TRANSPORTABLE GC/ION TRAP MASS SPECTROMETRY FOR TRACE FIELD ANALYSIS OF ORGANIC COMPOUNDS

Chris P. Leibman, David Dogruel, Health and Environmental Chemistry Group, HSE-9,
Eric P. Vanderveer, Instrumentation Group, MEE-3 Los Alamos National Laboratory,
M/S K-484, Los Alamos, New Mexico, 87545

Abstract

A transportable purge and trap/GC/MS based on the Finnigan Ion Trap Detector (ITD) has been developed at Los Alamos National Laboratory for the identification and quantification of volatile organic compounds present at chemical waste sites. This instrumentation is being evaluated for use to support environmental surveillance and the characterization/clean-up of hazardous waste sites. A custom purge and trap/GC sampling system was integrated with a modified ITD to achieve instrument operation consistent with field activities. The sampling system is controlled by an ancillary microprocessor designed at Los Alamos National Laboratory. The instrument is extensively automated and can be operated with minimal training. Instrument operation transparent to the field user has been achieved by integrating sampling system control software with the operating software of the ITD.

The instrumentation and associated methods parallel those outlined in method 8260, SW-846. Qualitative and quantitative analysis for the 68 target compounds and the associated internal standards and surrogates is completed in an automated sequence that is executed every 25 minutes. Sample purging, analysis, data reduction, and preliminary report generation proceeds automatically. The instrument can be operated in a continuous mode, pausing only for sample loading and data file specification. All data are archived on floppy disk for subsequent review by a skilled analyst.

Part-per-trillion detection limits can be attained for many compounds from either 5 gram soil or 5 milliliter water samples.

Introduction

The development and use of field transportable analytical instrumentation can significantly reduce the cost associated with environmental surveillance and restoration activities. Field analytical support minimizes the analytical data turnaround time, which can expedite site characterization and provide analytical data to field personnel for guidance of ongoing work. Clean-up personnel can be used more efficiently since these teams will not have to be released and reassembled weeks later after receipt of analytical results from a remote laboratory.

Field analytical support can directly impact the expense of environmental clean-up by reducing the cost-per-analysis. Cost for sample packaging, shipment, receiving and management are eliminated if analyses are performed on site. Field analytical support improves the chances that schedules and monetary constraints associated with remedial activities are met.

Performing analyses on-site can enhance the quality of analytical data generated. Field analyses reduce the possibility that samples will be compromised from transport and handling. Reduced sample handling and the analysis of samples within minutes of collection minimizes the potential loss of volatile components. Near real-time data can also be used to direct subsequent sampling efforts. Additionally, initial site characterization can help delineate the sampling grid used for collection of samples to be sent to a remote laboratory.

A transportable purge and trap/GC/MS has been developed at Los Alamos National Laboratory to provide field analytical support for environmental restoration activities. The instrument is based on a Finnigan Ion Trap Detector (ITD)[1], a rugged and simple mass spectrometer. This transportable GC/ITD has been designed specifically to support field operations and to provide analytical data of sufficient quality to meet higher level data quality objectives. Our focus has been to attempt to meet the quality control criteria outlined in chapter 1 of SW-846 and to use procedures which parallel method 8260, SW-846.

Experimental

Purge and Trap/Gas Chromatograph

A custom purge and trap/GC was fabricated for sampling volatile organics in water or soil samples. The purge and trap/GC has two sampling loops, each loop consisting of a needle sparger and an adsorbent resin trap. A schematic of this sampling system is shown in Figure 1. In position A, simultaneous with the purging and concentration of one sample onto trap B the contents of trap A are desorbed onto the capillary column. Subsequent to the analysis of trap A, the ten port valve (Valco Instruments Co.) is rotated to position B

and the contents of trap B are desorbed onto the capillary while purging/concentration occurs on the other sampling loop. Backpressure regulation via a split maintains column carrier gas flow. Splitless injection is performed for 20 seconds during adsorbent trap desorption. This is sufficient for quantitative transfer of trapped target analytes while serving to minimize water transfer to the analytical system. Additionally, the capillary column is maintained at 10 °C during desorption. This serves to cryofocus target analytes onto the head of the column while allowing any water to pass unretained.

The adsorbent traps are packed with equal amounts of 2,6-diphenylene polymer and silica gel. Traps are heated to 200°C at a rate of 500°C/min. Heater jackets are provided for the 5 milliliter sparger tubes and maintain a purge temperature of 35 °C. The temperature programmable GC oven can be programmed with up to 35 multiple ramps and is capable of sub-ambient operation. All sample transfer lines are deactivated fused silica and are heated to 85 °C. All valves, heaters and the GC oven associated with this sampling system are controlled by a dedicated microprocessor. A 30m x 0.32mm i.d. DB-624 (J&W Scientific) fused silica capillary column with 1 um film thickness was used. The capillary column was directly coupled to the ITD via a heated transfer line.

