A BACKPACK-PORTABLE MASS SPECTROMETER FOR MEASUREMENT OF VOLATILE COMPOUNDS IN THE ENVIRONMENT

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ABSTRACT

Environmental measurements of volatile pollutants and metabolic gases are preferably made *in situ*. *In situ* measurement provides immediate information to the investigator while minimizing disturbance and eliminating the need for sample collection, preservation, and transport. A self–contained mass spectrometer, capable of being carried by one person, has been designed and built for this purpose. The instrument is based on a compact crossed–field analyzer using a high–energy–product magnet and control circuitry optimized for low power consumption using a 12V DC primary power source. An internal, rechargable battery can provide up to several hours of operation in the field. Provision is made for interface, via RS–232, to a compact battery–operated laptop microcomputer. A variety of inlet configurations is possible, the simplest being a probe, containing a small silicone–rubber membrane, which may be inserted into a gas– or water–containing environment of interest.

INTRODUCTION

In situ Analysis

The ability to measure environmental chemical parameters *in situ* can offer many advantages. In hazardous waste detection, monitoring, and remediation efforts, immediacy of results may be of prime importance. In sediment geochemistry, minimization of disruption of sediment and porewater structure associated with classical sample collection and storage techniques may be important. The present paper describes a field–portable mass spectrometer which may be employed with a minimally–invasive membrane probe for *in situ* analyses of volatiles in either air or water. The ultimate objective is to provide a capability for *in situ* environmental chemical analysis which will offer immediacy of results, ability to measure without serious disrupt rom sampler installation or sample collection, minimization of gas exchange with the atmosphere, and freedom from sample transportation and preservation concerns.

Membrane–Inlet Mass Spectrometry

The use of a membrane interface and a mass spectrometer (MS) to measure gas and vapor content of fluids is now well established in laboratory, medical, and industrial settings (e.g., Westover et al., 1972; Brantigan et al., 1972; Greenwalt et al., 1983; Harland et al., 1987). A membrane interface is generally versatile and robust, and a mass spectrometer is a universal detector, capable of providing both identification and quantification of gases and vapors. However, MS has traditionally been of limited mobility and restricted to operation where electrical utilities are available, due to considerations of size, weight, and power consumption. Specialized instruments have flown on weight–critical space missions, and several vehicle–portable MS have been decribed. However, a MS suitable for general analysis of volatiles in the environment, which can be carried by a person into a field setting where electrical power lines do not exist and a

vehicle can not travel, does not appear to be available until now. The present paper describes the general features of a prototype of such an instrument.

Choice of MS Configuration

All mass spectrometers operate by ionizing analyte molecules and separating them according to their mass–to–charge ratio (m/e). The separations of ions can be accomplished by several means, as described in detail elsewhere (e.g., Watson, 1985). For vapor analysis requiring relatively modest resolution the common choice is between a magnetic analyzer and a quadrupole analyzer. The latter is free of the heavy magnet required by a magnetic machine. Many high–quality quadrupole analyzers are now available commercially.

However, operation without line power, large batteries, or a generator places premium on low power consumption. In this respect the otherwise compact, highly developed, and commercially available quadrupole mass spectrometer encounters a disadvantage, namely, the need for significant (a few 10's of watts) levels of precisely controlled radio–frequency power. Magnetic analyzers, while handicapped by the need for a magnet, require significantly less operating power. This factor was important in the choice of a magnetic analyzer for the present machine.

It is intended to use the mass spectrometer with no pre–separation of analyte (in contrast to a GC/MS). By employing a simple membrane interface between the mass spectrometer inlet and the water or gas to be analyzed, a very simple sample inlet system results. Resulting spectra, however, contain contributions from all gases and vapors present, thus requiring the mathematical separation of the resulting spectrum into the components due to each vapor. Such separations have been done in the past; in this application, we use the linear programming algorithm UNMIX (Doherty, Hemond, and Ernst, 1990). Because successful use of this or any other spectrum separation algorithm puts a premium on the reproducibility with which mass spectra can be obtained, an

additional incentive exists for gaining the stability and reproducibility which have traditionally been attributed to magnetic mass analyzers.

