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A TRANSPORTABLE TURNKEY GAS CHROMATOGRAPH/ION TRAP DETECTOR FOR FIELD ANALYSIS OF ENVIRONMENTAL SAMPLES

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ABSTRACT

We have developed two transportable gas chromatograph/ion trap detectors (GC/ITD) for the *in-situ* characterization of chemical waste sites. These instruments are based on a modular design and can be readily modified in the field for air, water, or soil sampling. A purge-and-trap GC is used for the separation of volatile organic compounds before their introduction to the ion trap for mass spectral analysis. A secondary, or daughter, microprocessor controls ancillary hardware by means of the ion trap software. Most analyses are accomplished in an automated 20-min procedure. The detection limit for trichloroethylene in water is in the low part-per-trillion range. The analysis of soil and water samples is demonstrated by using surrogate samples spiked with 24 volatile organic compounds. The first instrument has been used under field conditions for soil analysis at a chemical waste site. The second-generation instrument differs from the first in the extensive use of commercially available equipment. The second-generation instrument will be briefly described here and some preliminary comparisons will be made to the first instrument.

INTRODUCTION

We describe two modular field-deployable gas chromatograph/ion trap detector systems for the characterization of chemical waste sites [1]. Extraction of the analyte from the matrix occurs in the *sampling module*. Sampling modules can be interchanged to configure the instrument in the field for the extraction of volatile organic compounds (VOCs) from soil, air, or water. Soil and water analyses are described here. Air analysis can be done either in a continuous mode, without chromatographic separation, or in a batch mode, with separation of the individual constituents. A *separations module*, based on gas chromatography, has been designed for the separation of the extracted VOCs. A Finnigan MAT ion trap detector (ITD) [2] provides an easily modified mass analyzer on which to base field instrumentation. The ITD serves as a universal *detection module*. A turnkey operating system, which

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allows the instrument to be used by personnel with minimal technical background through the incorporation of additional hardware and software, has been developed for this instrument. Because the instrument operates under nearly full computer control, very little operator interaction is required.

EXPERIMENTAL

Ion Trap Detector

The ion trap detector was used in conventional fashion with minor modifications. In the first-generation instrument, the interelectrode TeflonTM spacers and open-split interface were eliminated and the standard 50 l s⁻¹ turbomolecular pump was replaced with a 240 l s⁻¹ turbomolecular pump to maintain the ion trap at the proper pressure (ca. 10⁻⁴ torr helium partial pressure) with the higher gas load imposed by the direct-coupled, wide-bore capillary column described below. The ion trap detector was used without modification in the second-generation instrument. An SRI 8610 gas chromatograph was connected directly to the ITD transfer line. Electron impact ionization was used with the Finnigan Version 4.0 software with automatic gain control (AGC) [3]. The Finnigan Programmer's Option Package was used to generate Forth subroutines and keystroke sequences. The ion trap was tuned using perfluorotributylamine (FC-43) as a tuning and mass calibration standard with the automated tuning procedures contained in the ITD software. The Finnigan "Autoquant" ITD software was used for quantitation.

A schematic diagram of the first-generation transportable GC/ITD is shown in Fig. 1. The ancillary hardware (valves, heaters, flow controller, etc) added to the mass spectrometer can be monitored and controlled by a daughter microprocessor connected to the serial port. Automation software consists of the host interface software, the extended Forth Finnigan ITD software, and keystroke sequences (i.e., macros) added to the ITD software. The major differences in the second-generation instrument lie in the use of the SRI Instruments Model 8610 gas chromatograph with built-in purge and trap and in the use of the DAP 1200/4 data-acquisition processor from Microstar Laboratories. In this fashion, all components required for the transportable instrument are readily and inexpensively available.

No special consideration was given to reducing size, weight, and power requirements of the instrument described here. The GC/ITD is self-contained in a housing approximately 60 cm on each side. This housing contains the gas chromatograph, ion trap detector, sampling system, and a 6.8-l cylinder of helium. The mechanical backing pump for the ion trap vacuum system was mounted next to this housing. The instrument required less than 3 kVA power.