In addition to soil or water sampling, soil gas analysis can be accomplished by replacing the needle spargers with an adsorbent trap thermal desorption unit. Soil gas or air samples are collected on an adsorbent trap using an air sampling pump. The air sampling tubes are then transported to the instrument and placed in a heater assembly whereby trap contents are thermally desorbed onto the primary adsorbent traps shown in Figure 1. Conversion from soil/water analysis to air analysis can be accomplished within 5 minutes. Instrument operation is modified via the computer to accommodate the air sampling trap desorption/analysis.

Mass Spectrometer

A Finnigan MAT Ion Trap Detector[1] was used with the following modification. The supplied transfer line and open split interface were eliminated. The 50 L/sec turbomolecular pump was replaced with a 240 L/sec turbomolecular pump. The larger pump was required to handle the increased gas load realized from the direct coupling of the capillary column to the ITD. The larger turbomolecular pump also reduces pump down time following system venting.
Electron impact ionization was used; the ionization period was regulated using Finnigan supplied automatic gain control software.

Data System/Automation

A Zenith Supersport 286 laptop computer was used for data acquisition and instrument control. All aspects of mass spectrometer and sampling system operation were controlled through the dedicated laptop computer. Finnigan supplied ITD control software (version 4.10) with the programmer's option served as the platform for system automation. FORTH subroutines and keystroke sequences were incorporated with the Finnigan supplied software to automate ITD data acquisition, quantitation, and report generation. Communication to the sampling system microprocessor was through the serial port of the laptop computer. Sampling system control was achieved using assembly language programs. Parameters for sampling system event sequencing and heater or GC oven temperatures were written into the Finnigan ITD software using the programming option.

Physical Requirements

The total instrument dimensions are 17.5" x 23.5" x 26" (H x W x D) exclusive of the laptop computer. The instrument can be deployed in a vehicle equipped with compressed gas supply and a small liquid nitrogen dewar if cryogenic operation is required. A portable generator or line power is required. Power consumption is less than 1.5 kW. For field test to date, the instrument has been deployed in a 12 foot trailer.

Methods/Operational Sequence

The methods used with the transportable purge and trap/GC/ITD parallel those outlined in method 8260, SW-846[2]. Following instrument pump down and warm up of all heated zones, filament continuity and water concentration in the ITD are checked. Mass calibration is verified using perfluorotributylamine (PFTBA). Depending on the end use of field generated data, different levels of quality control can be used. An ITD tuning check can be performed using 4-bromofluorobenzene (BFB) to ensure that abundance criteria recently specified in method 524.2 is met. Figure 2 shows ion chromatogram derived from the molecular ion of 4-bromofluorbenzene obtained by purging a solution containing 50 ng 4-bromofluorobenzene. The mass spectrum obtained at the scan indicated by the cursor shown in Figure 2, is shown in Figure 3. This mass spectrum meets the abundance criteria specified in method 8260, SW-846. Following tune verification, a calibration curve can be established or continued adherence to the calibration curve can be checked using a midpoint standard. The midpoint standard check can also be used to update retention times on a daily basis. Currently our target list comprises the 68 target compounds shown (with their corresponding internal standards and surrogates) in Table 1. Following analysis of a blank, sample analysis is performed in a continuous mode, pausing only for sample loading and data file specification. Data acquisition is followed automatically by data reduction. Target compounds are identified by 1) elution of sample component at the appropriate elution window and 2) comparison of the sample mass spectrum with the standard reference mass spectrum. Standard reference mass spectra are obtained from the analysis of calibration mixtures. If any targeted compounds are detected, a hardcopy preliminary report is generated immediately. All data are archived on machine readable media for subsequent review by a skilled analyst.

Results/Discussion

We have successfully deployed the transportable GC/ITD at waste sites at Los Alamos National Laboratory. To date field trials have been completed without significant instrument failures. The qualitative and quantitative analysis for the 68 target compounds and the associated internal standards and

surrogates is accomplished in the field in an automated sequence executed every 25 minutes. A portion of the total ion chromatogram obtained in the field from 5 mls of a 50 ppb water standard is shown in Figure 4. Retention times for the target compounds reflected in Figure 4 are given in Table 1. Chromatographic development is completed within 16 minutes.

The need to obtain the chromatographic resolution displayed in Figure 4 is dependent on the site specific data quality objectives established. If only screening is required or the target list is more limited, chromatographic development can be reduced by using a steeper GC oven temperature ramp for faster elution. An example of instrument operation in the fast screening mode is shown in Figure 5, representing a chromatogram obtained from the internal standards/surrogates spiking mixture used in this work.

