Journal of Chromatography, 555 (1991) 297–301
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 393

Short Communication

Trace determination of volatile organic compounds in soil based on thermal vaporization followed by Tenax-GC trapping and capillary gas chromatography–mass spectrometry

YOKO YOKOUCHI*
National Institute for Environmental Studies, 16–2, Onogawa, Tsukuba, Ibaraki 305 (Japan)
and
MASAFUMI SANO
Shiga Prefectural Institute for Public Health and Environmental Science, 13–45, Gotenhama, Otsu, Shiga 520 (Japan)

(Received April 23rd, 1991)

ABSTRACT

A simple method for the determination of trace volatile organic compounds in the soil was developed, based on the thermal vaporization of the volatile organics from the sample (1–3 g) and their entrapment on Tenax-GC adsorbent, followed by capillary gas chromatography–mass spectrometry. Using this method, volatile hydrocarbons, aldehydes, sulphides and ketones could be measured in garden soil.

INTRODUCTION

Many kinds of organic compounds are present in soil naturally and/or anthropogenically. They have been studied from the viewpoint of soil contamination [1] and soil chemistry [2], but might also be important in atmospheric chemistry, as volatile organics would be expected to migrate from the soil into the air.

Organics in the soil have usually been determined by gas chromatography (GC) or GC–mass spectrometry (MS) after extraction and concentration with a rotary evaporator. However, volatile organics are likely to be lost through the process of evaporative concentration, and for compounds having similar boiling points to solvents, solvent extraction cannot be applied.

We have therefore developed a technique for the determination of volatile organics in soil based on thermal vaporization from the sample under a flow of nitrogen and entrapment on Tenax-GC adsorbent, followed by capillary GC–MS. The use of a

0021-9673/91/$03.50

Poraplot Q analytical capillary column made it possible to refocus the organics introduced into the capillary without the necessity to cool them below 0°C, thus preventing the formation of ice. This method has been successfully used to determine volatile organics in garden soil.

EXPERIMENTAL

Apparatus

Fig. 1 shows the preconcentration–capillary GC–MS system. The preconcentration unit consists of a soil sample, a cold trap, a Tenax-GC trap and two six-port valves (VL1 and VL2) and is a form of the analytical system for atmospheric organics described elsewhere [3]. The soil sample is placed inside a 5-ml screw-capped vial sealed with a PTFE-lined silicone-rubber septum and an aluminium open-top screw cap, and is inserted into an aluminium heater block. The cold trap is an empty screw-capped vial maintained at 0°C with ice–water. The adsorption trap is a stainless-steel tube (4 cm × 3.2 mm), packed with 0.04 g of Tenax-GC and is set inside a PTFE tube (8 cm × 14 mm O.D.). The temperature around the trap can be regulated in the range from −60 to 300°C by a temperature regulator which controls both liquid carbon dioxide cooling and a heater. All the connections except for the soil sample and the water trap are of 1.6 mm O.D. stainless-steel tubing which is as short as possible. The soil sample and the cold trap are connected with a stainless-steel needle (7 cm long), and are connected to the valve VL1 with 1.6 mm O.D. PTFE tubing and 1.6 mm O.D. stainless-steel tubing, respectively, through the needle end. Screw vials, septa and needles were precleaned by heating at 150°C in an evacuated oven before use.

To avoid any adsorption of the compounds on the transfer lines, the valves and the stainless-steel tubes downstream of the cold trap were warmed at 115°C by wrapping with a flexible heater.

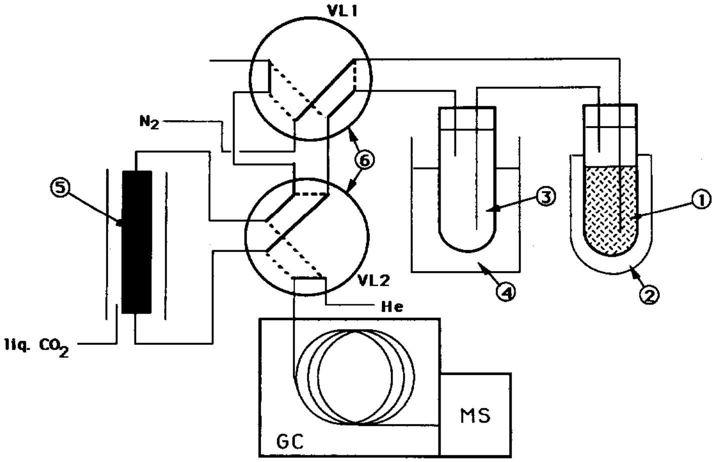

Fig. 1. Analytical set-up for the determination of volatile organic compounds in soil. 1 = Soil sample; 2 = heater block; 3 = cold trap; 4 = ice-water; 5 = Tenax-GC trap; 6 = six-port switching valve.