The instrument described here is based upon a magnetic analyzer of the crossed–field, or cycloidal, design (Bleakney and Hipple, 1938) which achieves both direction and velocity focusing in an exceptionally small volume. Such an analyzer is not without drawbacks; a cycloidal analyzer is difficult to equip with an electron multiplier, and the volume of magnetic field which must be established is relatively high. However, the former disadvantage is offset somewhat by the intrinsic linearity and minimal mass discrimination effects of a Faraday cup detector, and the latter by the use of modern high–energy–product permanent magnetic materials. From a control standpoint, the cycloidal analyzer is advantageous. Operating voltages are low compared to other magnetic machines. As in other magnetic analyzers, mass scanning can be accomplished by varying the output voltage of a single power supply.

INSTRUMENT CONFIGURATION

Figure 1 shows the overall system diagram for the portable mass spectrometer. Each of the major subsystems is described below.

Mass Analyzer

The mass analyzer employs a commercial cycloid tube originally used in machines manufactured by Consolidated Electrodynamics Corp., and utilized in the 21–620 mass spectrometer. (A very similar tube is used in the 21–614 residual gas analyzer.) The analyzer was designed for a m/e range of 2 through 150, with unit mass resolution. Sensitivity to N_2 for the 21–614 analyzer is indicated as "1 division" for 5×10^{-11} torr, implying that 5×10^{-11} torr of N_2 constitutes a useable source pressure. The magnetic flux density within which the analyzer operates is about 0.33 Tesla. For values of m/e between

2 and 11, the analyzer includes an auxiliary Faraday cup collector arranged such that, when the electric field is reduced to zero, the instrument behaves as a 180° magnetic sector analyzer. For the prototype machine, the analyzer was employed in its original stainless steel envelope, modified to accomodate the vacuum system.

For portable operation, it was necessary to effect a dramatic reduction of the weight of the magnet; the magnet originally used with this analyzer has a mass of 32 Kg. Although the flux density required is not exceptional, the pole pieces of the magnet are separated by about 2.6 cm, necessitating the production of a fairly high magnetizing force. This requirement was met using a neodymium–iron magnet, with mild steel pole pieces and magnet return path. Total mass of the magnet assembly is about 9 kg.

Vacuum System

For maintenance of the high vacuum required in the analyzer tube, a Varian 8 L/sec diode sputter–ion pump is used. Required +3000 volt power is supplied by a DC–DC converter capable of delivering up to 7 ma (Gamma High Voltage UC30–3.5 p/cm). While this power output is marginal during initial pumpdown of the instrument, it is more than adequate to maintain pumping speed during any normal mode of operation. No–load power consumption of the converter is of the order of 1 watt. Initial pumpdown is accomplished by a mechanical pump separate from the instrument. A resistor is provided in the return circuit of the high voltage power supply to monitor ion pump current (and, hence, gas pressure at the pump). A separate panel meter (Metrabyte model 2002) provides the operator with a continuous pressure reading. Should venting of the high vacuum envelope be required as part of field operations remote from a source of 110 volt AC electrical power, roughing can be accomplished by a battery operated vacuum pump constructed from a Sargent–Welch model 8804 direct–coupled pump and a 1/4 hp 12 volt DC motor (Pacific Scientific Model BA3618).

Emission Regulator

In order to minimize power consumption and simplify circuitry, the emission regulator circuitry was designed to run near ground potential with unregulated 12 volt power. Filament power is provided at approximately 60 khz by a push–pull pair of Darlington power transistors, operating through a toroidal transformer (Pico # 67490). ON time per cycle of each of power transistor is constant, and maximum filament current is controlled by varying the frequency of the driving circuitry. Emission current regulation is provided by feedback from a trap current sensor which is coupled, via optical isolation, back to the above power circuit; this feedback, compared with a reference voltage, is used to control a series pass resistor in the +12 V supply to the push–pull power transistors. Normally, the circuit is adjusted so that the desired emission current is achieved with only a small (1–2 volt) drop in the series pass transistor. In future versions, emission regulation will be provided directly by controlling the duty cycle of this inverter circuitry, thereby achieving additional power savings.