During field trials, co-located samples were taken for comparisons between the transportable GC/ITD and a laboratory based GC/quadrupole mass spectrometer. Table 2. shows the comparison between an analysis performed at a waste site with the GC/ITD and results obtained from the remote laboratory. The results shown in Table 2. reflect a 1 to 100 dilution (high level-methanol extraction method)[2]. Difference between the field results to those obtained at the remote laboratory may reflect the loss of volatile components during sample transport.

Low part-per-trillion detection limits have been achieved for some compounds from 5g soil or 5 mls water samples with this instrumentation. An extracted ion current profile of m/z 98, the quantitation ion of toluene d8 (a surrogate), obtained from a 20 ppt solution of the compounds listed in Table 1. (100 picograms/component in 5mls) is shown in Figure 6. The signal to noise ratio for m/z 98 in this chromatogram is approximately 10:1. The complete background subtracted mass spectrum for toluene d8 is shown in figure 7. No toluene d8 was detected in the blank which preceded the ion chromatogram shown in figure 6. Low part-per-trillion detection limits cannot be routinely achieved in the field. However, the high sensitivity of the instrument increases the degree of confidence in the automated mass spectral identifications performed in the field for a higher working concentration range. Our targeted working concentration range for field studies is from 100 ppt to 100 ppb for most compounds.

Conclusion

A transportable GC/MS for the qualitative and quantitative analysis of volatile organic compounds present at chemical waste sites has been developed at Los Alamos National Laboratory. System components have been integrated to produce an instrument which is extensively automated and can be operated with minimal training. Protocols for field technicians with subsequent data review by a skilled analyst ensure data quality. A high degree of specificity for compound identification is achieved with retention time and mass spectral information. The instrument is fast, analysis for the 68 target compounds outlined in method 8260, SW-846[2] can be achieved in 25 minutes. For screening, the chromatographic performance can be reduced to reduce analysis time. Additionally, part-per-trillion detection limits have been demonstrated for many compounds with this instrument.

References

1) Stafford, G.C., Kelley, P.E., Syka, J.E.P., Reynolds, W.E., and Todd, J.F.J. "Recent Improvements in and Analytical Applications of Advanced Ion Trap Technology " Int. J. Mass Spectrom. Ion Processes, 60, Special Issue, Sept., 1984, 85.

2) "Test Method for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Ed., Update I, Method 8260. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Acknowledgements

C.P.L. wishes to acknowledge the contributions of P.H. Hemberger, T.M. Cannon, and M.A. Wolf during the initial development of this instrumentation.

This work has been financially supported by the Department of Energy Office of Environmental Restoration and Waste Management, Los Alamos National Laboratory Environmental Restoration Program, Applied Instrumentation Technology.

TABLE 1.

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

	Ret. Time (min: sec)
Pentafluorobenzene	5:45
Dichlorodifluoromethane	:04
Chloromethane	:18
Vinyl Chloride	:28
Trichlorofluoromethane	1:18
1,1-Dichloroethene	2:00
Trichlorotrifluoroethane	2:03
Iodomethane	2:10
Carbon Disulfide	2:09
Acetone	2:08
Methylene Chloride	2:43
Acrylonitrile	3:13
trans-1,2-Dichlorethene	3:09
1,1-Dichloroethane	3:59
Vinyl Acetate	4:18
2,2-Dichloropropane	4:59
cis-1,2-Dichloroethene	5:02
2-Butanone	5:09
Bromochloromethane	5:28
Chloroform	5:28
1,1,1-Trichloroethane	5:34
Carbon Tetrachloride	5:45
1,1-Dichloropropene	5:46
Benzene	5:58
1,2-Dichloroethane-d4 (surrogate)	5:56
1,2-Dichloroethane	6:01
1,4-Difluorobenzene	6:24
Trichloroethene	6:36
1,2-Dichloropropane	6:48
Dibromomethane	6:54
Bromodichloromethane	7:04
2-Chlorovinylether	7:20
trans-1,3-Dichloropropene	7:26
Toluene d8 (surrogate)	7:38

