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## Note

### Analysis of tetrahydrothiophene in water by headspace high-resolution gas chromatography-mass spectrometry

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Tetrahydrothiophene (THT) is widely used as a warning odorant for odourless fuel, city and natural gases<sup>1-3</sup> and recently also for herbicides<sup>4</sup>. It appears to be moderately toxic, its LD<sub>50</sub> after inhalation in mice being 26.7 mg/l (ref. 5). This value is about one third that of thiophene. Chronic inhalation of 3 mg THT/ml for 2 h per day for 3 months caused behavioural and liver function disorders in mice<sup>5</sup>. No threshold limiting value (TLV) has been established<sup>6</sup>.

Sulphur compounds including THT have been assayed in gases by electroanalytical<sup>7</sup>, olfactory<sup>8</sup> and gas chromatographic (GC) methods, the latter coupled to various types of detectors (flame ionization<sup>9</sup>, flame chemiluminescence<sup>10</sup>, thermoionization<sup>11</sup> and flame photometric<sup>12</sup>). To our knowledge, only one method has been reported for THT determination in water samples<sup>13</sup>. In this method, headspace gas chromatography (HS-GC) was employed but the limit of sensitivity was not reported.

This paper reports a simple, highly sensitive procedure to quantitate THT in water using headspace high-resolution GC (HS-HRGC) combined with mass spectrometry and selected ion monitoring (MS-SIM). The method was developed to monitor THT contamination of soil and spring-waters surrounding an area where a container had been incorrectly disposed.

## EXPERIMENTAL

### *Apparatus*

An LKB 2091 gas chromatograph and low resolution mass spectrometer operated in the electron impact mode were equipped with an LKB 2130 computer for data acquisition and calculation. The MS-SIM instrumental conditions were as follows: electron energy, 70 eV; trap current, 50  $\mu$ A; ion source temperature, 250°C; separator temperature, 260°C; monitored ion for THT,  $m/z$  88.

The GC instrumental conditions were as follows: carrier gas (helium) headpressure, 1 atm; oven temperature, 55°C; injector temperature, 100°C.

The glass capillary column was prepared according to the following technique. A borosilicate (Pyrex) tube was drawn with a Shimadzu GDM1 glass drawing machine to obtain a 20-m-long capillary (0.3 mm I.D.); a 0.05- $\mu$ m-thick film of OV-1 was then coated on the deactivated glass surface, following the procedures described by Grob *et al.*<sup>14</sup>.

### Reagent

THT, used as reference standard, was from Janssen Chimica (Belgium).

### Analytical procedure

Glass vials (8 ml), of the type used for injectable antibiotics, were used as sample vessels. A 1-ml volume of water, saturated with sodium chloride, was placed in each and the vial was immediately sealed with an aluminium cap and a rubber septum bearing a PTFE disk (0.1 mm thick) in the inner part. The vials were then equilibrated for 15 min at 60°C using a thermostat bath (Reacti-Therm Heating Module; Pierce, Rockford, IL, U.S.A.).

Using a pre-warmed (60°C), gas-tight syringe (Cat. No. 1001-LTN; Hamilton, Switzerland), 500  $\mu$ l of headspace vapour were withdrawn and injected in the gas chromatograph in the split mode. The whole operation has to be carried out as quickly as possible to avoid cooling and vapour condensation.

Soil analyses were carried out on 1-g samples following the same procedure as described for water, except that 4  $\mu$ l of headspace vapour were injected.

### RESULTS AND DISCUSSION

Fig. 1 shows a total ion current (TIC) chromatogram obtained by analyzing 4  $\mu$ l of headspace from a soil sample taken close to a buried container leaking with an intense smell typical of sulphur compounds. Peak A has the same elution position as standard THT. The identity of THT was confirmed by GC-MS. The mass spectrum of peak A (Fig. 2) was identical to that of standard THT and to that previously reported for THT<sup>15</sup>. This result indicates that THT spillage had occurred.

