feasibility studies in 1980 with Varian Associates, Inc.[1] (Palo Alto, Calif.) and the Jet Propulsion Laboratory (JPL) of the California Institute of Technology (through an agreement with the National Aeronautics and Space Administration).[2] In each case the objective of the study was to propose designs for a portable mass spectrometer (MS) to meet specified performance goals. Basic subsystems of an MS were reviewed, including inlet systems, ion sources, mass analyzers, ion detectors, vacuum systems, and data acquisition, processing and display systems.

FEASIBILITY STUDIES

JPL Study

The JPL study indicated that three types of inlets were feasible: direct atmospheric sampling, sequential analysis of desorbed samples from enrichment cartridges, and the use of gas chromatograph (GC) columns for preselection of the elutant from an enrichment cartridge. The mass selector proposed was a Mattauch-Herzog double focusing magnetic sector design originally intended for space applications. It used an electron impact low conductance ion source and a special electro-optical detector, which consisted of a microchannel array coupled to a phosphor coated fiber-optic array coupled to a photodiode detector array.[2] Recently, JPL authors have described further combination gas chromatograph and mass spectrometer (GC/MS) development work similar to the above.[3]

Varian Study

The Varian study covered additional theory related to MS design. It was concluded that detection limits of materials are related to the partial pressure of the gas in the ionizer. The ionizer would normally be restricted to an upper pressure limit of approximately 10^{-5} Torr. It was indicated that typically, for adequate ion currents to be generated for detection, a concentration of greater than 1 ppm would be required at the MS inlet. Thus, for many applications an efficient real-time preconcentrator would be important to the success of a portable MS. Varian proposed a multistage silicone rubber membrane inlet system, stating that nearly all materials found in the vapor phase in air are dissolved well in silicone rubber. For example, normal hexane, or the chlorinated alkanes, are transmitted through the membrane with a preference of a factor of 1000 relative to the air gases. However, some compounds are not transported well across the membrane, including amines and acid gases. Results of the study showed that an enrichment factor of 10^6 could be achieved for a practical three-stage membrane separator.[1]

The mass analyzers examined by Varian were magnetic sector, quadrupole, and Fourier transform ion cyclotron (FTIC) types. Ion vacuum pumping on the analyzer section was proposed due to weight constraints. The results of the study indicated each of the three analyzers was feasible, with similar sizes, weights, power consumption, and volume production costs. The quadrupole was the most directly applicable, the FTIC required the most development work, and the magnetic sector system required the production of a special rare earth magnet to make a unit of practical size and weight. Varian also proposed a novel method for adding real-time GC to the inlet, using a thermally pulsed capillary column. It was reported that this was tried successfully on a prototype instrument and could greatly improve the specificity and sensitivity of the instrument.[1]

CURRENT STATUS OF TECHNOLOGY

Computer Technology

One of the big changes that has occurred since technology was reviewed in the JPL and Varian studies is in computer hardware and software. This allowed sophisticated data storage and processing not practical for earlier portable instruments. This is particularly important for multitask processing during the operation of an instrument and during processing-intensive tasks such as mass spectra library searches and the spectral deconvolution of FTIC raw data. Improved computers also enabled the commercialization of the FTIC by the Nicolet Instrument Corp., as a large laboratory system using a super-conducting magnet.

Mobile Field Laboratories

Some researchers have used laboratory GC/MS instruments in mobile field laboratories. One group used a Finnigan ion trap laboratory instrument for field use in detecting environmental pollutants. It was a relatively large and heavy laboratory instrument with a special short column GC inlet and was mounted in a mobile laboratory on a three-quarter ton truck.[4] In general, the ion trap mass detectors can be more sensitive than quadrupole mass detectors. However, they are usually best suited to the detection of known chemical species, as their mass spectra do not match those in the classical electron impact mass spectra libraries normally used for identifying unknown components. A large semitrailer-mounted commercial Sciex TAGA MS/MS unit has also been used for hazardous substance monitoring.[5]

Vacuum Technology

It was evident from these studies that fundamental limitations in the capabilities of the proposed instruments were related to the vacuum pumping systems. Both the Varian and JPL designs proposed the use of a small ion vacuum pump. A discussion of vacuum pumping in the Varian report mentioned the promise of combination turbomolecular and molecular drag pumps. The author speculated that a combination pump could, after initial pump down, pump directly to atmosphere, and also provide intermediate pressures for use with their proposed membrane separator. Unfortunately, the promise of direct-to-atmosphere pumping has not been realized. Turbomolecular pumps at that time were heavy and required several kilowatts of power to operate.[2] Vacuum system-related limitations were summarized in the JPL report: "A portable mass spectrometer-based analytical instrument has, by its size and weight limitations, very low pumping capabilities and therefore requires extremely low carrier gas flow rates and/or the use of a separator and effluent gas splitters." The JPL instrument, for instance, tolerated a gas load no greater than 0.005 Torr cm^3/sec. The ion pump flow rate capacity was very limited, meaning that use was entirely dependent on the exclusive use of a membrane separator or extremely low flow rates (0.0003 standard cm^3/min for JPL design). This could constitute an unacceptable limitation, due to membrane selectivity or an overall lack of instrument sensitivity. Also, the lack of an integral roughing pump would mean the instrument had no ability to recover from vacuum overpressures, which often lead to ion pump shutdown.

One of the major problems with portable MS instruments has been the compromises related to producing a vacuum system having sufficient pumping capacity available at several pressures for the operation of both the analyzer (high vacuum) and inlet systems (intermediate pressures). The high vacuum pumps often require intermediate pressure pumps for either start-up or backing. Most intermediate pressure pumps are rotary vane oil-sealed mechanical pumps, weighing a minimum of 8 kg. The oil in these pumps can also cause shipping problems. To help reduce vacuum system-related size and mass problems, some alternatives to present methods were considered, including the use of a lightweight cryosorption intermediate pressure pump and a small peristaltic backing pump. To help reduce the size and weight of field-deployable GC/MS instruments, development of both of these pumps was undertaken by NIOSH. This resulted in working models of the two pumps, and U.S. patents for each. The cryosorption pump was based on the use of a small, closed cycle cryorefrigeration system and a zeolite molecular sieve material.[6] The miniature peristaltic backing vacuum pump would successfully back a variety of high-vacuum pumps usable in portable instruments.[7]

Current Research on Portable GC/MS Units

Researchers at the University of Utah recently presented a design of a "Man-Portable" GC/MS, based on the use of a capillary column transfer line GC, the use of a Hewlett-Packard Co. (Palo Alto, Calif.) Model HP 5971A mass analyzer, an Alcatel Vacuum Products, Inc., (Hingham, Mass.) Model 5010 molecular drag pump, a laptop computer, and a vacuum storage tank for use in place of a backing pump for the molecular drag pump.[8,9] Researchers at Lawrence Livermore National Laboratory reported on their attempts to produce a portable GC/MS.[10]

Commercially Produced Field Deployable MS Systems

Bruker-Franzer MEM and EM640

Bruker-Franzer (Bremen, Germany) produced a transportable

GC/MS (model MM1) for chemical and biological warfare agent monitoring. This was a vehicle-mounted device having approximately 51 × 76 × 69 cm dimensions and a mass of approximately 180 kg. It was offered commercially as the MEM and was recommended for environmental monitoring.[11,12] Bruker also produced the EM640 Mobile Mass Spectrometer, with dimensions of approximately 55 × 45 × 35 cm and mass of approximately 70 kg. It used a quadrupole analyzer and an ion getter high-vacuum pump (with no internal roughing pump). Due to limited vacuum pumping capabilities, it is necessary that all samples be introduced through a membrane separator. The GC portion used either a 3.5 m fast GC-separator module, or a 20-m column, and N_2 or filtered air as a carrier gas.[13]

Leybold QAS100

Leybold A.G. Co. (Cologne, Germany) produced the QAS100 gas analysis system. It was an MS-only device, and included a 100 amu range, an integral turbomolecular vacuum pump, a variety of available inlet designs (a selective diffusion membrane, a capillary for direct atmospheric sampling, or direct sample introduction), a specially designed ion source to suppress CO production, and a computer control system with some data-handling software. It was supplied in two modules with dimensions and masses of 25 × 32 × 46 cm, and 37.5 kg and 45 × 13 × 45 cm, and 12.5 kg. No shipping containers were included. It was intended for use in a variety of applications including environmental monitoring. The QAS100 was not produced past an initial 25 units, due to a lack of sufficient customer interest.