	Ret. Time (min: sec)
Chlorobenzene d5	8:56
4-Methyl-2-pentanone	7:36
Toluene	7:42
cis-1,3-Dichloropropene	7:55
1,1,2-Trichloroethane	8:05
Tetrachloroethene	8:10
1,3-Dichloropropane	8:13
Chlorodibromomethane	8:25
2-Hexanone	8:19
1,2-Dibromomethane	8:31
Chlorobenzene	8:58
1,1,1,2-Trichloroethane	9:04
Ethylbenzene	9:07
m,p-Xylene	9:15
o-Xylene	9:39
Styrene	9:41
Bromoform	9:52
Isopropyl Benzene	10:04
1,4-Dichloroethane-d4	11:36
4-Bromofluorobenzene (surrogate)	10:15
Bromobenzene	10:24
1,2,3-Trichloropropane	10:29
1,1,2,2-Tetrachloroethane	10:26
n-Propylbenzene	10:33
2-Chlorotoluene	10:39
4-Chlorotoluene	10:46
1,3,5-Trimethylbenzene	10:46
t-Butylbenzene	11:09
1,2,4-Trimethylbenzene	11:12
S-Butylbenzene	11:24
1,3-Dichlorobenzene	11:31
1,4-Dichlorobenzene	11:38
p-Isopropyltoluene	11:34
1,2-Dichlorobenzene	12:03
n-Butylbenzene	12:04
1,2-Dibromo-3-Chloropropane	13:03
1,2,4-Trichlorobenzene	14:11
Napthalene	14:21
Hexachlorobutadiene	14:27
1,2,3-Trichlorobenzene	14:54

TABLE 2.

COMPARISON OF FIELD ANALYSIS TO LABORARORY BASED ANALYSIS*

Compound	Field	Laboratory
1,1,1-Trichloroethane	1900 ppb	1340 ppb
Tetrachloroethene	1800 ppb	1500 ppb
2-Butanone	140 ppb	40 ppb
Trichlorotrifluoroethane	2950 ppb	810 ppb

