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## Note

### Gas chromatographic–mass spectrometric identification of tear-gases in dilute solutions using large injection volumes

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The analysis of tear-gases such as  $\omega$ -chloroacetophenone (CN), *o*-chlorobenzylidenemalononitrile (CS) and dibenz[*b,f*]-1,4-oxazepine (CR) by gas chromatography–mass spectrometry (GC–MS) has been described in a number of publications<sup>1–4</sup>. Up to now this analysis has been carried out by injecting 1  $\mu$ l of a solution containing the tear-gases into a packed column. Since identification by GC–MS should preferably be based on a full mass spectrum, this analysis provides a sensitivity level of 1–10 ng/ $\mu$ l.

Recently, two investigations have been reported concerning the injection of large volumes (> 100  $\mu$ l) of solutions into an adsorption tube filled with Tenax. After removal of the major part of the solvent by passing a gas flow through the adsorption tube, the compounds trapped on the Tenax were analysed by thermodesorption followed by cold trapping, flash heating and separation using capillary gas chromatography. Verweij *et al.*<sup>5</sup> used this procedure for an ethyl acetate solution containing organophosphorus compounds. A volume of 500  $\mu$ l was injected in small portions onto a quartz-wool plug in front of the Tenax bed (25 mg). Most of the ethyl acetate was removed in *ca.* 45 min using a nitrogen flow of 30 ml/min. Kirschmer and Oehme<sup>6</sup> injected 100  $\mu$ l of an *n*-hexane solution containing polycyclic aromatic hydrocarbons directly onto the Tenax bed (200 mg) itself, which was connected on-line with the cold-trap kept at  $-20^{\circ}\text{C}$ . After about 3 min, with a helium flow of 60 ml/min, most of the *n*-hexane had passed the Tenax adsorption tube and the cold-trap.

In order to identify the above-mentioned tear-gases at levels below 1 ng/ $\mu$ l by GC–MS we investigated the application of this injection technique. Ethyl acetate and *n*-hexane were chosen as solvents. The latter has been recommended as a solvent for the extraction of clothing contaminated with CS<sup>2</sup>.

## EXPERIMENTAL

### Materials

$\omega$ -Chloroacetophenone (CN) was a commercial product (Aldrich). *o*-Chlorobenzylidenemalononitrile (CS)<sup>7</sup> and dibenz[*b,f*]-1,4-oxazepine (CR)<sup>8</sup> were prepared according to the literature methods and gave satisfactory elemental analyses, IR and NMR spectra. Dilute solutions of the tear-gases were freshly prepared from concen-

trated stock solutions. No decrease in concentrations of the dilute solutions was observed over a period of 1 week.

Ethyl acetate (Merck 868) and *n*-hexane (Merck 4391) were distilled before use.

Glass tubes (16 cm × 6 mm O.D. × 2.8 mm I.D.) were filled with 125 mg of Tenax TA. The tubes were first washed with 10 ml of acetone and *n*-hexane respectively, followed by heating at 280°C in a stream of helium ( $\geq 10$  ml/min) overnight.

Helium was purified with a home-made dry filter, an oxygen filter (Chrompack) and a cold-trap cooled with liquid nitrogen.

### *Instrumentation*

A Chrompack thermodesorption cold-trap (TCT) injector was used. This unit was built onto a Varian 1400 gas chromatograph using a specially designed injection block (temperature 240°C). A piece of fused silica (300 × 0.5 mm I.D.) coated with 5  $\mu$ m of CP Sil 5 CB was used as the cold-trap. The solenoid valve in the vent line of the TCT injector was removed.

Chromatographic separations were carried out on a fused-silica column (50 m × 0.3 mm I.D.) coated with CP Sil 8 CB (Chrompack). The temperature was raised from 80 to 240°C at a rate of 10°C/min. The column was directly connected to the ion source of a VG 7070F mass spectrometer. Electron-impact mass spectra were recorded at an electron energy of 70 eV and an ion-source temperature of 200°C. Spectra were repetitively scanned over the mass range  $m/z$  25–500 every 1.5 sec and stored in a VG 2050 data system.

### *Injection procedure*

A Hamilton gas syringe was used for the injection of 250  $\mu$ l of *n*-hexane or ethyl acetate through a septum cap into the Tenax adsorption tube. Air was carefully removed from the syringe. The temperature of the cold-trap, connected on-line with the Tenax adsorption tube, was set at -30°C. A helium flow-rate of 50 ml/min at a pre-pressure of 1.4 atm was established by means of a flow regulator in the vent line. This low pre-pressure reduced the amount of solvent entering the GC-MS system. After 5 min the Tenax adsorption tube was heated rapidly to 240°C and maintained at that temperature for 10 min. Upon completion of the thermodesorption step, the vent was closed and the pre-pressure was raised to 2.4 atm, providing a flow-rate of 1 ml/min through the capillary column. The cold-trap was flash-heated to 240°C, which temperature was maintained for at least 1 min. About 1 min after the flash heating the flow in the vent line was established again at 50 ml/min by means of the flow regulator. In this way a reduction in the solvent background during the GC-MS analysis was achieved.