V.G. Petra Survey

V.G. Gas Analysis Systems (Wythenshawe, Manchester, England) produced the Petra Survey MS, configured for use in industrial hygiene applications. It was packaged in two approximately 56 × 56 × 20 cm units and weighed approximately 20 kg and 35 kg. About 21 kg of that was due to the ion vacuum pump and its back-up battery. It had no internal roughing pump. A single-stage silicone preconcentration membrane was used at the sample inlet to reduce vacuum pumping requirements.

Viking SpectraTrak 600

In the consideration of developing a portable MS or GC/MS for field industrial hygiene applications, certain mass-sensitive detectors used with laboratory analytical instruments (usually GCs) were examined for their potential as portable MSs. Of particular interest was the Hewlett-Packard Co. Model HP 5971A mass selective detector, due to its performance specifications, weight, size, and vacuum system. The 650 amu mass range, with 0.5 amu resolution, excellent software, and its 20-kg weight and 34 × 17 × 65 cm size (less computer) made it attractive for incorporation as a module in a portable instrument. In 1990 the Viking Instruments Corp. (Rockville, Md.) produced the SpectraTrak 600 transportable GC/MS.[14] The MS portion was a HP 5971A mass selective detector, with minor modifications, a small Alcatel turbomolecular high-vacuum pump (Model 5081), and an Alcatel Model 2002B oil-sealed rotary vane backing pump. The instrument appeared to have many desirable features, including the direct injection of samples and an automated GC inlet system for GC/MS analysis of preconcentrated samples from thermal desorption of sample tubes. The unit also allowed direct MS analysis of atmospheric samples introduced through a single-stage silicone membrane separator. This allowed continuous real-time monitoring of one or more chemicals, using selected ion monitoring, provided the selected analytes had unique ions associated with them. Figure 1 shows a flow diagram of the unit. The main module had dimensions and a mass of approximately 35 × 53 × 78 cm and 55 kg. It also had an approximately 51 × 68 × 99 cm (20 kg) shipping crate, a backing pump (approximately 14 kg in its 30 × 30 × 45 cm shipping container), and a cart (approximately 6 kg), for a total mass and volume of approximately 95 kg and 0.38 m^3. The cost for the first generation of the instrument was approximately $125,000. The device's dimensions and mass discouraged its use for field industrial hygiene activities; however, the combination of instrument capabilities otherwise appeared to be similar to those that had been considered as desirable.

For purposes of this study, it was felt that a field portable instrument should be able to be moved and assembled by a typical industrial hygienist. This suggested that no single module of the instrument should weigh over approximately 27 kg (60 lb), including its shipping container. Convenient container handles and wheels on the container would be desirable

MATERIALS AND METHODS

An MS alone has significantly less versatility than a combination GC/MS. Where sample matrices are relatively constant and known via laboratory GC/MS analysis of samples, and when it has been determined that certain ions can be uniquely associated with the analytes of interest, using an MS could be adequate and at a lower cost than a more versatile instrument. This has been successfully done around certain manufacturing processes and in certain established bioassay procedures.[15–17] However, following a review of the needs of field industrial hygiene studies, it became increasingly apparent that some type of preseparation of chemical species prior to introduction to the MS would be necessary for the MS to identify the components of complex mixtures and to allow field identification of ions unique to a specific analyte in a mixture.

As the Viking SpectraTrak 600 appeared to be the commercial device closest to meeting all needs, it was decided that one should be purchased to gain experience with field use of a GC/MS, and to serve as a platform for changes found necessary for its use in field industrial hygiene applications. Initially, several months were spent learning to use the instrument, as well as dealing with many instrument malfunctions, including (a) failure of the computer display, (b) failure of the oven heater to follow programmed temperature profiles, (c) failure of the injection heater, (d) leakage of injection ports, and (e) two failures of MS quadrupole heaters. Following the first airline shipping of the instrument, the high-vacuum pump had separated from the MS analyzer vacuum manifold. Considering the complexity of the instrument and that it was new in the marketplace, these problems could be considered normal.

A series of tests was established to determine whether the instrument was functioning properly. These included tests of the instrument's limits of detection for several compounds (acetone, toluene, xylene, benzene, and methylene chloride), using the three means of introducing samples into the instrument. After determining that the instrument was working properly, researchers took it to field industrial hygiene study sites to gain experience and determine its usefulness in such applications. Those sites included (1) an industrial manufacturing facility using 1,1,1-trichloroethane as a cleaning agent, (2) a facility for cleaning of petroleum hauling barges, (3) a furniture paint stripping facility, (4) a facility for dry cleaning of clothes, and (5) a facility for printing on flexible vinyl material. After gaining operating experience with the instrument, a general approach was developed for field use. This included