Computerized GC–MS analyses were carried out on Finnigan MAT 90 with a Varian 3400 gas chromatograph.

Procedure

The soil sample is collected *in situ* by directly inserting the sample into 5-ml vials, which are subsequently sealed tightly with PTFE-lined silicone-rubber septa. The vial is connected to the valve by inserting the needle ends as shown in Fig. 1. The following analytical process is a variation of the purge-and-trap method. On purging, the positions of the two switching valves are at the position of the solid line, and the vial is heated at a preset temperature (150°C) for 7 min. Nitrogen purge gas at a flow-rate of 20 ml/min sweeps the evaporated compounds from the soil sample onto the Tenax-GC trap, which is maintained at 10°C, passing the cold trap where most of the water vapour is removed to avoid interference. The lines are then directly connected by removing the sample and the cold trap, and by inserting the two needle ends into an empty vial, and only nitrogen is passed through the Tenax-GC trap for 5 min to purge water from the adsorbent. After the purge, the switching valve VL2 is changed to the position of the broken line and the Tenax-GC trap is heated to a preset temperature (210°C). Helium carrier gas at a flowrate of 1.4 ml/min transfers the adsorbed compounds onto the analytical capillary column for 7 min. The GC oven temperature is maintained at 55°C during this transfer and then programmed to 220°C at 12°C/min. MS measurements are started immediately after the transfer. The conditions are summarized in Table I. During GC–MS measurements, the valve VL2 is kept in the position of the solid line to allow pure nitrogen to flow through the Tenax-GC trap to remove any remaining trace contaminants.

Calibration is performed by analysing standards (0.1–100 ng of authentic samples dissolved in 0.5 μl of methanol) injected into the vial in place of the soil sample in Fig. 1.

RESULTS AND DISCUSSION

Recovery and precision

The breakthrough volume for *n*-pentane on the Tenax-GC adsorbent was found to be 25 l per gram of Tenax-GC (1 l per 0.04 g of Tenax-GC) at 10°C. As the total amount of nitrogen purge gas flowing from the soil sample into the Tenax-GC trap is only 140 ml, *n*-pentane and less volatile hydrocarbons are considered to be trapped without any loss.

Studies on recovery and reproducibility were done for eleven volatile halogenated hydrocarbons (the most volatile being dichloromethane and the least volatile

TABLE I

GC–MS CONDITIONS

Column	Poraplot Q, 10 m × 0.32 mm I.D.
Oven temperature	Programmed from 55 to 220°C at 12°C/min
Ionization	Electron impact
Scan range	m/z 35–500

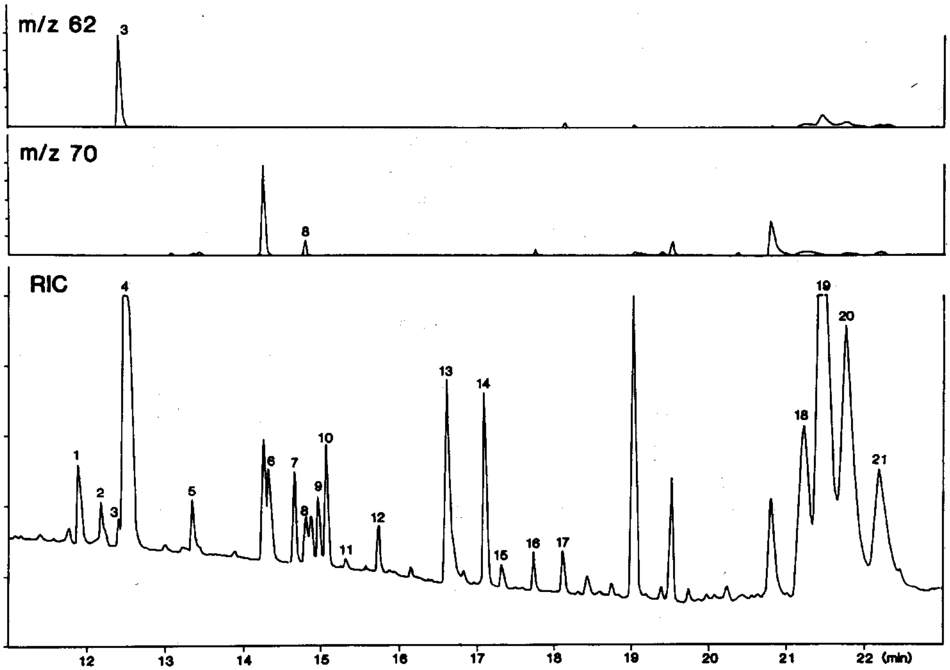

Fig. 2. Reconstructed ion chromatogram (RIC) and ion chromatogram (IC) traces for *m/z* 62 and 70 obtained from a garden soil sample.

