

## Notes

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CHROM. 5917

### Gas chromatographic determination of riot-control agents

There are very few references in the literature to the analysis of the irritants used as riot-control agents<sup>1-4</sup>. Most of the procedures described are based on the general properties of war gases and, therefore, are not specific and/or sensitive enough either for the identification of an unknown and its quantitative evaluation in trace amounts or for the demonstration of its presence in mixtures with parent compounds. Some of these difficulties were recently overcome by the separation and detection of these chemical agents using thin-layer chromatography<sup>5</sup>. However, this method is not suitable for quantitative analysis of this group of compounds.

This paper describes a gas chromatographic (GC) method which is not only able to separate several riot-control agents in a mixture, as well as some common impurities, but also to quantify each component by comparison with adequate control standards.

The chemical agents studied in this report, used at one time or another by military and law enforcement agencies, include benzyl bromide, xylyl bromide (mixture of isomers),  $\alpha$ -chloroacetophenone, *o*-chlorobenzalmalononitrile (CS) and diphenylaminechloroarsine (adamsite). The important impurities determined include diphenylamine and bromotoluene (mixture of *o*- and *p*-isomers).

### EXPERIMENTAL.

*Reagents and materials.* The riot-control agents used in this work were acquired from the following sources:  $\alpha$ -chloroacetophenone, xylyl bromide and benzyl bromide in neutral glass sealed vials from H. Stolzenberg (G.F.R.); diphenylaminechloroarsine and *o*-chlorobenzalmalononitrile from Aldrich (U.S.A.). Diphenylamine and chloroform were obtained from Merck (G.F.R.) and dimethylsulphoxide from Schuchardt (G.F.R.).

Chromatographic materials, Silicone OV-17 and Varaport 30 100/120, were obtained from Varian Aerograph (U.S.A.).

*Standard solutions.* Known amounts of the riot-control agents were weighed and dissolved in chloroform (except for diphenylaminechloroarsine which was dissolved in dimethylsulphoxide) to give stock solutions having a concentration of 10 mg/ml. Appropriate dilutions of the stock solution were then used as working standards.

*Apparatus.* The instrument used for this work was a Varian Aerograph 1522-B temperature-programmed chromatograph equipped with dual flame detectors, a Varian Model 20 1 mV recorder and a 6 ft.  $\times$  1/8 in. Pyrex column packed with 3% OV-17 on 100/120 Varaport 30, prepared by the rotating evaporator technique<sup>6</sup>.

It was found necessary to use glass columns in order to avoid decomposition of the compounds by catalysis on a hot metal surface. This effect is particularly marked with benzyl bromide.

The column was conditioned for 8 h at 250°, followed by the injection of Silyl 8 (Pierce Chemical Co., U.S.A.).

The instrument was operated at the following experimental conditions: inlet temperature, 200°; detector temperature, 240°; column temperature, programmed at 12°/min from 55° to 210°; nitrogen carrier flow, 25 ml/min; hydrogen flow, 30 ml/min; air flow, 300 ml/min.

### Results and discussion

The relative retention times (taking  $\alpha$ -chloroacetophenone as reference) as well as the elution temperatures of the compounds tested are given in Table I.

Some of the compounds used as riot-control agents are not pure entities. They either contain impurities or they are mixtures of more than one compound. For example, benzyl bromide used as a lachrymating agent gave two peaks on GC, which NMR analysis showed to be benzyl bromide itself and an unresolved mixture of *o*- and *p*-bromotoluene. GLC analysis by area normalization showed the benzyl bromide and the bromotoluene isomers to be in the same ratio as calculated by NMR (65:35).

TABLE I

RELATIVE RETENTION TIMES AND ELUTION TEMPERATURES OF RIOT-CONTROL AGENTS AND RELATED COMPOUNDS

<i>Compound</i>	<i>Relative retention time</i>	<i>Elution temperature (°C)</i>
<i>o</i> - and <i>p</i> -Bromotoluene	0.64	91
Benzyl bromide	0.74	106
Xylyl bromide	0.92	131
$\alpha$ -Chloroacetophenone	1.00	143
<i>o</i> -Chlorobenzalmalononitrile	1.27	182
Diphenylamine	1.34	192

<sup>a</sup> Relative to  $\alpha$ -chloroacetophenone.

