CHROMSYMP. 2285

Modern approach to the quantitative determination of volatiles in solid samples

Multiple headspace extraction gas chromatography for the determination of cyclohexanone residues in soil

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ABSTRACT

The application of multiple headspace extraction gas chromatography to the quantitative determination of volatiles in soil samples has been studied by means of a simulated system represented by cyclohexanone absorbed on a soil. An example of fast and accurate determination is reported. It has been experimentally demonstrated that this technique may overcome the problems linked to the handling of a solid matrix contaminated by volatiles, because it is not required to reproduce the solid matrix to perform a quantitative determination, it being sufficient to obtain complete vaporization of the calibration standard.

INTRODUCTION

The importance of environmental monitoring with respect to ubiquitous contaminants, has long been recognized, and this has led to the availability of standardized monitoring methods and reference materials [1].

A different situation pertains in the field of the accidental contamination of the environment caused by unforeseeable events, such as spillages, illegal waste, or accidents in chemical plants, ships, tanktrucks etc. In almost all such cases, besides the environmental "first aid" measures, it is necessary to perform quantitative determinations of the substances accidentally present in the environmental matrices. It is quite common to deal with volatile organic substances; their analysis is not too difficult in air, by means of absorbent tubes [2], and in aqueous samples, by means of static or dynamic headspace techniques [3–5]. When the polluted matrix is the soil, however, many difficulties arise. It is very difficult to carry out accurately liquid–solid extractions when the substances are volatile. Also, headspace techniques, calibrated by the usual methods, such as standard additions, internal standard or external calibration, rarely produce accurate results. This inadequacy is due to the practical impossibility

of overcoming matrix effects that dramatically influence partitioning of the volatile between the soil and the headspace [6], leading to highly inaccurate results [7].

A modern solution to these problems is an improvement of the automated headspace gaschromatographic analysis, a discontinuous gas extraction technique, calles multiple headspace extraction (MHE-GC).

This technique is a repeated withdrawal of headspace in equilibrium with a solid sample, followed by a GC separation of the components in the headspace. If repeated extraction steps are performed the resulting chromatogram shows a series of peaks decreasing in their areas according to a logarithmic law. Theoretically extraction could be carried out until all the volatiles had been removed. However, after few steps (from six to nine) a mathematical extrapolation may be applied, to obtain the total amount of the compound to be determined. In fact, as extensively described by Kolb [8], it can be assumed that the chromatographic peak area is proportional to the concentration:

$$A_n = A_1 e^{(1-n)k*} \tag{1}$$

where A_n is the peak area of the nth step, and $k*$ is a constant including both chemical and instrumental parameters.

Eqn. 1 can be treated as a geometrical progression:

$$\Sigma A_n = A_1(1 + e^{-k*} + e^{-2k*} + e^{-3k*}...) \tag{2}$$

and calculated according to:

$$\Sigma A_n = A_1/(1 - e^{-k*}) \tag{3}$$

Therefore, the total amount of a volatile in a vial is obtained from Eqn. 3, where A_1 is the experimental value of the peak area of the first MHE step. The value of $k*$ can be experimentally obtained by plotting the natural logarithms of the area values *versus* the number n of extraction steps (injections); in fact, at equilibrium, a straight regression line is obtained and the regression coefficient of this straight line corresponds to $k*$.

To perform an accurate quantitative determination, calibration is carried out by submitting a vial containing only few microlitres of the volatile to the MHE procedure under the same instrumental conditions adopted for the solid matrix. By multiplying the response factor obtained from the standard by the total area value of the analyte peaks in the sample, the amount of the volatile in the sample can be easily obtained.

The suitability of this procedure for the fast quantitative determination of residual volatiles in contaminated soils has been experimentally studied by means of a simulated system of contamination. This system consists of a soil contaminated by a known amount of a volatile substance. Cyclohexanone was chosen as the volatile substance, and garden soil as representative of a common soil.