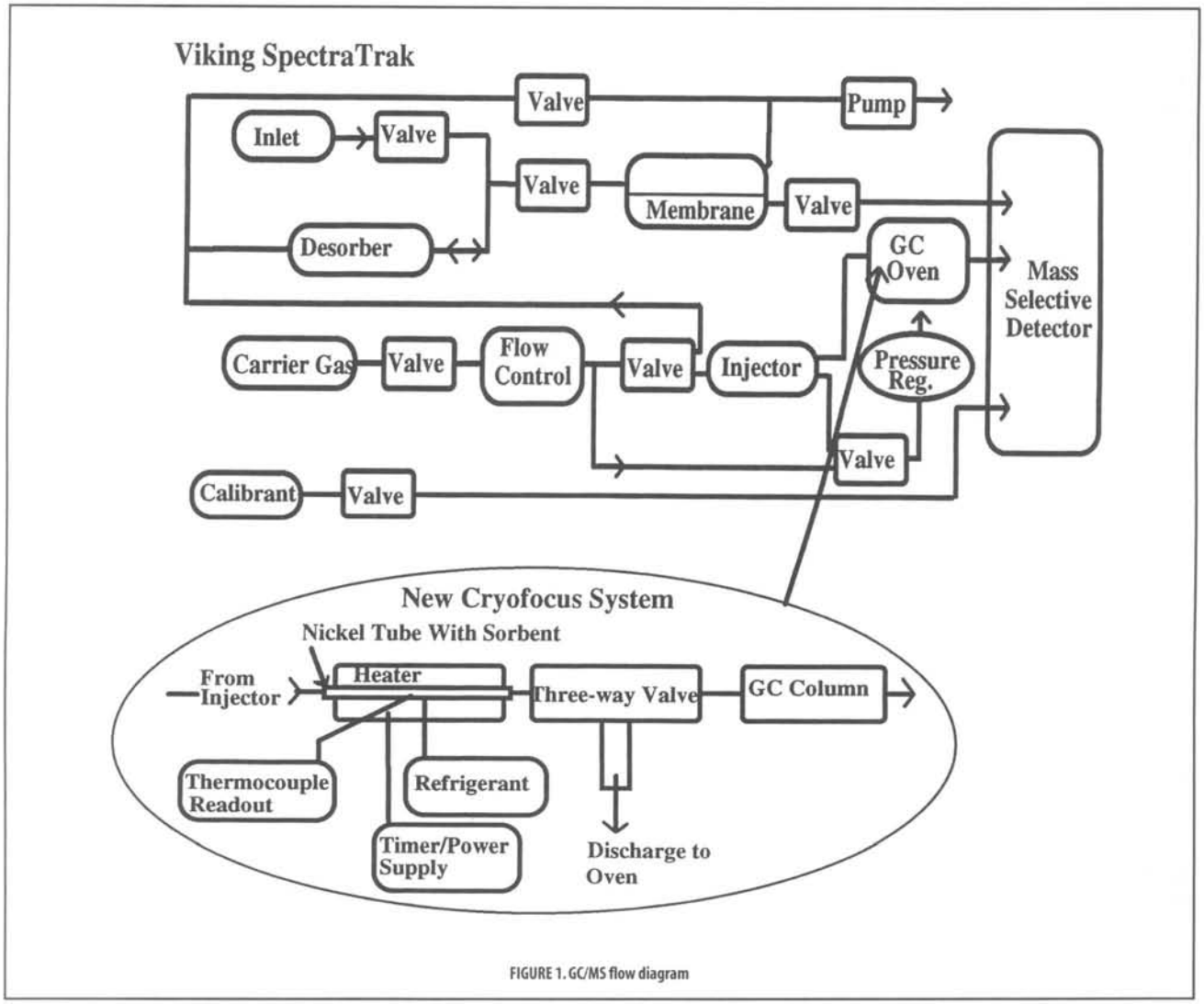

FIGURE 1. GC/MS flow diagram

gathering information from the facility on the chemicals used that were likely to produce significant workplace airborne gases and vapors; performing initial laboratory studies using samples of those chemicals, including making gas standards to see what their detectability was, and to establish an analysis method (sample introduction, temperature programming of GC; and choosing ions that were likely to uniquely identify the materials in a given sample matrix). The first on-site analysis would normally be of a representative sample of the air being monitored, using GC/MS. By observing selected ion chromatograms, and with the knowledge of which chromatographic peaks represented specific analytes, it could be determined whether a selected ion uniquely represented that compound in that specific sample matrix. That analysis would also indicate whether other unanticipated analytes were evident. Following a successful selection of ions unique to the analytes of interest, real-time monitoring of workplace air would be possible using selected ion direct MS analysis (via silicone membrane inlet).

Redesign and Reconstruction of GC/MS

Following the first four field studies with the GC/MS, major changes were made to the instrument to make it easier to use in field studies. Due to the sample processing problems identified in the first two field trips, some changes were made to the GC inlet. One change consisted of the design and construction of a miniature cryofocusing/flash desorption assembly placed in the oven between the GC injection port and the GC column head. An existing cryofocus trap consisted of a refrigerated section (approximately 2 cm) of GC column at the start of the GC column. This trap did not produce consistent trapping of a wide variety of materials. Its warm-up was slow, and its small bore was prone to plugging due to the freezing of water vapor desorbed from sample tubes. The new cryofocus trap (see Figure 1) contained a small amount of Tenax® GR sorbent placed in an approximately 1-cm length of a 1-mm bore pure nickel tube. The tube was enclosed in a high-power nichrome heating coil that was ballistically heated with a constant current. This allowed the trap to be heated to approximately 200°C in 5 sec. The trap then cooled to oven temperature. The temperature of the nickel tube at the location of the sorbent was monitored with a small thermocouple brazed to the nickel tube. During trapping, the trap was cooled using a low environmental hazard fluorocarbon refrigerant. A nozzle in the oven directed the liquid refrigerant onto the trap, maintaining its temperature at the approximately –30°C boiling point of the refrigerant. Between the cryofocusing assembly and the column head was a three-way valve, which allowed the injection of large-volume air samples through the cryotrap without the air going onto the GC column. The valve also allowed the desorption/purging of the cryofocus sorbent prior to introducing a new sample. In each of those cases the valve was opened, providing a low-resistance path out of

the valve port and into the GC oven (as compared to the high resistance to flow into the column head) for gas passing through the cryofocus trap. The valve was then closed, allowing flow gas and flash desorbed sample from the cryofocus trap to pass into the column head. Laboratory tests of the modified inlet showed that it could cryofocus the contents of 10 cm^3 air samples in approximately 4 min. That sample could then be thermally desorbed in approximately 5 sec. This resulted in a substantial reduction in sample processing time, while significantly improving chromatographic resolution.

Other changes involved splitting the main unit into two parts: GC/MS hardware, and computer. The miniature peristaltic backing pump[7] was incorporated directly into the GC/MS unit, replacing the separate oil-sealed rotary vane backing pump. The MS analyzer vacuum housing was redesigned to smaller dimensions and mass. High efficiency, low mass power supplies were adapted for use in the unit. A 250 L/sec Varian Model V250 combination turbomolecular-molecular drag high-vacuum pump was substituted for the Alcatel 60 L/sec turbomolecular high-vacuum pump, greatly increasing the pumping capacity of the unit. High-power heaters (GC oven, transfer lines, etc.) were converted to 110 V operation. The original computer was very slow, causing much wasted time. Its display was also difficult to see in bright lights and to view off angle. A higher performance computer (Dolch Computer Systems, Milpitas, Calif., Model PAC 486-33) was substituted for the original. It was selected based on its rugged construction, its small size and mass, its superior screen visibility, and its capacity to accept the necessary interface boards for the GC/MS. It was upgraded with a 486 DX 100 processor, and two 1-gigabyte hard disks (one used to back up the other). The chassis for the GC/MS was also redesigned to be lower mass. A new combination shipping case and cart was designed and constructed (see Figure 2). All of these changes resulted in a substantial reduction of size and mass while significantly improving the performance of the instrument. The main instrument had dimensions of 27 × 45 × 50 cm, and a mass of approximately 27 kg. In its shipping container (also used as a cart for the instrument), it had dimensions of approximately 43 × 53 × 63 cm and a mass of approximately 34 kg. The computer had dimensions of 21 × 24 × 39 cm and weighed approximately 7.7 kg. In its shipping case (also used as a seat for operator, as shown in Figure 2), it had dimensions of 34 × 46 × 57 cm and a mass of approximately 10.5 kg. The total mass and volume of the instrument was approximately 45 kg and 0.23 m^3. This represented a reduction of approximately 50% in mass and volume from the SpectraTrak 600. An interior layout of the redesigned GC/MS is shown in Figure 3.

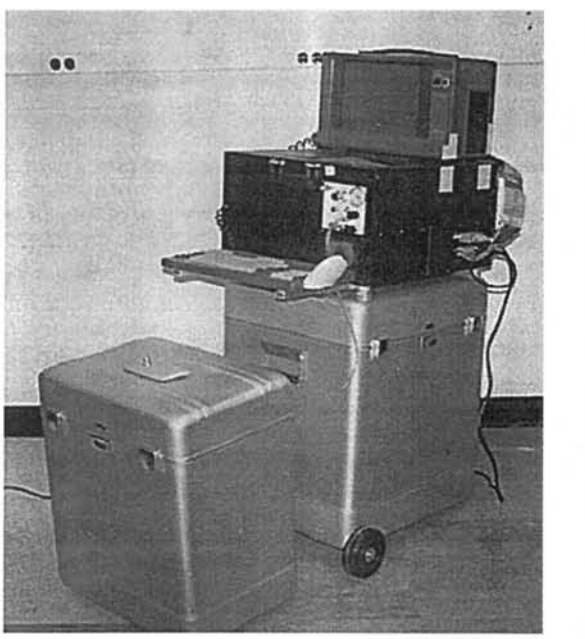

FIGURE 2. NIOSH-redesigned GC/MS on shipping container/cart

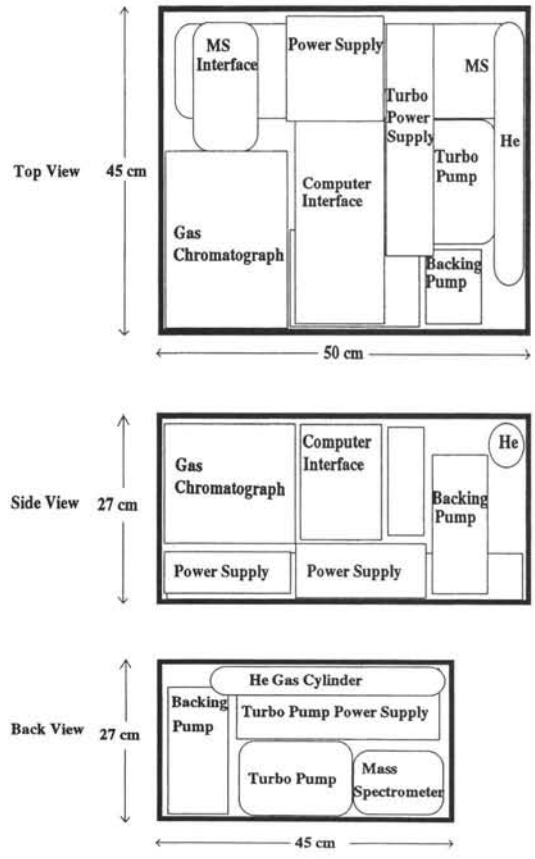

FIGURE 3. Interior layout of NIOSH-redesigned GC/MS

Assembly and Startup of GC/MS

The assembly and power-up of the GC/MS typically took approximately 10 min. This was followed by an initial vacuum system pump down, which could take from 5 to 40 min, depending on whether the analyzer section had lost vacuum during transportation. After operating vacuum was established, the MS quadrupole heaters started, and typically achieved operating temperature within 10 min. This would normally be followed by a 5-min purge of the vacuum system with helium flow gas to eliminate residual air, and an autotune of the MS analyzer, taking another 5 min. Thus, the time to get started with field measurements could typically range from approximately 30 to 60 min.