Small DC–DC converters (Pico 12A250S and 12A48D)are used to provide the necessary electron accelerating voltage and trap voltage for the source. These devices incorporate the necessary isolation for the electrically floating ion source. Simple zener diode voltage regulation is employed for both voltages. In addition to the emission current signal, the emission regulator incorporates a filament current sensing circuit whose output is coupled to a panel meter via an optical isolator.

Mass Scanning

Mass scanning is provided using high voltage operational amplifier (Apex PA88). The circuit provides a 0–300 volt output when a 0–5 volt control signal is applied. DC–DC converters (Pico 12A100S) and a simple zener regulator provide operating power to the op–amp, and the output is divided along a resistor chain which provides appropriate voltages to each field electrode of the cycloid tube as well as the repeller and the injector.

The control signal is provided either by a stable 0–5 volt source controlled with a 10–turn potentiometer on the front panel or the output of a digital to analog converter associated with a microcomputer interface. Output of the mass scanning circuit is also made available to a front panel connector for use, if desired, with an external x–y recorder.

Cycloid Tube Heaters

The cycloid tube has both filament and plate heaters, which are useful for degassing of the analyzer. The two plate heaters are series connected and driven by the paralleled output of four unregulated DC–DC converters in parallel (Pico 5E5S) while the filament heater is driven by a pair of unregulated DC–DC converters (Pico 12E5S). In future versions, a single DC–AC converter with a transformer having 2 appropriate secondaries might be used as an alternative power supply.

Electrometer

In the analyzer tube, positively charged ions are collected by a Faraday cup. Ion current is sensed using an electrometer based on an ultra–low bias current operational amplifier (Teledyne–Philbrick model 1702). The op–amp input circuitry is mounted on Teflon standoff insulators, and a feedback resistor of 10^{11} ohms paralleled by about 2 pF provides a time constant of about 1/2 second. The entire assembly is mounted in a rigid aluminum box bolted to the cycloid tube envelope.

Primary Power Supply

For operation in the laboratory or from a motor vehicle, external 12 volt power can be supplied through a cigarette lighter plug. The internal nickel–cadmium battery pack for self–contained operation is nominally rated at 12 volts and 7 amp–hours at a 10–hour rate.

Typical current draw of the mass spectrometer with all systems operating except for

the filament and plate heaters is about 2 amps; at this rate, the battery pack capacity must be somewhat derated. Separate power switches are provided for each subsystem of the mass spectrometer so that circuits not actually in use may be shut down to conserve power. For example, between measurements or while waiting for vapor flow to reach a steady–state value, it may be appropriate to shut down the scanning circuitry or even the emission regulator. Under such conditions, some (thus far unquantified) stability may be sacrificed to gain extended battery life.

Inlet System

The mass spectrometer is provided with an isolation valve connecting a sample inlet port on the front panel to the inlet tube of the analyzer itself. A capacitance manometer vacuum gauge (MKS 122A), having a resolution of 0.2 torr, is connected to this inlet manifold via a second valve, which may be closed to reduce inlet system volume under conditions where the existence of appropriate inlet pressures (no more than a few microns of mercury) are known to exist. The inlet system is initially rough–pumped externally, after which low pressure is maintained by gas flow into the analyzer.