*100x Dilution Required Prior to Anaylsis

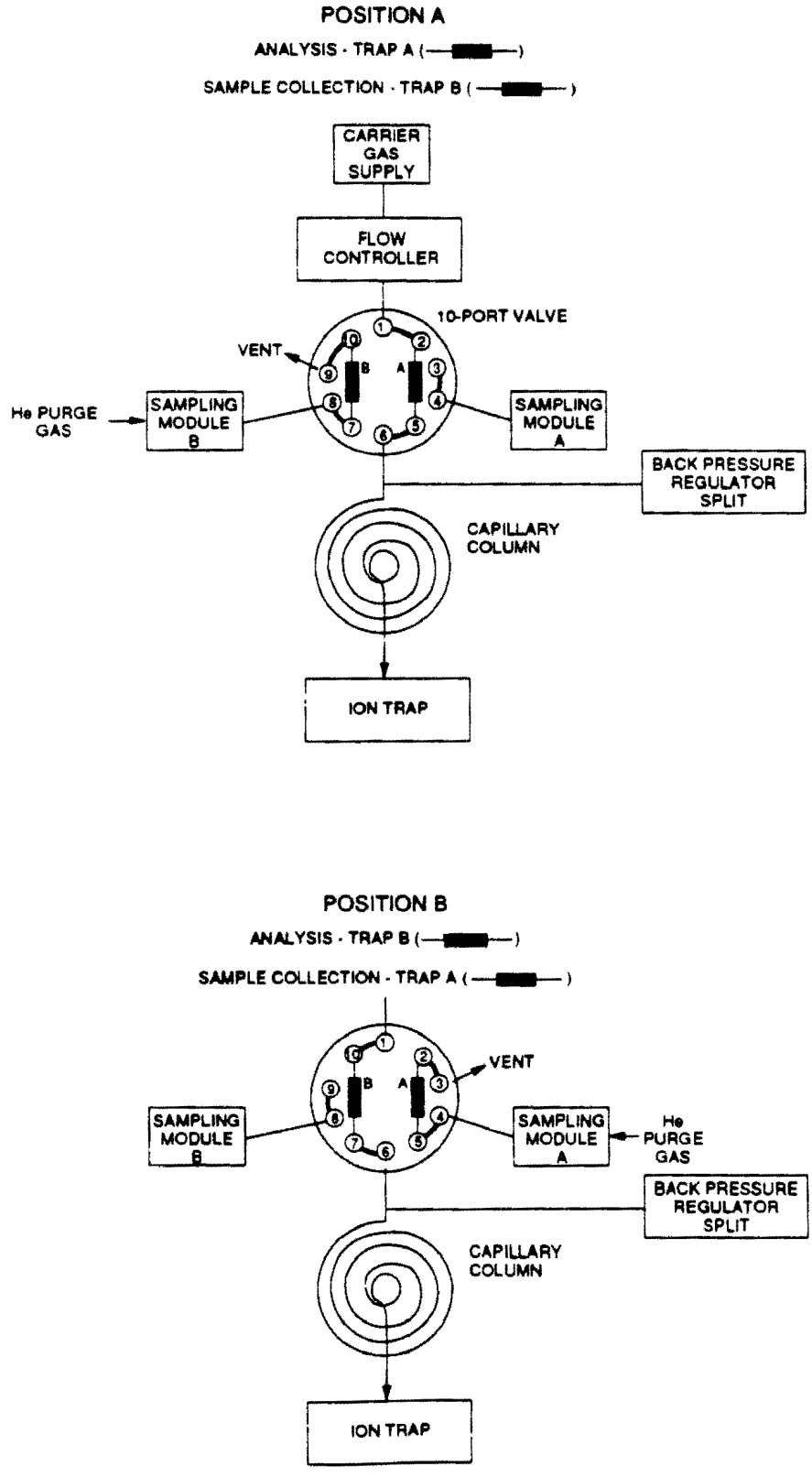

Figure 1. Schematic of Transportable GC/ITD Sampling System.

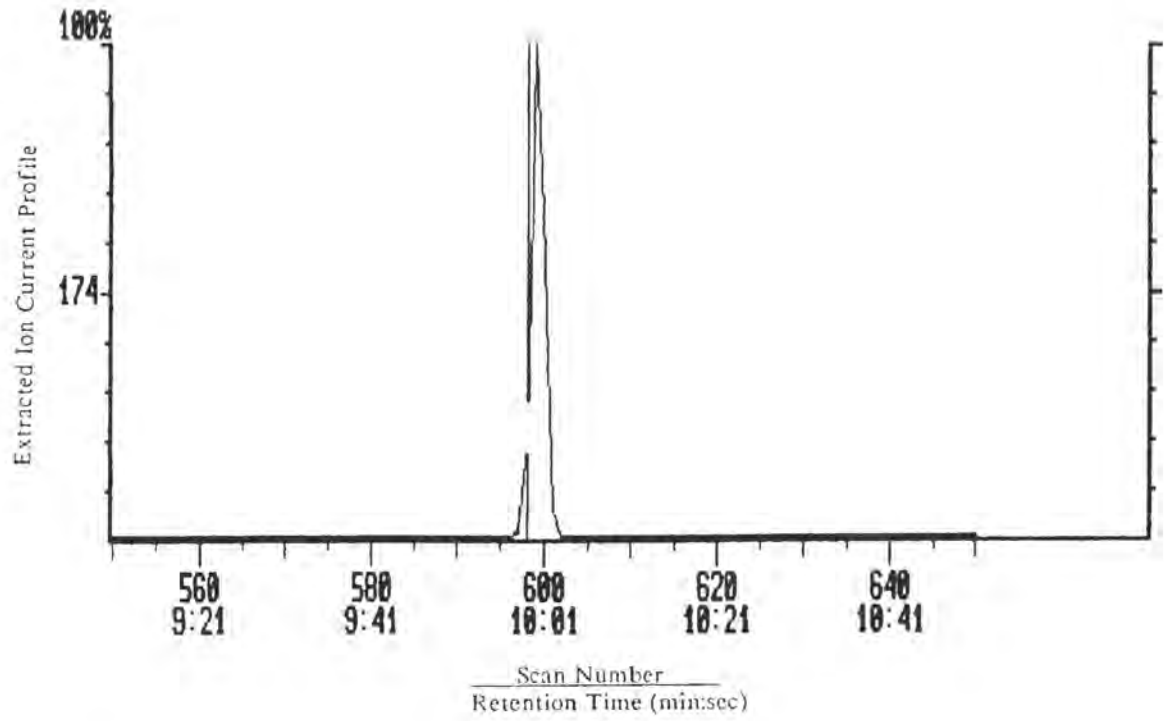

Figure 2. Extracted Ion Current Profile Derived from Molecular Ion of 4-Bromofluorobenzene (50ng).