Measurement Error

The principal measurements in this study were ion chromatograms from GC/MS samples and selected ion graphs showing concentrations of analytes as a function of time. Error and bias

associated with the results of GC/MS analysis can be difficult to characterize. While certain specific parameters of the instrument can be characterized, the bias and error associated with the total analysis process are complicated by the large number of variables involved, including the substantial bias and error that can be associated with the operator of the instrument and the preparation and introduction of the sample. Where many samples of a given type and with identical analysis procedures are to be analyzed routinely, repetitive quality control runs performed using standards replicating the standard sample matrix can be performed, and statistics associated with the analysis developed. However, for typical field use of the instrument where analytes of interest, sample matrices, and analysis procedures vary widely, and relatively small numbers of replicate analysis are performed, the investment of time and resources to develop dependable statistics associated with a particular analysis type may be impractical. In such cases conservative estimates of performance statistics must be made, based on long-term experience with the instrument and similar analysis. To give readers an idea of what may be expected, a few estimates of performance statistics are included, based on the author's experience. In the case of GC/MS chromatograms, the principal source of error is associated with the time position of a given chromatographic peak, and the intensity of that peak. With careful operation, chromatographic peak time position should have a random error typically less than ±10 sec (2σ), and a bias < 3 sec. Using m/z scanning over a range of approximately 250 amu, the peak intensity may have a random error of ±100% (2σ). Thus, quantification using scanning GC/MS is not excellent. For the selected ion direct MS real-time measurements, the principal source of error is in the relationship between the ion signal and the concentration being measured. Using calibration samples at the start of each sampling run, random error is typically < ±10% (2σ), and bias < 5% (error in producing standard concentrations).

Results and Discussion

Parts Vapor Degreasing Operation

For the initial field study the instrument was taken to a local industrial manufacturing plant. During that survey Tenax-filled sample tubes were used to gather air samples around a parts vapor degreasing operation using 1,1,1,-trichloroethane. After thermal desorbing of the sample tubes, identification of the solvent was successful, using a mass spectral library search.

Cleaning of Petroleum Hauling Barges

In the second field study, the instrument was used as part of a field investigation of air concentrations of benzene associated with cleaning operations on petroleum hauling barges.[18] These barges were used primarily on the Mississippi River, and the barge cleaning facility was near New Orleans, La. For barges to be entered by personnel for cleaning operations, it was required that the atmosphere be tested specifically for benzene concentration. This was normally being done by marine chemists using indicator tubes. However, there were concerns in the marine chemistry community that the indicator tubes were not adequate. Others had proposed the use of a portable GC as a superior testing means. The author's study of the barge cleaning operations was conducted to compare the results of the two methods. The GC/MS was also included as an additional tool. In the study certain samples run by GC and sample tubes were also examined using GC/MS.

Figure 4A shows a total ion chromatogram and Figure 4B a selected ion chromatogram of Sample A from a barge carrying quench oil. In that case the single ion chromatogram (ion 78 for benzene) appears to appear almost uniquely at the benzene peak, and the mass spectrum (Figure 4C) is similar to that of benzene. Figure 4D shows a total ion chromatogram for Sample B from another barge. Several possible ions associated with benzene were selected for extracting single ion chromatograms from that file. Ion 78 yielded the most sensitivity and specificity (see Figure 4E); however, it clearly had substantial responses for materials present other than benzene. Thus, it was clear from the selected ion chromatograms that a unique ion for benzene did not exist for that sample matrix. Consequently, it was not possible to utilize the direct MS feature of the instrument (through the silicone membrane inlet) for real-time monitoring of benzene. The results of the GC/MS analysis indicated that there was more than benzene under the benzene chromatographic peak. This can be seen when the mass spectrum of sample data under the benzene peak (Figure 4F) is compared with that of Figure 4C. This was a clue as to why the GC methods did not produce consistent results. Similar results were later obtained using sample tubes and a laboratory GC/MS analysis.[18]

This study also demonstrated that the use of sample concentration tubes for preconcentrating samples prior to introduction to the GC/MS took unacceptable amounts of time (up to 1 hour/sample including prepurging of tube, desorbing tube, running GC/MS analysis, and postdesorbing the tube, thus preparing it for the next run). The thermal desorption of a sample tube also resulted in broadened chromatographic peaks. Moisture released from the sorbent typically precluded the use of the original cryofocus, due to column freeze-up.

Furniture Stripping

Next the GC/MS was taken to a paint stripping firm that had been the site of a previous NIOSH study. The paint stripping operation made use of several solvents, including methylene chloride, methanol, acetone, xylene, and toluene. It is possible there were some minor amounts of other solvents present that were components of finishes being applied to stripped furniture. Also, it was reported that there was a change in the stripper formulation, which added perchloroethylene and 1,1,1,-trichloroethane to the stripping mixture. In preparation for the survey, standards of the major components were produced by placing known amounts of the solvents in sample bags having known volumes of air. Subsequently, total ion chromatograms of these standards were run, and the positions of chromatographic peaks for the solvents were noted. Next, a sample of headspace gas from a sample of stripping solution was run, and both total ion and selected ion chromatograms were generated. From those it was possible to see whether ions could be selected that were unique for each of the solvents. It can be seen from Figures 5A–K that by selecting the following certain ions—acetone (58 amu), methylene chloride (84 amu), methanol (31 amu), toluene (92 amu), and xylene (106 amu)—a substantially interference-free simultaneous real-time sensing of these solvents could take place, using direct MS in the selected ion mode. Figures 6A–G show the total ion chromatogram and selected ion chromatograms for air above a stripping tank. It can be seen that several of the expected solvents were present. While there appeared to be a small amount of 1,1,1-trichloroethane (99 amu), there was no evidence of perchloroethylene (166 amu). It was subsequently learned that the use of those two solvents had been discontinued. An example of a survey using selected ion monitoring is shown in Figure 6H. The 84 amu ion associated (in this case uniquely) with methylene chloride was monitored with the air sample stream flowing across the silicone membrane of the MS membrane

separator inlet. This resulted in a real-time record of the 84 amu ion signal. This was calibrated with a standard concentration of methylene chloride in air, to yield methylene chloride air concentration in the sample stream.

Dry Cleaning

NIOSH has been investigating potential workplace hazards in dry cleaning establishments. During a visit to a large central dry cleaning plant, measurements of workplace air were made, looking for the principal solvent present (perchloroethylene [166 amu]), as well as some solvents used for spot removal purposes (1,1,1,-trichloroethane [99 amu], amyl acetate [70 amu], and 1,4-dioxane [88 amu]).