Mechanical Assembly

The mass spectrometer is assembled within a rectanglular framework of welded 3/16" by 1 1/8" aluminum angles, having dimensions 20 cm x 36 cm x 60 cm. The cycloid tube is mounted in yokes which allow small angular adjustments of the cycloid tube about an axis perpendicular to the magnetic field. The magnet is mounted directly to the aluminum frame, and provides a small angular adjustment about a second axis perpendicular to the magnetic field. The sputter–ion pump, mounted on a 2.75" knife–edge flange, is cantilevered from the vacuum envelope. Individual circuit boards for the emission regulator, mass scanning, and heater power supplies are mounted to the aluminum frame using metal spacers. Space and power are available for a microcomputer

interface to be mounted inside the frame. All controls and meters are clustered on a removable front panel. Total mass including battery and optional pack frame is about 32 Kg. The completed instrument is shown in Figure 2.

Field Transportability

To facilitate transport to field setting, a three–point attachment is provided to mount the MS on a conventional welded aluminum pack frame. The pack–mounted instrument is shown in Figure 3.

PERFORMANCE TESTS

Figure 4a shows a spectrum of air as measured on the mass spectrometer. Figures 4b, 4c, and 4d show spectra obtained from the headspace of an isopropanol solution, a water sample containing CH_4, and water containing approximately 50 ppm of trichloroethelene, respectively. Sample was admitted via a single silicone rubber membrane interface of estimated area of 1 mm^2 and thickness of 0.2 mm, connected to the mass spectrometer inlet via a length of 0.55 O.D. stainless steel tubing, with no other provision for sample enrichment or water vapor removal.

The air spectrum shows the expected peaks for water (m/e 18, 17, 16), nitrogen (m/e 28), and oxygen (m/e 32) plus small unidentified peaks at m/e 43, 41, and 27. When the probe was placed in tap water a similar spectrum (not shown) was observed, except that the water peaks were very much larger. Additional peaks in the isopropanol spectrum (Fig. 4b) include m/e 14, 15, 19, and 45. An aqueous solution prepared by briefly bubbling tap water with CH_4 (Fig. 4c) yielded the spectrum of tapwater with additional signal due to CH_4 at m/e 16, 15, and 14, while a solution of about 200 ppm of trichloroethylene in tap water (Fig. 4d) had additional peaks at m/e 57, 60, 95/97, and 130.

Demonstrable baseline resolution is evident near m/e 40. This falls short of the unit

resolution at m/e 150 which can in principle be obtained with the 21–620 cycloid tube. Numerous possible factors, such as chart recorder noise, sub–optimum adjustment of the instrument, magnetic field inhomogeneity, or electrical noise in the scan circuitry, have not yet been investigated.

Sensitivity of the analyzer was measured using a calibrated leak which releases 4.4 x 10^{-7} torr – L/s of argon into the instrument. Faraday cup current, measured with a Keithley electrometer, was .76 pA, giving a sensitivity of about 1.7 x 10^{-4} A per g/s for Argon. If 4 x 10^{-14} amperes of Faraday cup current is considered the minimum required to reliably detect a signal (this is conservative with respect to the capabilities of a modern electrometer, and varies with the time available to make a measurement), the sensitivity corresponds to about 50 pg/sec (≈ 1.2 picomole sec) of argon. This is indistinguishable from the author's observations of the usable sensitivity of a commercial CEC 21–620 mass spectrometer.

CONCLUSIONS

Operation of the prototype described here demonstrates the feasibility of building a useful mass spectrometer for true portable operation in terrestrial or aquatic environments. The machine is not yet fully developed to its maximum potential; several items have been identified which could yield improvements in power consumption, weight, size, and performance. In addition, the microcomputer interface will greatly facilitate the routine collection of environmental data using this machine. Further gains may be made by incorporating more sophisticated environmental probes. Use of multiple–membrane probes and appropriate vapor drying techniques could considerably expand the capabilities of the overall system. However, even in its present demonstrated configuration with the simplest of inlet probes, the machine performance is adequate to make many environmental measurements, such as *in situ* identification of spilled or leaked volatile chemicals, or

high–resolution *in situ* measurement of oxygen, carbon dioxide, methane, and other metabolic gas profiles in waters, soils, and sediments.