Shown in Fig. 3 are typical mass fragmentograms ( $m/z$  88) of a blank solution,

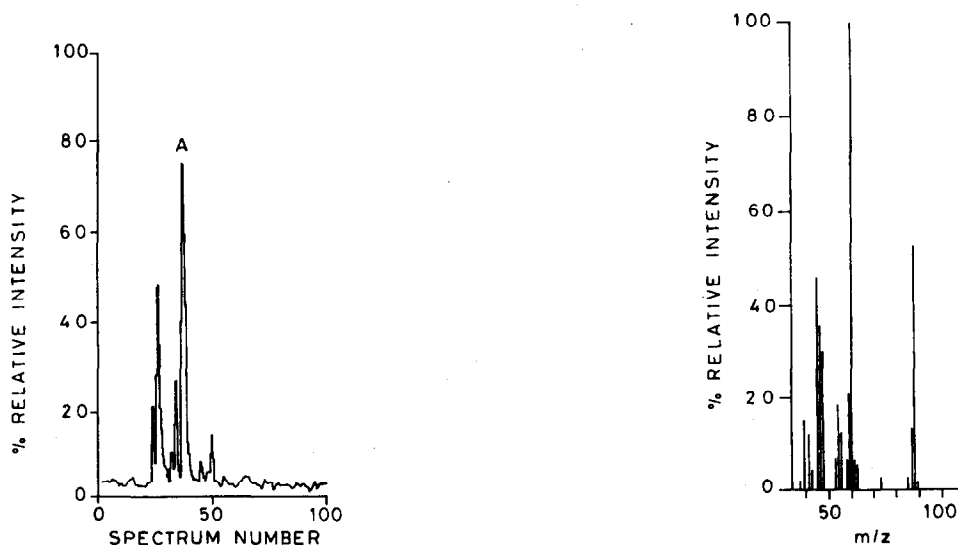


Fig. 1. Total ion current chromatogram of the headspace from a soil sample.

Fig. 2. Mass spectrum of peak A in Fig. 1.

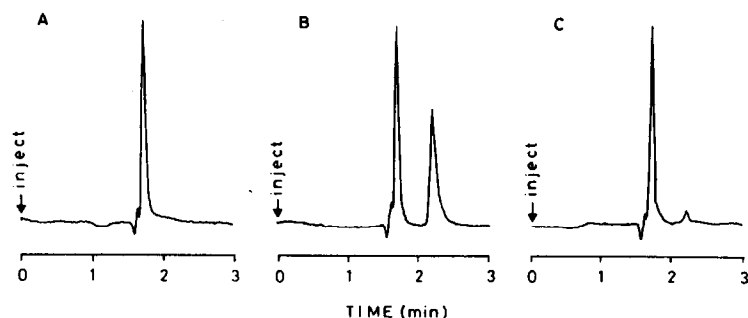


Fig. 3. Mass fragmentograms ( $m/z$  88): A, blank solution; B, standard THT (50 ng/ml); C, water sample.

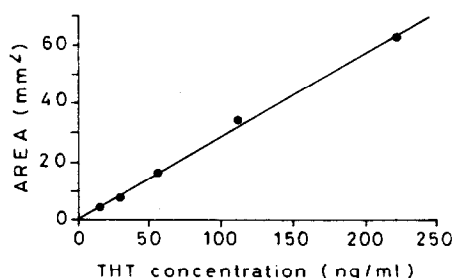


Fig. 4. Calibration curve of the peak area of THT vs. its concentration in water.

a standard THT preparation (50 ng/ml) and a water sample. The determination was made by use of a calibration curve where the THT peak area was plotted against its concentration in ng/ml (Fig. 4). As shown, a linear response ( $r = 0.999$ ) was obtained for concentrations of THT ranging from 10 to 250 ng/ml, passing through the origin, indicating that no absorption occurs in the sampling system and that quantitative analysis was accurate even at a concentration of 10 ng THT per ml water.

The recovery of different amounts of THT (10–250 ng) added to 1 ml of water was  $84 \pm 2\%$  (mean  $\pm$  S.D.).

THT was present at trace levels ( $< 10$  ng/ml) in only one of seven samples of different spring-waters analysed with the method described. The method appears to be useful for detecting water contamination by THT at levels as low as 10 ng/ml.

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