Surrogates and Samples

Soil standards and surrogates were prepared by adding the Purgeable Mixture A (200 $\mu\text{g ml}^{-1}$ of each of 13 VOCs) and Purgeable Mixture B (200 μg of each of 11 VOCs) (Supelco, catalog nos. 4-8851 and 4-8852, respectively) to 100 g of soil. The soil had been baked for 12 hours at 150°C before addition of the purgeable mixtures. Analysis of blank soil samples baked in this fashion showed no residual volatile organic compounds. For soil standards from 1 ppm by weight to 10 ppm, the purgeables A and B were added directly to the soil. For soil spiked with less than 1 ppm of purgeables, the purgeable mixtures were diluted with reagent-grade methanol (J.T. Baker) before their addition to the soil. In an attempt to homogeneously distribute the VOC standards throughout the soil, the soil/standard mixtures were periodically shaken for several hours. The results shown in this paper for surrogate soil samples are representative of a number of analyses of different aliquots from that soil.

Purge and Trap Chromatography

A schematic of the purge and trap GC developed as a separations module is shown in Fig. 2. For soil analysis, 1 g of soil was loaded into a PyrexTM glass tube (11.5-cm length by 9-mm i.d.). The soil surrogates and samples were spiked to 100 ppb by weight with fluorobenzene (Chem Service). Sufficient distilled water was added to cover the soil to improve purge efficiency and to ensure that channels were not formed in the soil during the purge. In general, 5 ml of water was added to the soil samples; when foaming of the sample occurred during purging, the amount of water added was reduced to 2 ml.

After the sample purge, the TenaxTM trap was ballistically heated to 150°C and flushed with helium at the gas chromatograph carrier flow rate of 8 ml min^{-1} (carrier gas velocity 63 cm s^{-1}). A thermocouple inserted into the TenaxTM trap indicated that the internal temperature reached 150°C in less than 10 seconds. The analytical column, a fused silica capillary column (30-cm length by 0.53-mm i.d.) with a 3.0- μm bonded cross-linked cyanopropylphenyl dimethyl-polysiloxane polymer film (DB-624) (J&W Scientific), was coupled directly to the ion trap by a deactivated fused silica line (60-cm length by 0.53-mm i.d.). For the analysis of soil samples, the oven temperature for the chromatography column was programmed as described in Table 1. The mass flow controller was stepped to full-scale flow (15 sccm helium) for approximately 30 seconds after data acquisition to flush the column. The flow controller was reset to its original value and the separations module was cooled by forced air.

RESULTS

Water Samples

A list of the 24 purgeable volatile organic compounds in the A and B standards is given in Table 2. Figure 3 shows the reconstructed ion

chromatogram (RIC) from the purge and trap GC/ITD analysis of 5 ml of water containing 50 ppb of these 24 compounds. In these experiments, the GC oven was operated from 30°C to 115°C with a programmed temperature increase of 7.5°C min⁻¹. The working calibration curve for trichloroethylene from 10 ppt to 10 ppm in 5 ml of water is shown in Fig. 4. Calibration curves at high and low sensitivity were obtained by adding and subtracting, respectively, 2000 from the sensitivity factor B, determined by the Finnigan AGC software.

The use of the automatic gain control does not in itself ensure that the ion trap will not operate under space-charge conditions. At higher sample concentrations (microgram levels), the AGC should be manually tuned to prevent mass spectral degradation caused by space-charging. The data shown in Fig. 4 do not display the nonlinearity at the higher sample concentrations within the low- and high-sensitivity calibrations that would indicate space-charging. This nonlinearity would be manifested as a saturation in response as a result of ion-ion repulsions within the trap. Moderate space-charge effects can be observed as mass shifts and loss of mass resolution in the mass spectra. These effects were not observed in the data of Fig. 4. There is, however, poor linearity in the data at lower sample concentrations in the high- and low-sensitivity calibrations. This nonlinearity cannot be explained on the basis of space-charge phenomena, especially since a linear increase in signal with increasing amount of sample is observed at higher sample concentrations. Figure 4 does show that usable calibration curves can be obtained over three decades of concentration for a given value of B and that the usable dynamic range can be extended to five decades of concentration if two windows of dynamic range are combined.