EXPERIMENTAL

Contaminated soil sample

A 30-g sample of the soil was accurately weighed and placed in a glass flask with a ground glas stopper. Then, 30 μl of an aqueous cyclohexanone standard solution (9420 mg/l) were added by means of a microsyringe, and the flask was slowly shaken mechanically, to allow the cyclohexanone to be absorbed homogeneously by the soil. The sample was shaken for 2 h at room temperature. The concentration of cyclohexanone in the soil was 9.42 μg/g.

Analytical samples

A 1-g sample of the contaminated soil was placed in a 20-ml headspace vial, 100 μl distilled water were added, and the vial was sealed with an open-centre aluminum cap and PTFE-faced butyl rubber septum. A small amount of water was added to promote the release of the volatile. This addition will be further discussed later. Six replicate soil samples were prepared. A blank sample was prepared by placing 1 g of uncontaminated soil and 100 μl of distilled water in a headspace vial.

Calibration standard

A 1-μl volume of the aqueous cyclohexanone standard was placed in an empty headspace vial, through the septum of an already sealed vial, by means of a 1-μl microsyringe. This calibration vial contained 9.42 μg of cyclohexanone in 1 μl of water. Three replicate calibration standards were prepared.

Instrumentation

The GC system consisted of a Perkin-Elmer 8500 gas chromatograph, equipped with a Perkin-Elmer HS101 automatic headspace sampler and a flame ionization detector. Data collection and handling were performed with an Epson PCAX2 and Perkin-Elmer Nelson 2600 chromatography software.

Operating conditions

The fused-silica column (10 m × 0.53 mm I.D.) was CP-Sil-19 CB, with film thickness, 2 μm (Chrompack, the Netherlands). The GC operating conditions were as follows: oven temperature, 60°C (isothermal); injector temperature, 160°C; detector temperature, 220°C; carrier gas, nitrogen; headpressure, 40 kPa; run time, 6 min. The MHE operating conditions were as follows: thermostat temperature, 100°C; needle temperature, 110°C; transfer line temperature, 120°C; injections per vial, 9; thermostatting time, 45 min (soil samples), 15 min (standards); pressurization time, 1 min; injection time, 0.10 min; withdrawal time, 0.20 min; number of vents, 1. It must be stressed that thermostatting times are different between samples and standards. In fact, to perform an accurate MHE determination, it is of fundamental importance to evaporate the calibration standard totally. Therefore, some preliminary tests were carried out by analysing identical standards after increasing thermostatting times; it was observed that 15 min were sufficient, at the selected temperature, to ensure the complete vaporization of cyclohexanone standard.
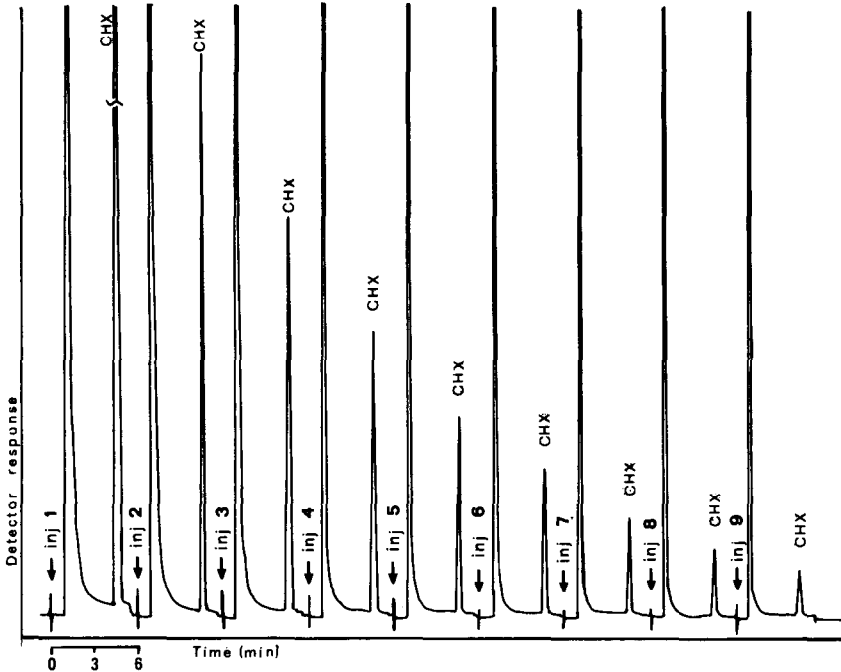
Fig. 1. Chromatograms from a nine-step MHE determination of cyclohexanone in a contaminated soil sample.