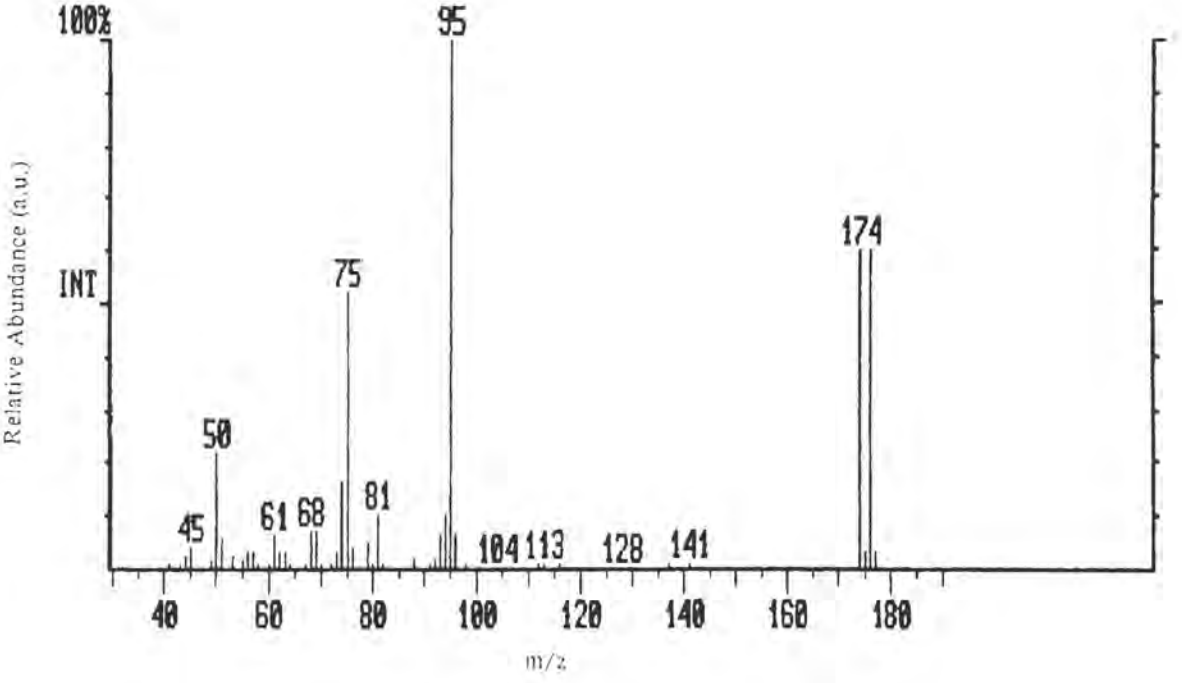

Figure 3. Mass Spectrum of 4-Bromofluorobenzene Which Meets Tune Criteria.