During the survey a bag sample of workplace air near a spotting table was analyzed by GC/MS to help determine its principal constituents (see Figure 7A). Selected ion chromatograms were made, readily identifying 1,1,1,-trichloroethane (a spotting solvent), and perchloroethylene (principal dry cleaning solvent) (see Figure 7B and C). Although not anticipated, it was found that trichloroethene was very likely present. This was based on a mass spectrum library search of the 9.7-min peak. Based on selected ion

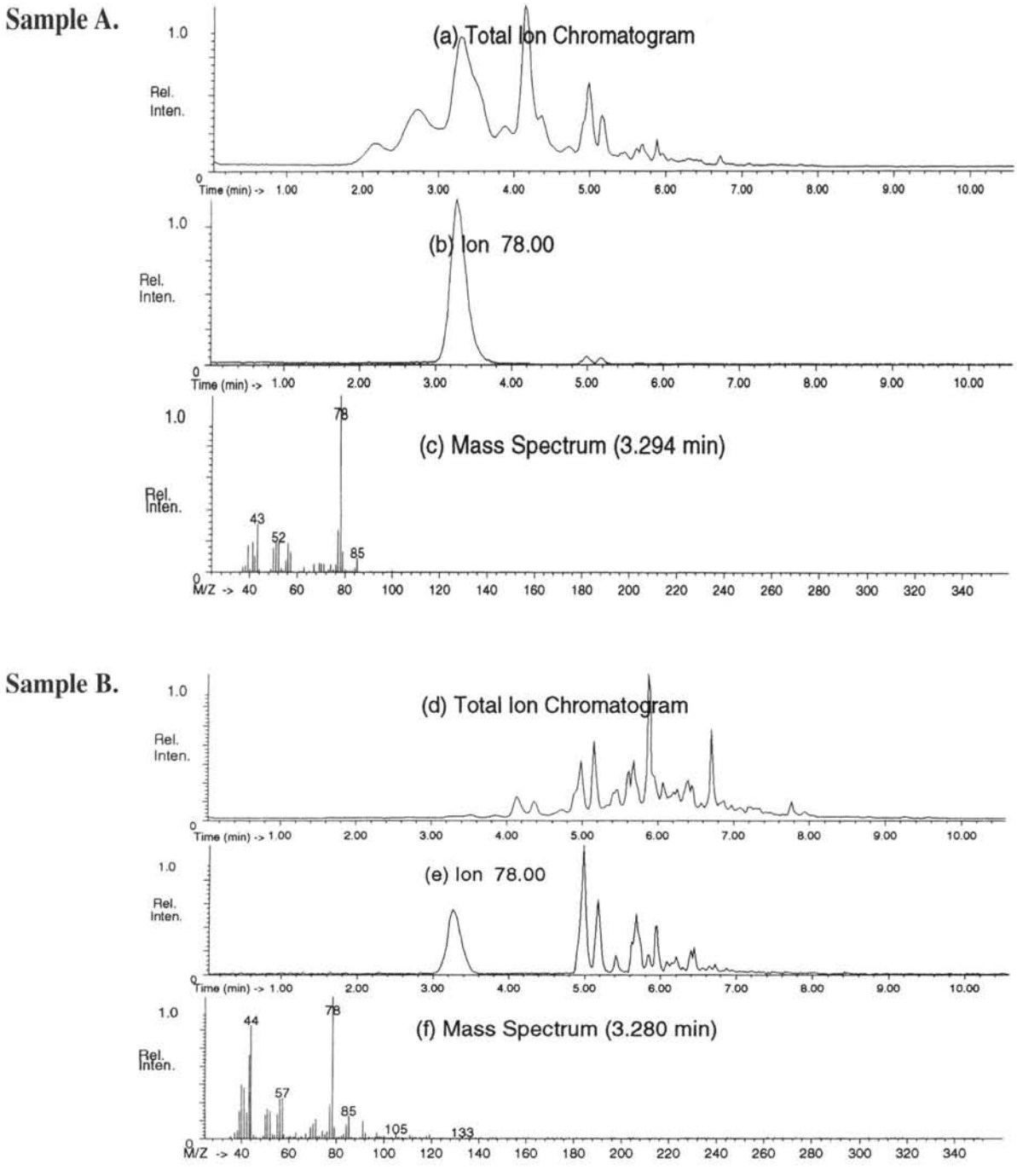

FIGURE 4. Ion chromatograms and mass spectra associated with vapors from a petroleum barge

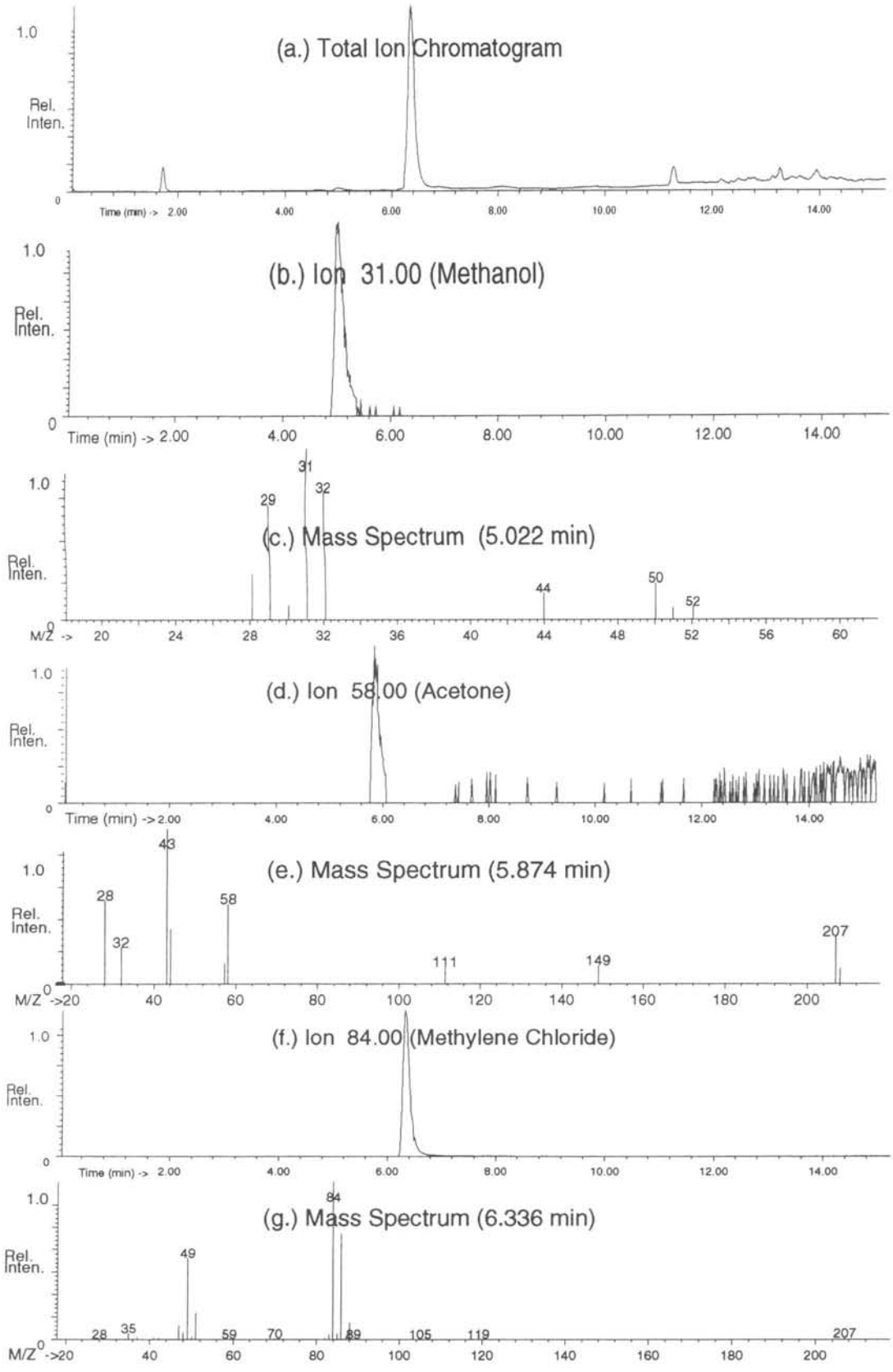

FIGURE 5. Ion chromatograms and mass spectra associated with stripping solution headspace vapors (continued)