MHE-GC determination

Analytical samples, calibration standard and blank samples were submitted to the nine-step MHE-GC determination of cyclohexanone in contaminated soil, under the above described conditions. The chromatograms obtained from a contaminated soil sample are shown in Fig. 1.

RESULTS

Computing of the results

By plotting the natural logarithms of the peak area *versus* the number of the injection, straight regression lines were obtained for both the standards and the samples. Fig. 2 shows the plot of two straight regression lines obtained from the averaged standards and from one of the six replicate soil samples.

The straight regression line calculated from the standards was:

ln area $=$ -0.35 (number of injection) $+$ 7.79

with a linear correlation coefficient r_{xy} $=$ 0.9999.

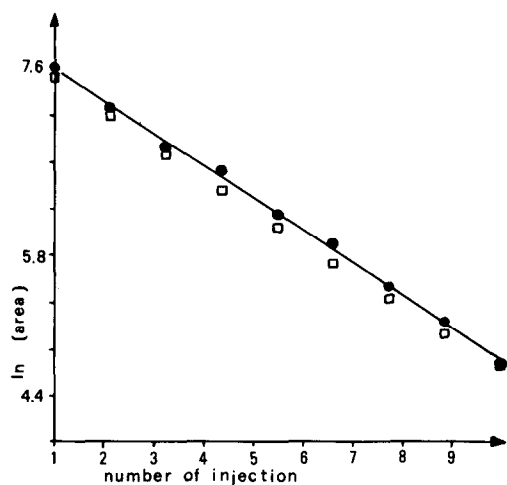The value of k^* (0.35) obtained for the standard was inserted into eqn. 3,

Fig. 2. Straight regression lines from MHE determinations of cyclohexanone in standards (□) and in a contaminated soil sample (●).

together with the experimental A_1 value (1777.2), and the total area value for cyclohexanone standard was computed:

$$\Sigma A_n = 1777.2/1 - e^{-0.35} = 6078.7$$

The total area value corresponding to 9.42 μg of cyclohexanone yields a response factor of amount per unit peak area, *i.e.*:

9.42 μg/6078.7 area unit = 0.0015

TABLE I

RECOVERY OF CYCLOHEXANONE FROM CONTAMINATED SOIL SAMPLES BY MHE-GC

Cyclohexanone added to soil, 282.6 μg per 30 g; soil aliquot submitted to MHE determination, 1 g; cyclohexanone theroretically present in 1-g soil aliquot 9.42 μg; number of replicate determinations, 6.

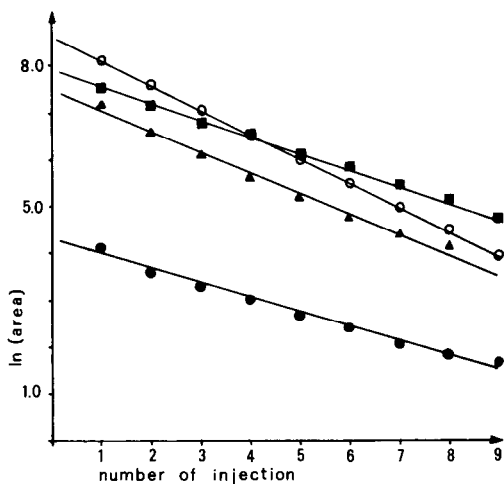| Sample	Cyclohexanone		Recovery (%)	Total area
	Theoretical (μg)	Experimental (μg)		
1	9.42	10.08	107.0	6505.9
2	9.42	8.98	95.3	5794.8
3	9.42	9.76	103.6	6298.1
4	9.42	8.74	92.8	5639.9
5	9.42	9.83	104.4	6343.3
6	9.42	8.76	93.0	5652.8
Mean values	9.42	9.36	99.4	6039.1
S.D.		0.6	6.4	386.2
R.S.D. (%)		6.4	6.4	6.4