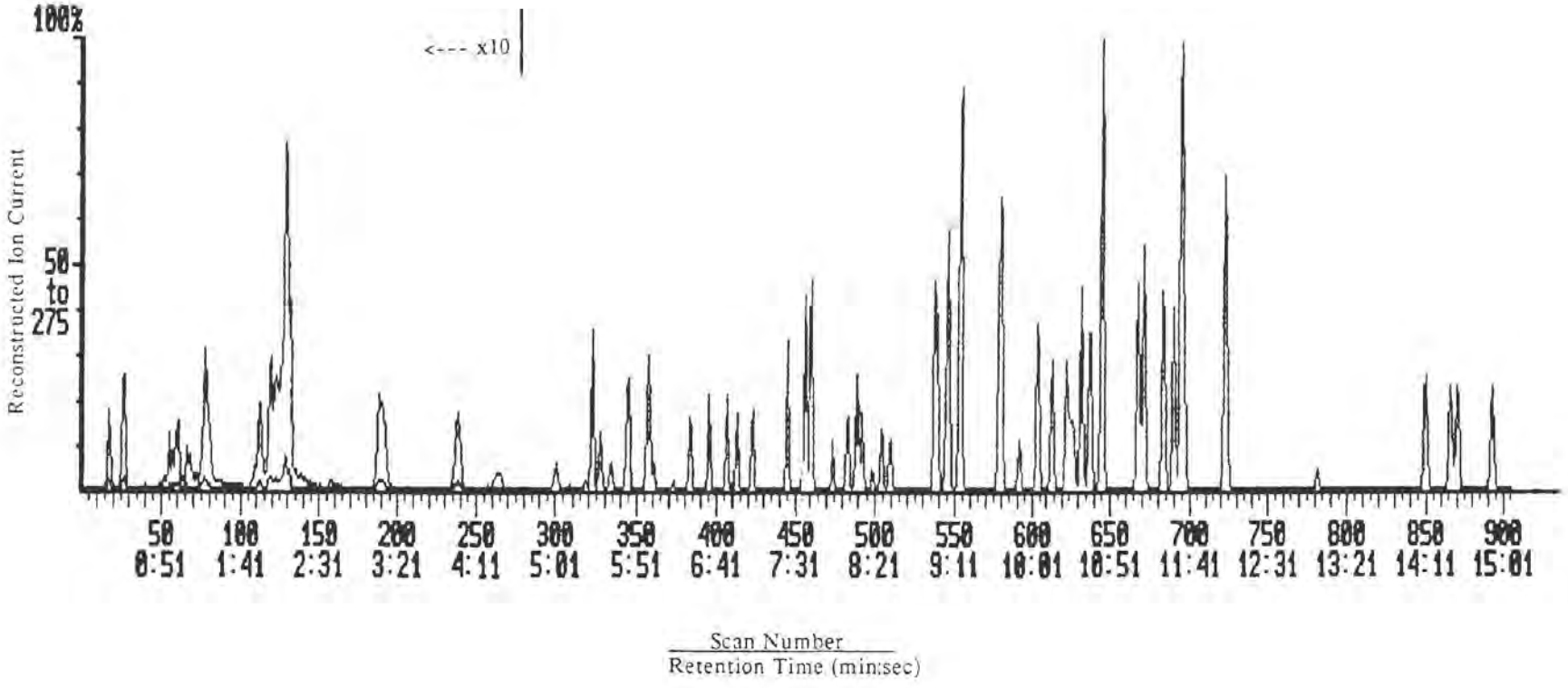

Figure 4. Total Ion Chromatogram Obtained in the Field from 50 ppb Standard.

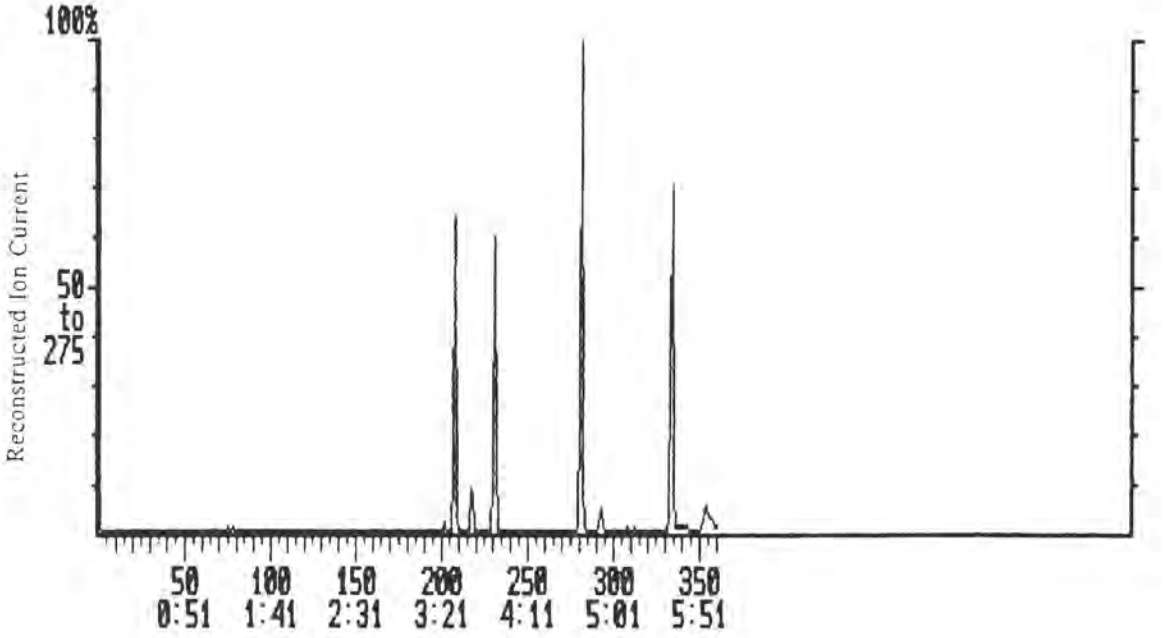

Figure 5. Total Ion Chromatogram of Internal Standards Obtained in Fast Screening Operational Mode.

