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## Chromatographic characterization of lachrymatory agents in tear gas aerosols

During the past few years a variety of aerosol sprays containing tear gases has become available to the public in a number of countries. In the United Kingdom, however, tear-gas aerosols are classified as offensive weapons and their possession is illegal. Because of the legal restrictions on these products, methods for the identification of the active ingredients are of forensic interest, and this paper describes the chromatographic procedures used in this laboratory.

The lachrymatory materials commonly used are α-chloroacetophenone (CN), *o*-chlorobenzylidenemalonitrile (CS), chloroacetone and oleoresin capsicum, (a mixture obtained by extracting capsicum seed pods with acetone, this contains capsaicin — *trans*-8-methyl-N-vanillyl-6-nonenamide — as its active ingredient). In commercial aerosol products, these materials are present with a propellant and a suitable organic solvent.

Very little information is available in the literature concerning the gas chromatography of these lachrymatory agents. SREENIVASON AND BOESE[1] were unable to distinguish lachrymators from solvents in the samples they examined, but STAHL *et al.*[2] reported the detection of CN in commercial products. A method for the gas chromatographic characterization of capsaicin has been described[3], and its thin-layer separation on polyamide plates has also been reported[4].

*Experimental*

Standard solutions of the lachrymators were prepared in acetone and when kept refrigerated were stable for long periods.

*Gas chromatography.* A number of stationary phases were investigated but on most of these appreciable tailing was displayed by the lachrymators. The most useful column was found to be a 0.9 m × 2.2 mm stainless-steel column containing 2% Carbowax 20M on Chromosorb G, acid washed and silanized, 80–100 mesh. Symmetrical peaks were obtained on this column. Both flame ionisation and electron-capture (tritium) detection were used. Because of the widely different volatilities of the compounds two different isothermal operating temperatures (60° and 180°) were found to be necessary.

The procedure adopted with samples was to spray a short burst from the aerosol container into a weighed beaker. After standing at room temperature for about 30 min to allow all the propellant to evaporate, the beaker was reweighed. The residue was dissolved in acetone and after suitable dilution was injected on to the column at the two different temperatures.

*Thin-layer chromatography.* Thin-layer chromatography was only applied to solutions containing oleoresin capsicum. Separations were carried out on a 250-μ layer of Silica Gel G (Merck). Portions of the solutions derived from the aerosol cans together with oleoresin capsicum and capsaicin standards were spotted on to the plate. This was developed in a benzene–ethanol–ethyl acetate (5:1:1) solvent mixture. The visualizing agent used was a mixture of 2% ferric chloride and 1% potassium ferricyanide (prepared by mixing the fresh aqueous solutions immediately before use). This was oversprayed with 2 *N* HCl.

*Results*

With the exception of oleoresin capsicum the lachrymatory agents gave well characterized gas chromatographic peaks displaying a high response to electron-capture detection. Oleoresin capsicun. BP, gave a few minor peaks at *RRT* (180°) of 30, 34, 136. These peaks were not detected by electron-capture and the low response with flame ionisation detection indicated that the bulk of the material injected did not elute from the column. Capsaicin did not gas chromatograph under the conditions used.

In most of the tear gas samples claimed by the manufacturers to contain oleoresin capsicum, gas chromatography revealed two components with *RRT* (180°) of 45 and 280. Both these components gave strong electron-capture response but did not correspond to the behaviour of standard oleoresin capsicum BP solutions and may well derive from components in the solvents used.

The retention time data for the other lachrymators, relative to normal paraffins, are shown in Table I. The detection limits with flame ionisation detection were in the range 2–5 ng and an approximately tenfold improvement was obtained with electron-capture detection.

TABLE I

GAS CHROMATOGRAPHIC PROPERTIES OF LACHRYMATORS

Column conditions: 0.9 m × 2.2 mm stainless-steel column containing 2% Carbowax 20M on AW-DMCS, 80–100 mesh, Chromosorb G. Temperatures: injector 205°, detector 210°, column as above. Carrier gas: nitrogen at 30 ml/min.

| *Compound* | *Column temp.* (°C) | *Relative retention time* |
|---|---|---|
| Octacosane | 180 | 100 (20 min) |
| α-Chloroacetophenone (CN) | 180 | 7.5 |
| *o*-Chlorobenzylidene malonitrile (CS) | 180 | 26 |
| Tetradecane | 60 | 100 (6.7 min) |
| Chloroacetone | 60 | 24 |

With the thin-layer separation, capsaicin gave an intense blue spot at $R_F$ 0.63 with a fainter spot at $R_F$ 0.54. Oleoresin capsicum BP gave the same two spots together with a band of brown-coloured material which ran with the solvent front. Aerosol contents containing oleoresin capsicum displayed the same behaviour. About 10 μg of active ingredient was required for successful visualization. The other lachrymatory agents were not detected by the visualization agent used.

*Discussion*

The inability to detect capsaicin by gas chromatography accords with the previously reported behaviour of this material[3], which showed that glass columns and low-loaded glass bead supports were necessary for successful separations. Pure samples of the other lachrymatory agents were readily detected by gas chromatography but when different manufactured brands of tear gas were examined using flame ionisation detection, interferences were frequently encountered. These interferences took the form of a broad unresolved solvent peak obscuring the lachrymator

peak and were assumed to derive from the commercial solvents used. When electron-capture detection was used, however, no response was obtained from the solvents and the lachrymator could be readily characterized. If electron-capture detection is used, it is essential that all the propellant be allowed to evaporate as these fluorinated compounds are strong capturers.

The combination of gas chromatography (with electron-capture detection) and thin-layer chromatography has been found to provide an effective method of characterizing the active ingredients in all the tear gas aerosols so far examined in this laboratory.

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