The high sensitivity of the instrument is demonstrated in Fig. 5, a mass chromatogram of m/z 130 from trichloroethylene. These data were obtained from the analysis of 5 ml of water containing 10 ppt of each of the 24 A and B purgeables (corresponding to 50 pg of each component). Full-scan mass spectra can be obtained at this concentration level. The signal-to-noise ratio (S/N) of this mass chromatogram is 6:1. Scaling response as a linear function of amount of material to S/N = 2 yields an estimated detection limit for trichloroethylene of less than 20 pg. The experimentally obtained mass spectrum of 50 pg of trichloroethylene in water agrees well with the reference spectrum obtained by an automated library search procedure (Fig. 6). In general, a purity search was used for compound identification. We have found that the number of correct first-ranked library identifications for the A and B purgeable standards is higher for the system in which the GC is coupled to the ion trap by the open-split interface rather than by the direct-coupling scheme used in the first instrument. This is most likely due to better regulation of the buffer gas partial pressure in the trap using the open-split interface. Exceptions include cases in which there were co-eluting components and at higher concentrations (greater than 5 µg per compound).

Readjustment of the B-value as described above improved the library matches for species at higher concentrations.

Soil Samples

The transportable GC/ITD was mounted in the back of a panel van and taken to a chemical waste impoundment area for actual field testing. Figure 7 is the reconstructed ion chromatogram from a 1-g soil sample taken from a partially excavated waste site. Fluorobenzene (100 ppb) was added to the 1-g sample as an internal standard. The concentration of 1,1,1-trichloroethane in the soil was calculated to be 5 ppm. A matrix-spiked sample containing a mixture of 60 VOCs (most of which are contained in the EPA Priority Pollutant List and the National Primary Drinking Water List) at the 400-ppb level in a 1-g surrogate soil sample is satisfactorily analyzed in the field with the transportable GC/ITD.

DISCUSSION

The modular design of this transportable instrument, coupled with the flexible control system provided by the custom daughter microprocessor or the Microstar Laboratories data-acquisition processor, is well suited to problems in field analysis. The ability to address and control interchangeable ancillary instruments, such as sampling devices or the purge and trap GC, by means of the host computer provides great flexibility for different analytical problems. The host interface software is written in Forth and is implemented as an extension of the existing Finnigan control software. Finally, keystroke sequences can provide customized data-reduction procedures for different applications.

The combination of the daughter microprocessor (or the data-acquisition processor), Forth interface software, and Forth keystroke sequences added to the ITD software allow the instrument to be operated in a turnkey fashion. That is, in the intended mode of operation for the transportable GC/ITD, the operator need only "log in" at a menu window and select the appropriate analytical procedures from the menu. For example, one can choose to analyze for a suite of VOCs in soil or to monitor a single compound in groundwater. Figure 8 is a flow chart of the analysis sequence. Operator interaction is required in the first step (labeled "Log-In"); the remainder of the analytical procedure (from a brief instrument check to report generation) is done under computer control.

The gas chromatograph/ion trap detector (GC/ITD) configuration described here has, in addition to the modular turnkey design, other advantages over commercially available transportable gas chromatograph/quadrupole mass spectrometers [4]. Ion trap detectors are inherently simple. The ion trap does not suffer from the complexity added by external ion sources and ion lenses. The ion trap electrode assembly is small and rugged although the radiofrequency and power transformers, gas supplies, data system, and other equipment can offset the size advantage. When operated as an ion trap detector (that is, as a simple single-stage mass

analyzer), no direct current potentials are applied to the trap electrodes. Charging phenomena of the ion trap electrodes as they become dirty are minimized. Another advantage derives from the inherently high sensitivity of the ion trap detector. The ITD is roughly 10 to 100 times more sensitive than a conventional transmission quadrupole [5]. This sensitivity advantage can be pushed even further with the addition of axial modulation to the ion trap [6]. Finally, the ion trap can provide mass spectrometry/mass spectrometry capabilities [7] far more simply than tandem quadrupole instruments, which require at least two independent quadrupole mass filters [8].