tetrachloroethylene), where soil sample, standard (16 ng of each halogenated hydrocarbon in 0.5 μl of methanol) and standard added soil sample were analysed, and the results were compared [4]. A quantitative recovery (90–101%) was obtained for each of the tested components. The relative standard deviation (five repetitions) for each component was in the range 1–5%.

TABLE II

TENTATIVELY IDENTIFIED COMPOUNDS IN THE SOIL

Compound	Peak No.[a]	Retention time (min:s)	Compound	Peak No.[a]	Retention time (min:s)
Acrolein	1	11:52	Hexane	12	15:44
Propanal	2	12:11	3-Methylbutanal	13	16:36
Dimethyl sulphide	3	12:24	Pentanal	14	17:06
Acetone	4	12:28	Dimethyl disulphide	15	17:19
Pentane	5	13:21	Heptane	16	17:45
2-Methylpropanal	6	14:19	Toluene	17	18:06
2-Methylfuran	7	14:39	$C_{10}H_{16}$	18	21:12
Methyl vinyl ketone	8	14:48	α-Pinene	19	21:35
Butanedione	9	14:57	Camphene	20	21:43
Methyl ethyl ketone	10	15:04	$C_{10}H_{16}$	21	22:11
2-Methylpentane	11	15:19			

[a] See Fig. 2.

Blank

A blank test with a pre-baked vial showed no detectable contamination.

Analysis of garden soil

Garden soil (2–3 g), collected in the grounds of the National Institute for Environmental Studies, was analysed by the proposed method. Fig. 2, which is an example of a reconstructed ion chromatogram (RIC) obtained for these soil samples, shows good chromatographic separation. Compounds identified tentatively on the basis of their mass spectra are summarized in Table II with the corresponding peak numbers and retention times in Fig. 2. A variety of volatile compounds, including hydrocarbons, aldehydes, ketones, ethers and sulphides, were found to be present in the soil. Most of these compounds have not been reported previously. Several other soil samples showed different compositions, but acetone was always the major component.

Regarding their sources, monoterpene hydrocarbons ($C_{10}H_{16}$) such as α-pinene and camphene are well known secondary products of higher plants. Aldehydes, ketones and sulphides are also likely to be derived from terrestrial plants and/or bacterial production [5], although very little is known about their behaviour.

Ion chromatography (IC) can be used for the selective detection of overlapping compounds. In Fig. 2, IC traces for ions of m/z 62 and 70 show the selective peaks of dimethyl sulphide and methyl vinyl ketone, respectively. For known compounds, more sensitive MS analysis can be done using selected ion monitoring.

A significant feature of the compounds detected with the present method is that all of them seem to migrate easily into the atmosphere owing to their high volatility. This suggests that they participate in atmospheric chemistry. For example, dimethyl sulphide emitted from the soil might contribute to the production of sulphate, in addition to that from the oceans [6]. The amount of dimethyl sulphide detected in the soil was in the range of several nanogram per gram, which is higher than its average concentration in the oceans [6].

REFERENCES

1 J. S. Warner, M. C. Landes and L. E. Slivon, in R. A. Conway and W. P. Gulledge (Editors), *Hazardous and Industrial Solid Waste Testing, Second Symposium* (*ASTM STP* 805), Amercian Society for Testing and Materials, Philadelphia, 1983, p. 203.
2 G. Eglinton and M. T. J. Murphy (Editors), *Organic Geochemistry*, Springer, Berlin, 1969.
3 Y. Yokouchi, Y. Ambe and T. Maeda, *Anal. Sci.*, 2 (1986) 571.
4 Y. Sano, *Master Thesis*, Tsukuba University, Tsukuba, 1991.
5 T. E. Graedel, D. T. Hawkins and L. D. Claxton, *Atmospheric Chemical Compounds—Sources, Occurrence and Bioassay*, Academic Press, Orlando, 1986, Ch. 6, 7.
6 M. O. Andreae and H. Raemdonck, *Science* (*Washington, D.C.*), 221 (1983) 744.