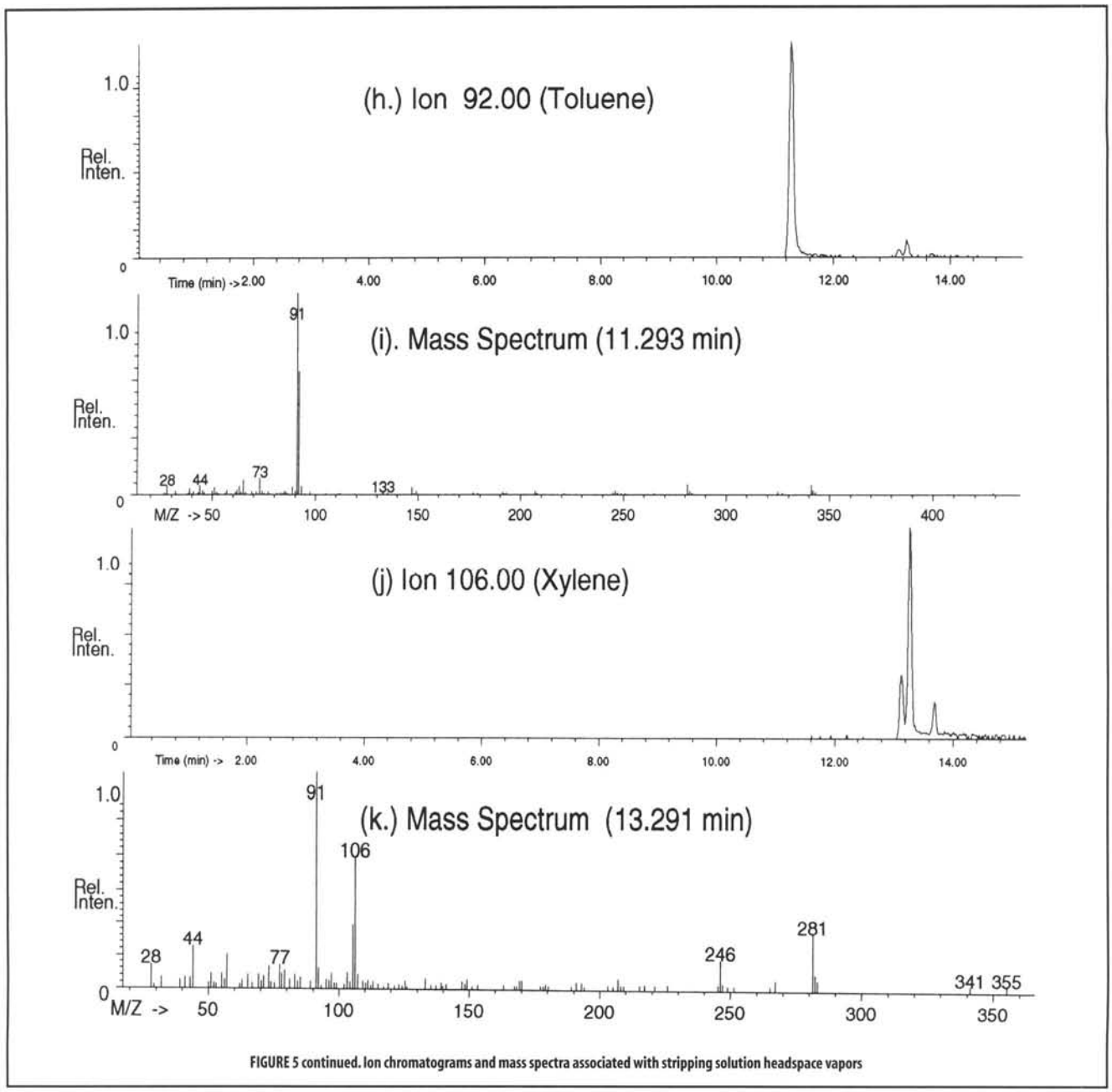

FIGURE 5 continued. Ion chromatograms and mass spectra associated with stripping solution headspace vapors

chromatograms using ions present in the trichloroethene library mass spectrum, the identifying ion selected for further measurements of trichloroethene was 95 amu (see Figures 7D and E). Its concentration was probably lower than perchloroethylene and 1,1,1,-trichloroethane; however, a calibration standard for trichloroethene was not available. Two commercial spotting materials (R.R. Street and Co., Oak Brook, Ill., Streetex and Picrin) were in use at the time of the survey. Amyl acetate and 1,4-dioxane were not detected. Real-time surveys were then conducted around solvent use areas. At the beginning of the measurements, pure air followed by 11 ppm perchloroethylene was introduced at the sampling port to establish a calibration reference. Figure 8A shows the concentration as a function of time of perchloroethylene for various areas around the dry cleaning machine and over clothes recently and just removed from the machine. Figure 8B shows a similar survey for 1,1,1,-trichloroethane near a spotting table while steam was applied on a treated spot. Figure 8C shows a survey for trichloroethene near the spotting table, while a mixture of two spotting agents was used. In a survey at another dry cleaning facility, perchloroethylene and Stoddard solvent were used in separate cleaning machines, as the principal dry cleaning solvents. These were separated chromatographically and unique ions identifying each solvent were selected.

Printing on Flexible Vinyl

NIOSH has been investigating potential worker health hazards at a facility that uses a silk screen process to print large images on a flexible vinyl sheet. The ink used relatively volatile solvents to produce rapid drying and secure adhesion of the image. This was necessary, as the printing process used several colors, each of which must dry before another is applied. The principal solvents were acetone (55%), methyl propyl ketone (MPK; 35%), and propylene glycol methyl ether acetate (PGMEA; >10%). Due to the nature of the printing process, large quantities of these solvents evaporated into the workplace air and produced time-weighted average concentrations close to or exceeding acceptable values. Worker personal respirators were being used as a temporary measure to lower worker exposure.

The GC/MS was used in this setting to produce real-time simultaneous measurements of the concentrations of the three principal solvents. This was useful, both in the workplace setting as well as in associated laboratory work, to study the evaporation of

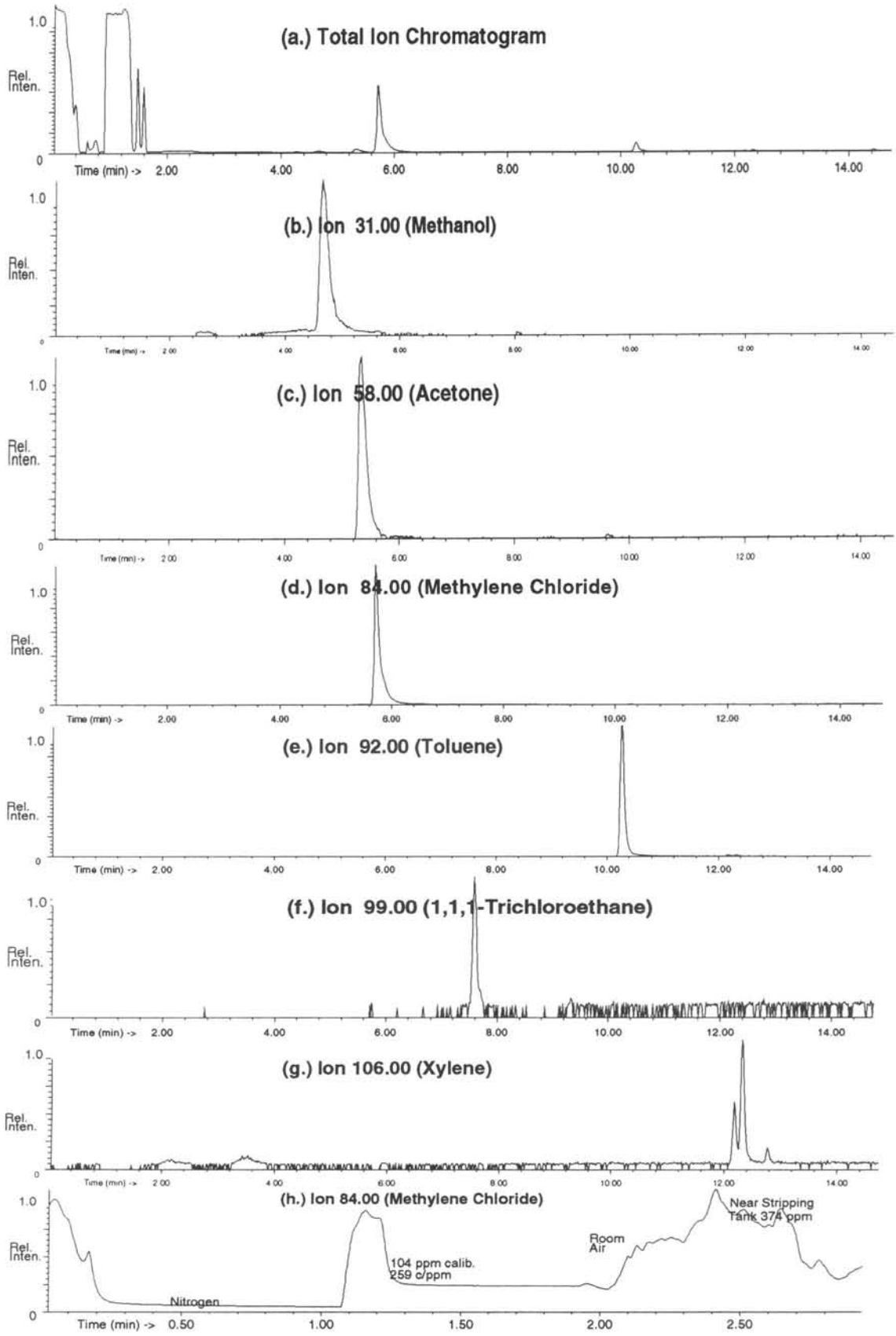

FIGURE 6. Ion chromatograms and selected ion monitoring associated with vapors above a stripping tank