Fig. 3. Effect of increasing addition of water on the recovery of cyclohexanone from contaminated soil: (●) no addition, 4% recovery; (▲) 0.005% (v/w) addition, 48% recovery; (■) 0.01% (v/w) addition, 99.4% recovery; (○) standard, theoretical amount of cyclohexanone.

The same procedure was followed for the samples, and the total area values were computed. By multiplying these values by the above-reported response factor, the amount of cyclohexanone in the samples was easily obtained. The results from the six replicate samples, the corresponding recovery percentages, and the total area values are shown in Table I.

DISCUSSION

As described in Experimental, small amounts of water were added to the sample, to promote the release of cyclohexanone from the soil. This system is typical of a medium-polar compound absorbed on a strongly polar matrix. In these cases, small amounts of another polar compound, with a greater affinity for the matrix than the analyte, will facilitate the release of the absorbed compound, and also enhance the analytical recovery from the sample.

In this study, it was experimentally observed that the addition of increasing amounts of water to the soil samples led to the optimization of the recovery of cyclohexanone. This effect is illustrated in Fig. 3, which shows four straight regression lines corresponding to the addition of increasing amounts of water: 0%, 0.005%, and 0.01% v/w. The fourth line is that of the reference standard. It can be seen that the addition of 0.01% water led to quantitative recovery of cyclohexanone, and the corresponding regression line is superimposed on that of the standard. Therefore, the addition of 0.01% water was deemed essential to carry out the determination.

The analytical procedure was applied to six replicate soil samples; in all the tested samples, the recovery of cyclohexanone was practically quantitative. The amount of cyclohexanone theoretically present in the 1-g soil aliquots submitted to the MHE-GC determination was 9.42 μg; the amount found was 9.36 μg (mean value from six determinations; range, 8.74–10.03 μg).

The repeatability of the developed method, expressed as percentage relative standard deviation (R.S.D.) was 6.4%. This relatively high value may be explained taking into account the inhomogeneity of cyclohexanone in the soil and the intrinsic variability due to handling of volatiles. However, this situation reflects what may actually happen in authentic samples of a contaminated soil. On the other hand, the study was aimed at solving analytical problems linked to the handling to contaminated soils.

The addition of a small amount of water may be reasonably proposed as a systematic step in the determination of volatiles in a contaminated soil sample, when the determination is extremely urgent, as in the case of accidents, spillages, etc. In fact, if the contaminating compounds have a good affinity for soil (*i.e.* with polar groups in their structure, and not too high a volatility), they will be better released to the headspace by the action of water. In contrast, if the compounds have poor affinity for soil (*i.e.* non-polar structures, high volatility) they will not remain strongly absorbed by the soil and are likely to escape to the atmosphere. Therefore, there is a low probability of finding large amounts of this type of compound in soil. In any case, a small amount of water is very unlikely to interfere with the determination of non-absorbed compounds; on the other hand, if the time available for the determination if not too short (*i.e.* soil-monitoring programs, routine procedures, *etc.*) it is advisable to evaluate the water content of the soil samples before defining the correct amount of water to add.

CONCLUSIONS

The developed procedure may be considered as a validated example of a rapid and simple quantitative determination of volatiles in a contaminated soil sample. By and large, MHE-GC appears to be the most convenient technique to use when a solid sample has to be tested; it requires minimal sample handling, minimal consumption of materials and, most important of all, it is unnecessary to reproduce the matrix to perform accurate determination of volatiles. It is sufficient to ensure the complete vaporization of the calibration standard.

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