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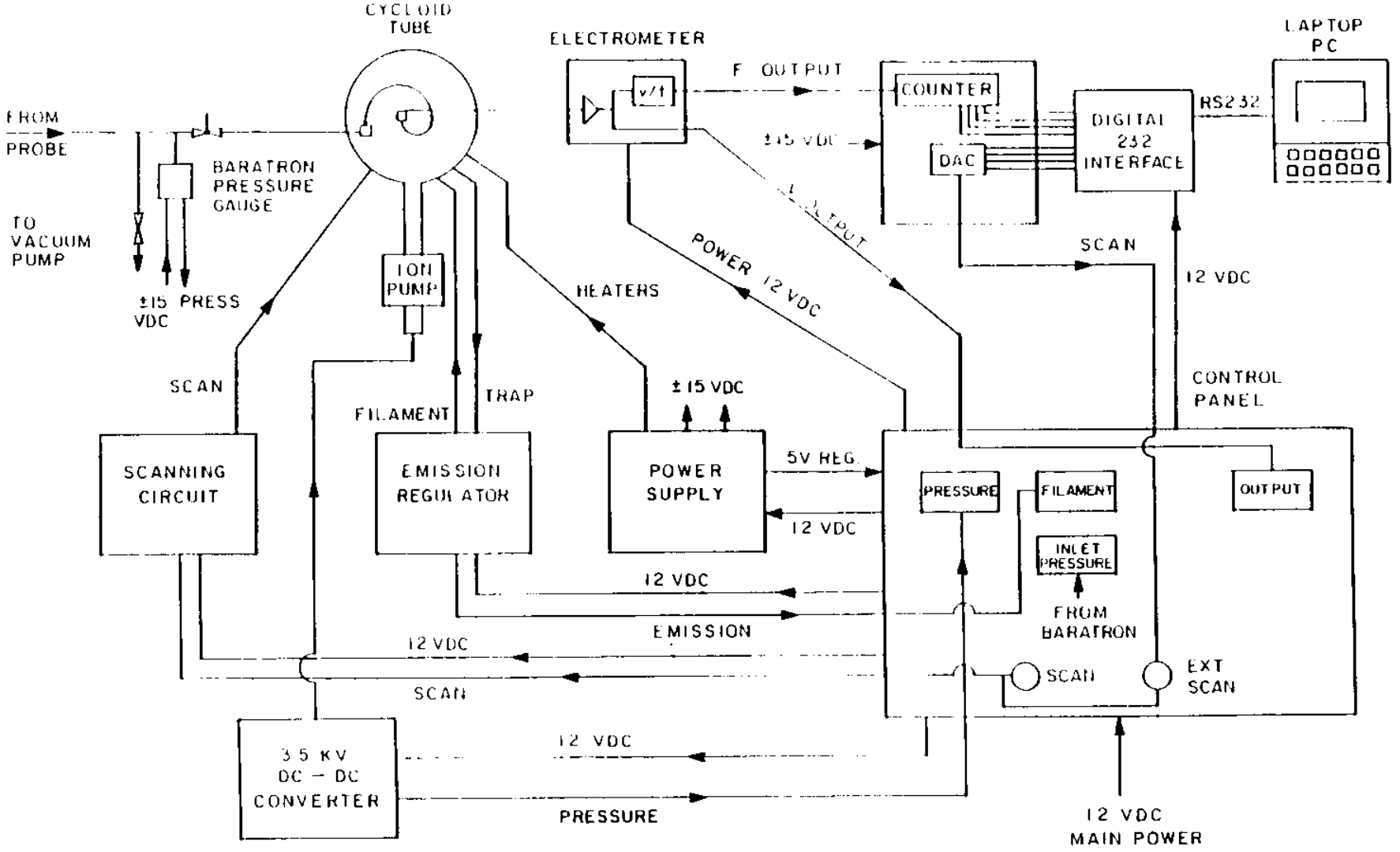
LIST OF FIGURES