In the case of adamsite, we were not able to detect diphenylaminechloroarsine under the experimental conditions used. Our attempts to prepare a trimethylsilyl derivative of this compound were unsuccessful. All the samples of adamsite tested gave a major peak apparently due to diphenylamine, as its retention time agrees very well with that of a pure sample of this compound. When removal of diphenylamine from adamsite was necessary, this was accomplished by repeated ethanol extraction until the diphenylamine peak no longer appeared in the chromatogram.

All the compounds tested gave good linear quantitative responses within the range of the concentrations employed (Fig. 1). The method of height  $\times$  width at half-height has been employed in order to calculate the peak areas, as this method

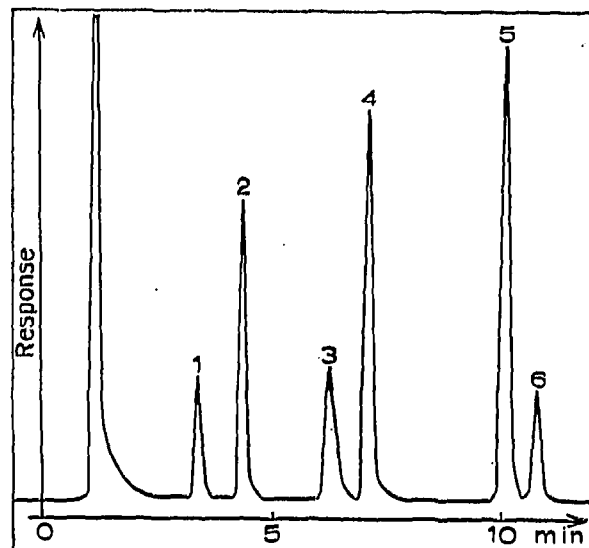
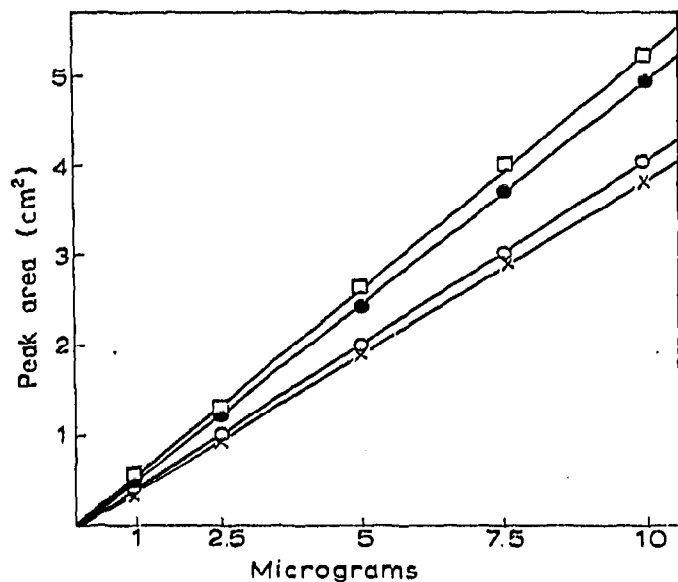


Fig. 1. Standard curves for *o*-chlorobenzalmalononitrile (□),  $\alpha$ -chloroacetophenone (○), xylyl bromide (●) and benzyl bromide (×). ( $256 \times 10^{-10}$  a.f.s.).

Fig. 2. Chromatogram of the mixture of bromotoluene (1), benzyl bromide (2), xylyl bromide (3),  $\alpha$ -chloroacetophenone (4), *o*-chlorobenzalmalononitrile (5) and diphenylamine (6).

is useful in the calculations of symmetric peaks and quantitation may be easily achieved by employing this technique.

Besides the possibility of identifying or determining the concentration of any of the riot-control agents, this procedure was found to be adequate for the separation of any mixture of them. Fig. 2 shows a typical chromatogram of these compounds and their usual impurities. As one can see, a neat separation of all the components is achieved using temperature programming.

The application of this separative GC technique coupled with the use of an electron capture detector may extend the application of the method to the nanogram level.

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