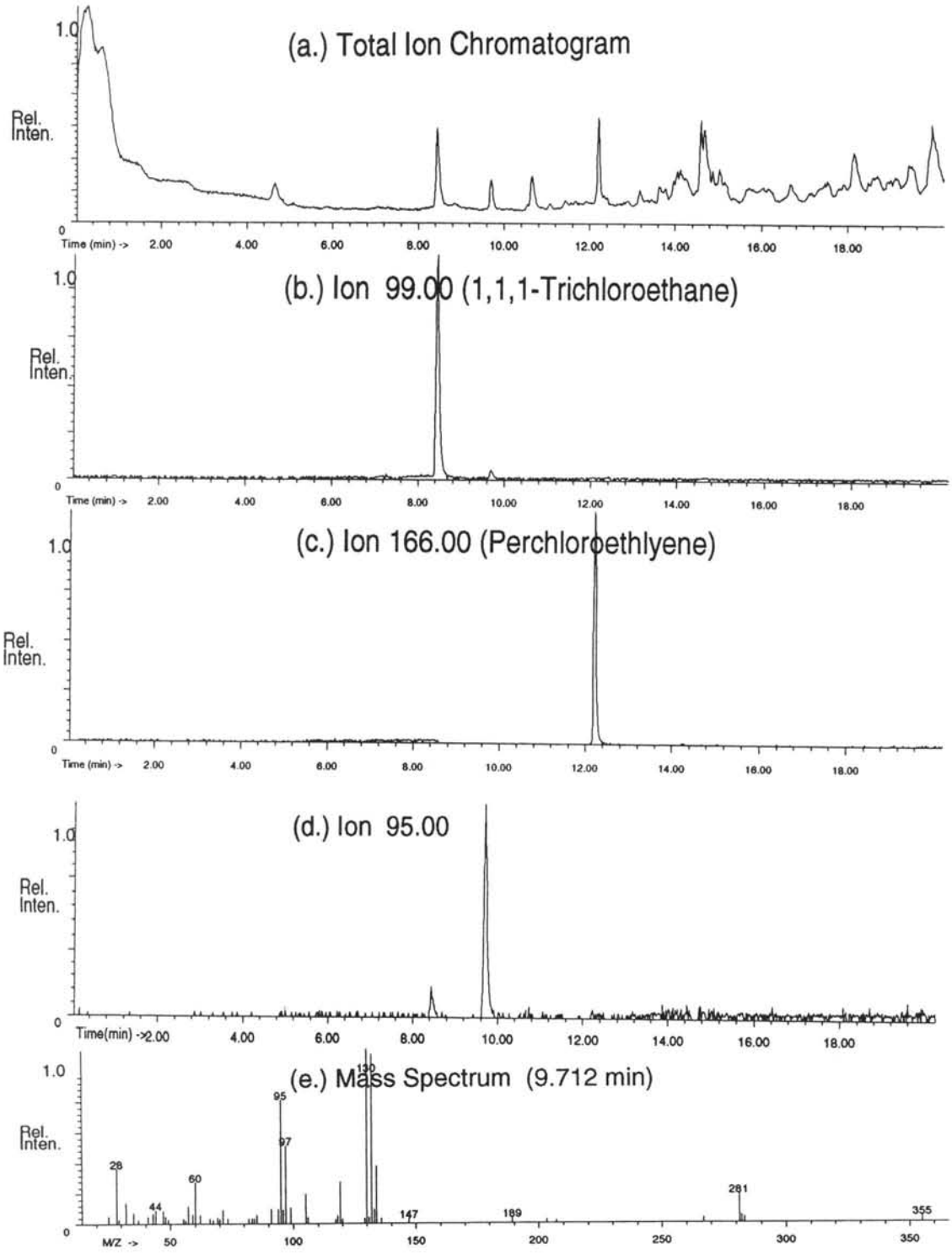

FIGURE 7. Ion chromatograms and mass spectra associated with air sample near spotting table

the solvent components from the printing process as a function of time after printing. This was also useful in designing control measures for the process. Figures 9A–C show a GC/MS analysis of workplace air, where the three components of the solvent are readily identified. The ions identified for the selected ion monitoring simultaneous measurement of the components was complicated by the fact that the principal identifying ions for acetone (43 and 58 amu) were present in the other two compounds. Those compounds had identifying ions unique to them (86 amu for MPK and 72 amu for PGMEA; see Figures 9D–F). By running separate standards of the three compounds, a ratio was established for the 86 and 72 amu ions to the 43 or 58 amu ion for MPK and PGMEA. Thus, in the selected ion monitoring mode for the 43 (or 58), 72, and 86 amu ions, the contribution to the 43 or 58 amu ion signal from the MPK and PGMEA was first calculated, and subtracted from the 43 or 58 amu total, leaving the remaining 43 or 58 amu signal due to acetone. This processing was done after gathering the data. Consequently, it could be said that the measurement of MPK and PGMEA concentrations was real-time; whereas, the measurement of acetone concentration was reconstructed later. However, it was time-coordinated to the MPK and PGMEA concentrations. Using this method, it was possible to measure the concentration of