## RESULTS AND DISCUSSION

The resulting total-ion-current gas chromatogram obtained after the injection of 250  $\mu$ l of an *n*-hexane solution containing 20  $\mu$ g/ $\mu$ l of each of the tear-gases CN, CS and CR into the Tenax adsorption tube, followed by removal of *n*-hexane, thermodesorption, cold trapping, flash heating and capillary GC-MS analysis, is presented in Fig. 1. Residual *n*-hexane together with some higher boiling impurities

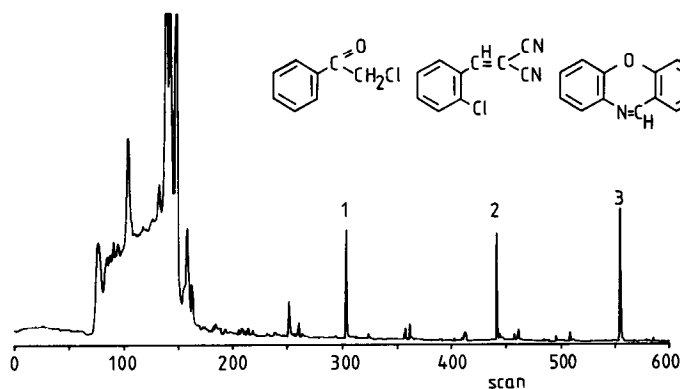


Fig. 1. Total-ion-current gas chromatogram obtained after the injection of 250  $\mu$ l of an *n*-hexane solution containing 20 pg/ $\mu$ l of each of the tear-gases CN (1), CS (2) and CR (3).

appear at the beginning of the chromatogram. If purified *n*-hexane is used the peaks of the tear-gases (each representing an amount of 5 ng) are clearly visible. Slight variations in the peak heights were observed during various experiments, mainly due to the relatively slow scan speed of the mass spectrometer compared with the width of the chromatographic peaks. The intensities of the ions in the mass spectra were comparable with those obtained after the injection of 1  $\mu$ l of a 250 times more concentrated solution, indicating that losses in this injection technique are negligible. Similar results were obtained with dilute ethyl acetate solutions of the tear-gases. Volumes greater than 250  $\mu$ l could not be injected on adsorption tubes filled with 125 mg of Tenax TA.

Problems were encountered with CS, which seems to be very sensitive to oxygen. Care has to be taken to prevent the diffusion of oxygen into the injection system, otherwise the peak of CS will be considerably reduced compared with those of CN and CR. The appearance of 2,2-dicyano-3-(*o*-chlorophenyl)oxirane (CS-epoxide)<sup>9</sup> eluted before CS under the prevailing chromatographic conditions may also serve as an indication that oxygen has penetrated into the injection system.

The principal ions in the mass spectra of the tear-gases obtained after the analysis of a dilute (20 pg/ $\mu$ l) solution are presented in Table I. Due to the weak molecular ion ( $m/z$  154), ca. 5 ng were necessary for the identification of CN under electron-impact conditions. Therefore, with an injected amount of 250  $\mu$ l, a minimum

TABLE I  
PRINCIPAL IONS IN THE MASS SPECTRA OF THE TEAR-GASES CN, CS AND CR

Compound	MW	$m/z$ (% relative intensity)
CN	154	50 (25), 51 (33), 77 (71), 78 (8), 91 (9), 105 (100), 106 (8), 154 (2)
CS	188	50 (16), 51 (15), 74 (10), 75 (16), 76 (17), 99 (11), 100 (12), 126 (18), 137 (14), 153 (100), 154 (14), 161 (18), 188 (67), 190 (22)
CR	195	50 (13), 51 (19), 62 (11), 63 (31), 97.5 (7), 139 (24), 140 (12), 166 (25), 167 (45), 168 (9), 195 (100), 196 (15)

concentration of 20 pg/ $\mu$ l was necessary. Both CS and CR exhibit intense molecular ions and high mass fragments, permitting their identification at a lower level.

Our mass spectrum of CR is rather different from that recently published by Tripathi *et al.*<sup>4</sup>. It seems unlikely that 10 ng of CR injected into a GC-MS system would produce such a prominent  $[M + H]^+$  ion as noticed in their spectrum. Moreover, our spectrum is in agreement with a published spectrum<sup>10</sup> which was verified by high resolution mass measurements.

#### REFERENCES

- 1 H. W. Avdovich, A. By, J.-C. Ethier and G. A. Neville, *Can. Soc. Forensic Sci. J.*, 14 (1981) 172.
- 2 J. Nowicki, *J. Forensic Sci.*, 27 (1982) 704.
- 3 R. M. Martz, D. J. Reutler and L. D. Lasswell, *J. Forensic Sci.*, 28 (1983) 200.
- 4 D. N. Tripathi, R. C. Malhotra and A. Bhattacharya, *J. Chromatogr.*, 315 (1984) 417.
- 5 A. Verweij, M. A. van Liempt-van Houten and H. L. Boter, *Int. J. Environ. Anal. Chem.*, in press.
- 6 P. Kirschmer and M. Oehme, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 306.
- 7 B. B. Corson and R. W. Stoughton, *J. Am. Chem. Soc.*, 50 (1928) 2828.
- 8 F. Hunziker, F. Künzle, O. Schindler and J. Schmutz, *Helv. Chim. Acta*, 47 (1964) 1163.
- 9 E. R. J. Wils and A. G. Hulst, *Fresenius Z. Anal. Chem.*, 320 (1985) 357.
- 10 J. Enqvist, *Identification of Non-phosphorus Warfare Agents*, ISBN 951-46-6386-1, Ministry of Foreign Affairs of Finland, Helsinki, 1982, p. 140.