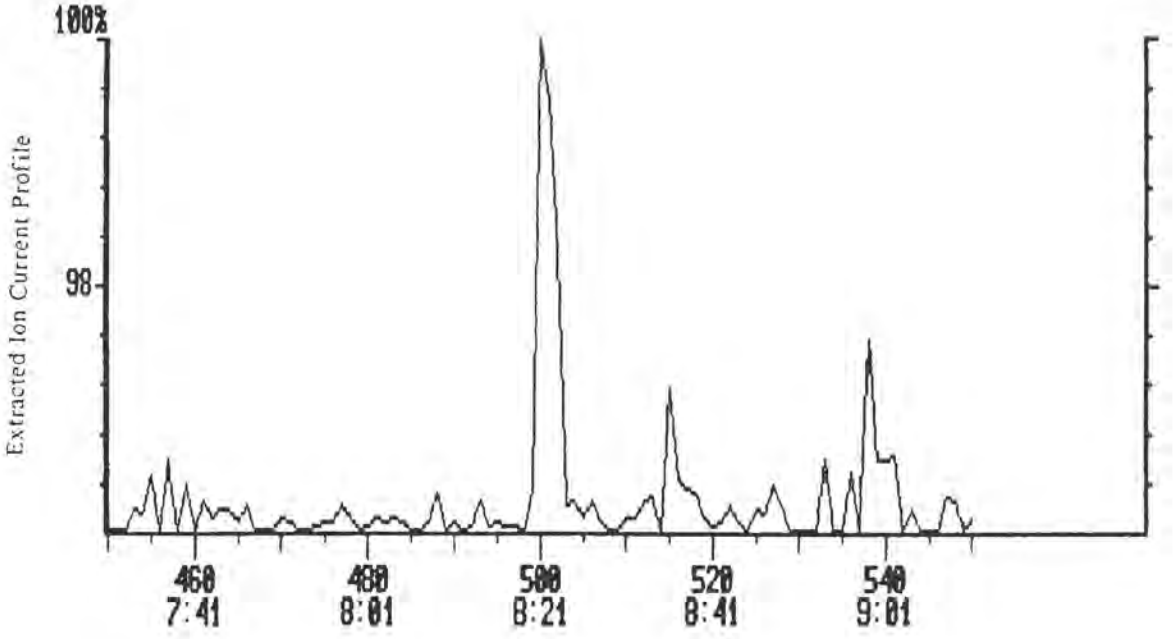

Figure 6. Extracted Ion Current Profile of Toluene d8 Molecular Ion from 20 ppt Standard Solution (100 picograms/5 mls water).

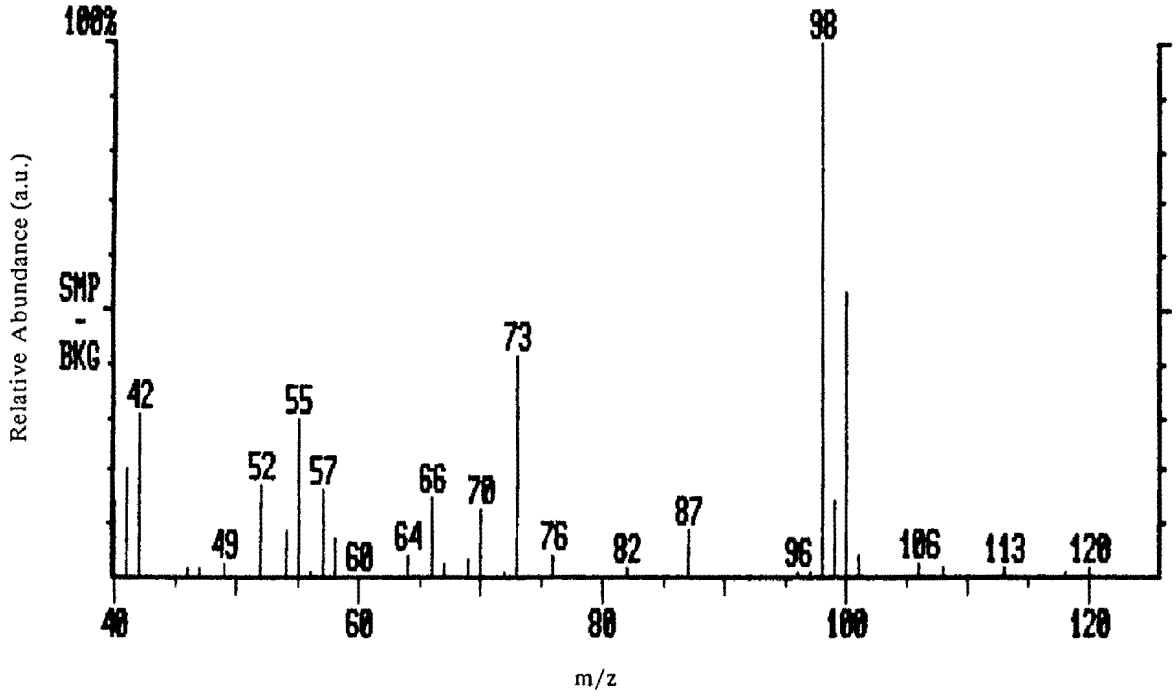

Figure 7. Background Subtracted Mass Spectrum Obtained from 20 ppt Standard Solution.

Second International Symposium

FIELD SCREENING METHODS FOR HAZARDOUS WASTES AND TOXIC CHEMICALS

February 12–14, 1991

Symposium Proceedings

SECOND INTERNATIONAL SYMPOSIUM

FIELD SCREENING METHODS FOR HAZARDOUS WASTES AND TOXIC CHEMICALS

February 12–14, 1991

CO-SPONSORS

U.S. Environmental Protection Agency

U.S. Department of Energy

U.S. Army Toxic and Hazardous Materials Agency

U.S. Army Chemical Research, Development and Engineering Center

U.S. Air Force

Florida State University

National Environmental Technology Applications Corporation

National Institute for Occupational Safety and Health