CONCLUSION

Work is currently in progress to fully characterize the second-generation instrument, especially in the areas of reproducibility and quantitation accuracy, and to establish detection limits for a wide number of compounds of environmental significance. Results from this second-generation instrument, along with some comparisons to the first instrument, will be the focus of the oral presentation. Our primary goal in the work reported here was to demonstrate the viability of an *automated* GC/ITD system for the *in situ* monitoring of chemical waste sites. The ion trap detector provides many advantages as a mass analyzer in this application. It is simple to maintain and operate. The high sensitivity of the ion trap and the inherent universality of the modular mass spectrometer system are perhaps the most important features for a field analytical instrument. The two-dimensional information provided by chromatographic retention time and mass spectral library identification gives the instrument high specificity for compound identification. Mobile ion trap mass spectrometers operating in the MS/MS mode have been successfully applied for the direct, continuous, or near-continuous analysis of permanent gases and condensable vapors [9]. Other instruments used in field applications, such as a gas chromatograph [10] or Fourier-transform infrared spectrometer [11], do not provide the combination of sensitivity, specificity, and universality demonstrated by the transportable ion trap instrument.

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TABLE 1

Temperature programming of the column oven for VOC analysis in soil with the transportable GC/ITD

Initial temperature 30° C
Heated to 35° C at 1.2° C/min
Heated to 78° C at 3.9° C/min
Heated to 103° C at 7.5° C/min
Heated to 148° C at 11.7° C/min
Held at 148° C for 2 min

TABLE 2

Components^a (200 µg each in 1 ml of methanol) in purgeable mixtures A and B

Purgeable A	Purgeable B
1. Carbon tetrachloride	14. Benzene
2. Chlorobenzene	15. Bromodichloromethane
3. 2-Chlorovinyl ether	16. Bromoform
4. Chloroform	17. 1,2-Dichloroethane
5. Dibromochloromethane	18. <i>trans</i> -1,2-Dichloroethene
6. 1,1-Dichloroethane	19. <i>cis</i> -1,3-Dichloropropene
7. 1,1-Dichloroethene	20. <i>trans</i> -1,3-Dichloropropene
8. 1,2-Dichloropropane	21. Ethylbenzene
9. Methylene chloride	22. 1,1,2,2-Tetrachloroethane
10. Tetrachloroethene	23. Toluene
11. 1,1,2,2-Tetrachloroethane	24. 1,1,1-Trichloroethane
12. Trichloroethene	
13. Trichlorofluoromethane	

^aThe number of each compound identifies the chromatographic peaks in Fig. 3.

FIGURE CAPTIONS

Fig. 1. Block diagram of the transportable GC/ITD showing the interchangeable sampling and separations modules and the daughter microprocessor for control of ancillary equipment.

Fig. 2. Schematic of the separations module. In this work, a self-contained purge and trap gas chromatograph was developed for the separation of VOCs.

Fig. 3. Reconstructed ion chromatogram from the purge and trap analysis of 5 ml of water spiked with 500 ppb each of the 24 organic compounds from purgeable mixtures A and B (cf. Table 2).

Fig. 4. Calibration curve for trichloroethylene in water. A composite calibration curve spanning 6 decades of concentration (10 ppt to 10 ppm) can be constructed from high- and low-sensitivity curves obtained at different ionization times.

Fig. 5. Mass chromatogram of m/z 130 from trichloroethylene. This mass chromatogram was derived from the full-scan mass spectra of trichloroethylene at the 10-ppt level in 5 ml of water.

Fig. 6. Comparison of the mass spectrum of 50 pg of trichloroethylene with the NIST Library spectrum.

Fig. 7. Reconstructed ion chromatogram from the analysis of 1 g of soil from a chemical waste site. This analysis was done in the field at the site.

Fig. 8. Flow chart of the automated analysis sequence. Operator input is required only to select a preprogrammed analytical procedure.

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6

Formula: $C_2H_3Cl_3$ Rank 1 Index 3000
Molecular weight 130 Purity 688 Cas# 0-00-0
Fit 943 Rfit 705

Fig 7

Fig 8

END

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