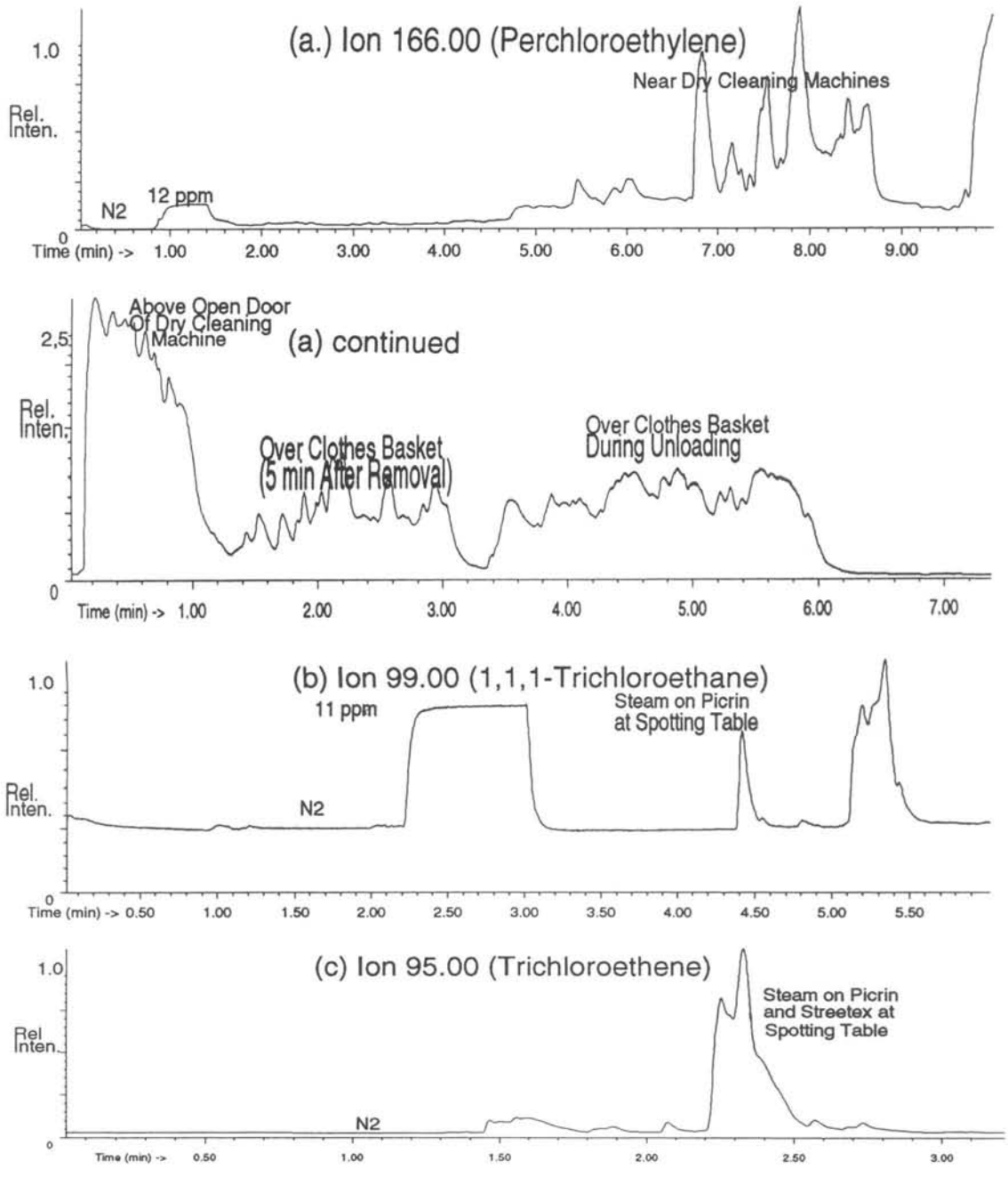

FIGURE 8. Survey for perchloroethylene, 1,1,1-trichloroethane, and trichloroethene in dry cleaning plant air

the three solvents as a function of time for a variety of exposure conditions. The resulting data made it possible to see that the ratio of the concentration of the three solvents changes significantly with the exposure conditions. As the allowable concentrations of the analytes were quite different, the data suggested that measurements with other types of survey instruments that did not independently measure the separate analytes would not be appropriate.

Considerations for the Field Use of a GC/MS

The competent use of a GC/MS requires significant operator training and experience. Potential users should have a physical sciences background, with experience in laboratory analysis. Specific training and experience in GC/MS analysis is also necessary. While training courses exist for orienting a user to a specific instrument, many months of hands-on experience must follow. In addition, a field instrument is more likely to have repair problems due to transportation trauma. Downtime would be minimized if the operator had significant experience in the instrument's maintenance and repair. It is unlikely that someone with modest training and only an occasional use of GC/MS would be able to carry out analysis tasks dependably.

It is clear that the cost of such an instrument (approximately $150,000) and the level of training required to use it preclude its use for a large class of field surveys. However, the results of this study indicate that there are circumstances under which it can be very useful for field GC/MS analysis, and when it uniquely allows real-time monitoring. In general, the field use of GC/MS could be appropriate when the sample matrix or specific analytes being monitored were such that other less costly real-time monitoring instruments were not appropriate. Other factors could include when

(1) the survey requirements are such that very large numbers of laboratory-analyzed sample tubes would be required (typically costing >$40.00 each),
(2) the logistics of the survey require immediate results to operate efficiently (such as when construction or decontamination crews are waiting for results), and
(3) field conditions of exposure, and the agents involved are unknown.

Under these circumstances, the GC/MS's sensitivity and versatility in identifying unknowns may justify its use.

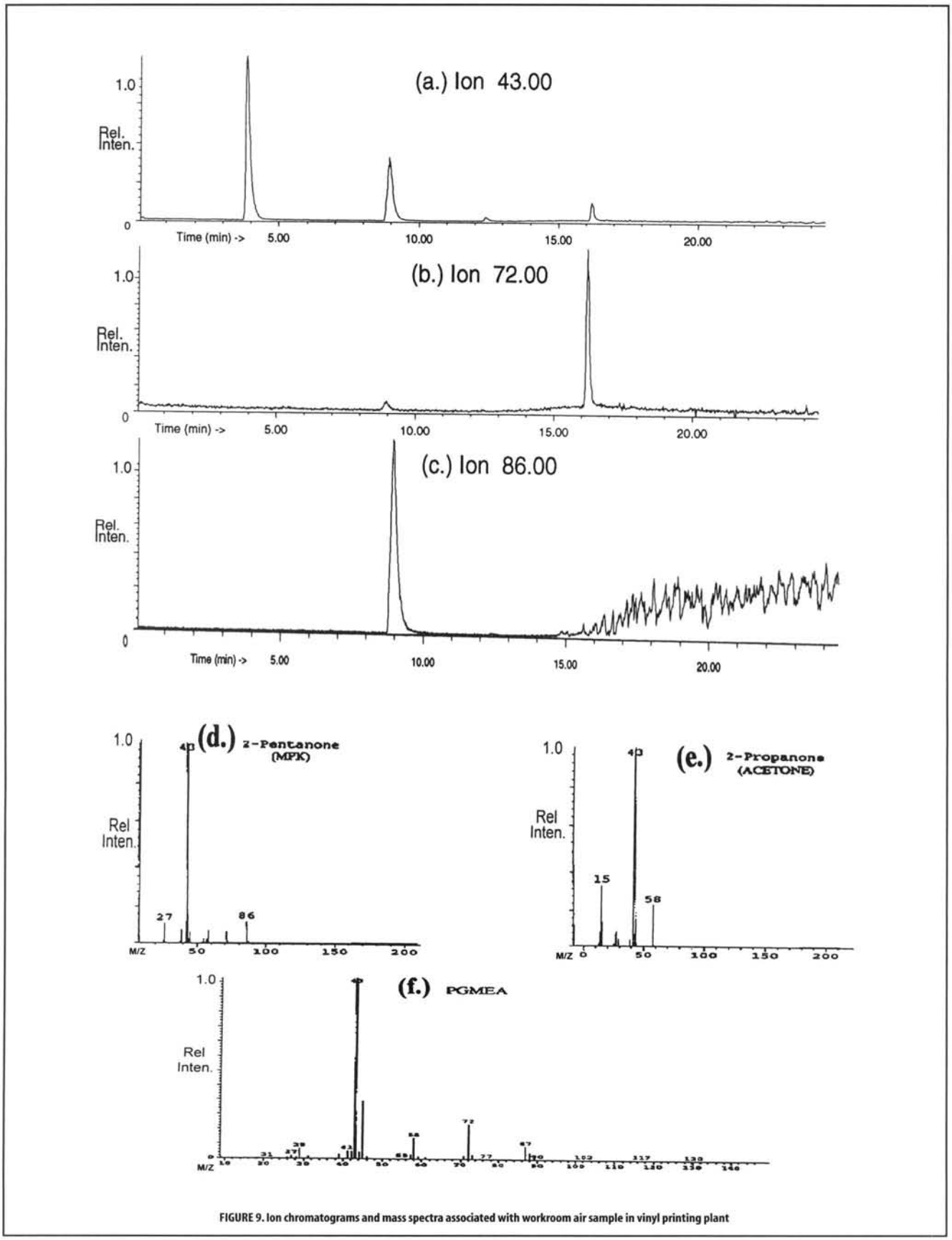

FIGURE 9. Ion chromatograms and mass spectra associated with workroom air sample in vinyl printing plant

CONCLUSIONS

In the author's limited field experience with the GC/MS, it was found that GC/MS always provided information useful to the study being conducted. The ability of the instrument to provide direct MS real-time monitoring of gases and vapors depends on the chemical matrix of the sample, as well as the sensitivity of the instrument for particular analytes. Under less ideal circumstances, all that could be accomplished may be to perform GC/MS analysis of either cryofocused air injections or highly concentrated air samples using sampling tubes, possibly yielding an identification of some significant pollutants present. Under more ideal conditions, this could result in the identification of ions unique to the principal pollutants of interest and allow direct MS simultaneous real-time monitoring of those. That was the case in three of the five surveys we conducted. The NIOSH-redesigned and reconstructed GC/MS, through its reduced size and mass and its improved capabilities substantially improved the ability to utilize a GC/MS in field industrial hygiene studies.

The field use of a GC/MS may be restricted by the cost of the instrument, the training required for the operator, and the technical capabilities of the instrument. Its use may be most appropriate when the cost of alternative analysis is very high (large numbers of laboratory-analyzed sample tubes), and/or the logistics of the survey demand real-time measurement capabilities and other real-time survey instruments are not technically adequate.

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