HAND-PORTABLE MASS SPECTROMETER
SYSTEM DIAGRAM



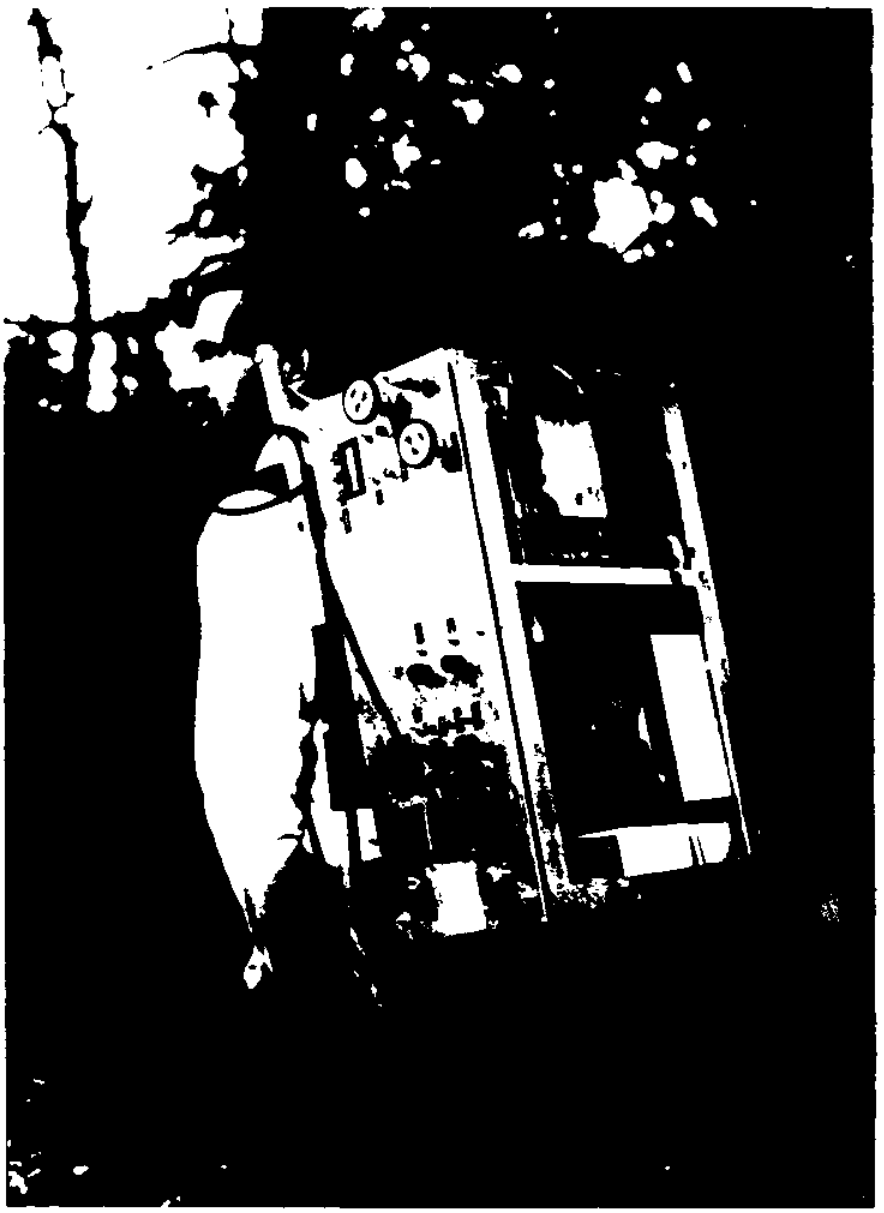


FIG 3

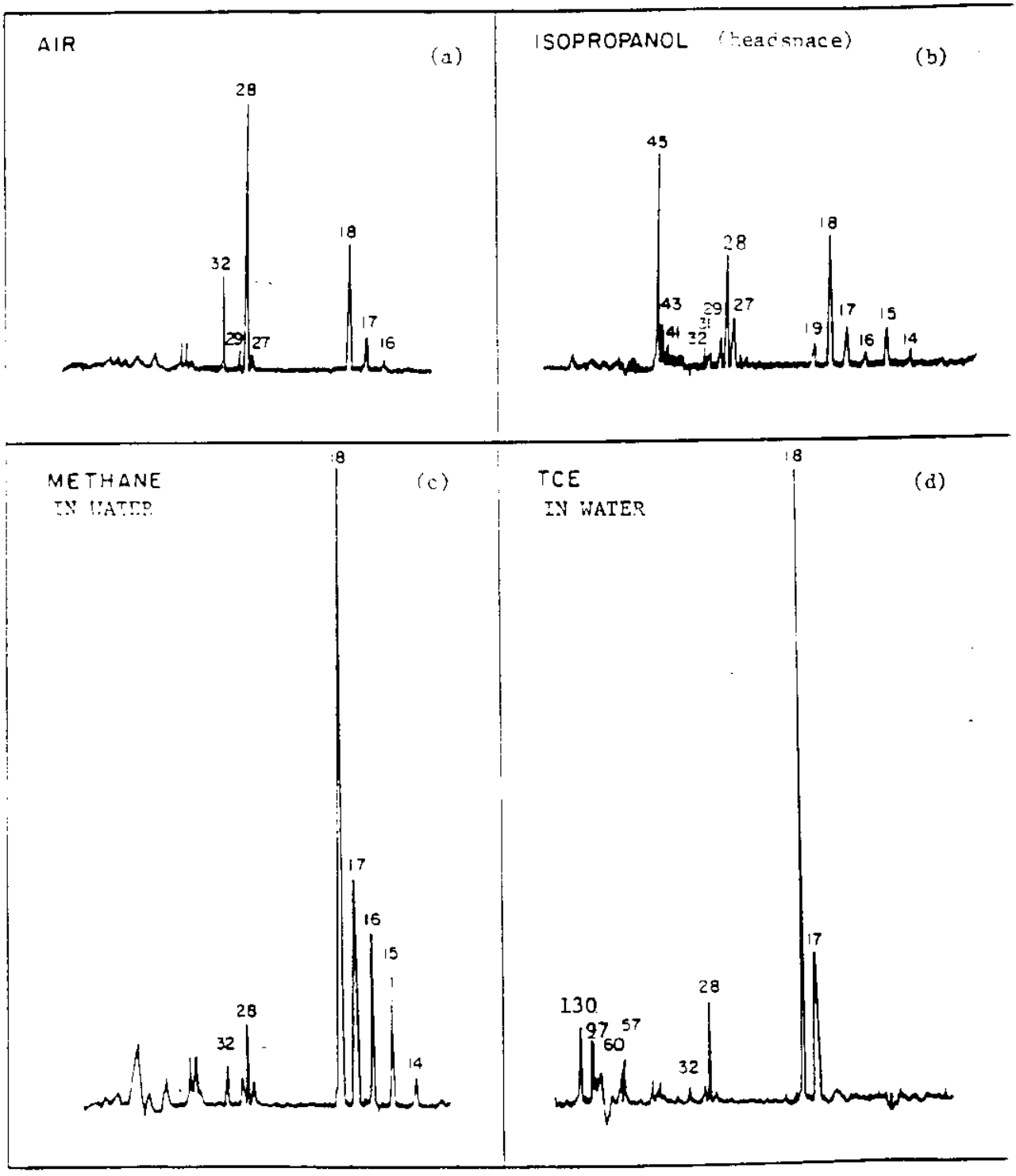

AIR
(a)
28
32
18
29
27
17
16
ISOPROPANOL (headspace)
(b)
45
28
18
43
29
27
17
15
41
32
19
16
14
METHANE
IN WATER
(c)
18
17
16
15
28
32
14
TCE
IN WATER
(d)
18
17
28
130
97
57
60
32

FIG 4