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A GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC METHOD FOR ANALYSIS OF THE CONTENTS OF AEROSOL IRRITANT PROJECTORS*

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SUMMARY

A convenient method for the sampling and total analysis of the propellents and active agents contained in aerosol irritant projectors has been developed. A gas chromatograph equipped with a column packed with 6% Carbowax 20M on Chromosorb G and coupled to a mass spectrometer provides both quantitative and qualitative analysis for the components of a typical irritant projector. The main lachrymator, bromoacetone, represented 1.5% and the propellents dichlorodifluoromethane and trichlorofluoromethane, comprised 97.7% of the aerosol mixture.

INTRODUCTION

Efforts to provide military and police forces, custodial officers and individuals with alternatives to traditional weapons has resulted in the development of a variety of non-lethal devices[1]. One of the most popular of these is the aerosol irritant projector[2], which has been used with increasing frequency in counter-insurgency activities and riot control, to facilitate capture or for self-defence during the past few years. Although the compounds contained in irritant projectors are classified as non-lethal[1], it has been pointed out that the improper use of these devices[2] can cause some degree of physical injury. Concern has also been expressed regarding the incomplete assessment of the physiological effects of irritants, solvents and propellents used[1–3]. Furthermore, it has been emphasized[1] that two serious problems associated with the use of aerosol irritant projectors is the apparent lack of quality control in their manufacture and unreliable information concerning the performance or composition of the formulations provided by manufacturers. A convenient method for sampling and analysis of the contents of aerosol irritant projectors is clearly required. This report describes a receiver designed to collect irritant mixtures delivered from projectors, a gas chromatographic (GC) method used to separate the components of a typical formulation, and their identification by IR and mass spectrometry.

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EXPERIMENTAL

Instrumentation

An F&M Scientific Research Chromatograph, Model 5750 (Hewlett-Packard Ltd.) equipped with a thermal conductivity detector (TCD; bridge current 150 mA) and flame ionization detector (FID) was used for all GC separations. Two columns, one (6 ft. × 1/8 in. O.D. stainless steel) filled with Porapak Q, 80–100 mesh and one (15 ft. × 1/8 in. O.D. stainless steel) packed with 6% Carbowax 20M on Chromosorb G, AW and DMCS-treated, 80–100 mesh were employed. The injection port and detector (TCD and FID) temperatures were kept at 170 ° and 190°, respectively. Carrier gas (helium) flow-rates were set at 25 ml/min and 30 ml/min, depending on whether the Porapak Q or Carbowax 20M column was involved, while the fuel gases (FID), hydrogen and air, were maintained at 10 p.s.i. and 36 p.s.i., respectively. The Porapak Q column was operated isothermally at 170°, the Carbowax 20M column required temperature programming from 60° to 180° at 8°/min.

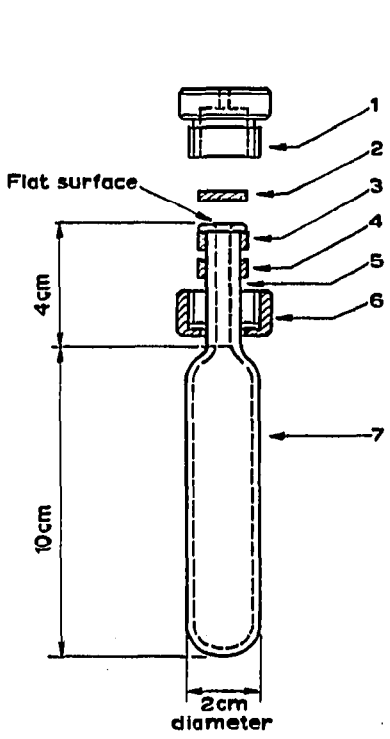
IR spectra (for propellent identification) were obtained with a Perkin-Elmer Model 221G spectrophotometer incorporating a minimum-volume gas cell (Beckman 7.5-cm path-length fitted with Irtan-4 windows).

The qualitative identification of all components other than the propellent was accomplished by coupling a fast-scanning Atlas CH4 mass spectrometer directly to the gas chromatograph at the exit port of the detector (TCD). The coupling was made with a 1/16-in. O.D. stainless-steel tube and a splitter valve. Pressure was held at 5×10^{-6} torr, ionizing voltage was 70 V and the ion-source temperature was 250°.

Sample collection and analysis

A Pyrex bomb of the type shown in Fig. 1 was used for sample collection. Similar bombs were used many years ago in this Establishment by King for high-pressure studies[4], at which time it was established that they could withstand a pressure of 2000 p.s.i. We modified the original design slightly by removing a neck consisting of 1/4 in. × 1-1/16 in. pressure tubing from the top of the adapter and substituting a standard Hamilton 3/8-in. silicone rubber gas chromatograph injection port septum for the usual rubber gasket.

A 1-3/4 in. × 3/16 in. O.D. stainless-steel tube was threaded at one end and soldered to the hub of a Becton Dickinson Luer-Lok 2 in. No. 17 hypodermic needle at the other. The plastic release cap of the aerosol can was tapped to accommodate the threaded hypodermic needle assembly described above as a substitute for the regular spray nozzle. Transfer of a sample of the contents of the aerosol irritant projector was then accomplished by inserting the needle "nozzle" through the silicone septum seal of the weighed, prechilled (dry ice–acetone bath for 15 sec) glass bomb and briefly operating the aerosol pressure release. This dispensed 12–15 g of stock sample into the tube, where it immediately formed a slurry. The dry ice–acetone bath was then allowed to warm to −40° and samples (0.25 ml) of head gas were taken with a Hamilton gas syringe for injection into the gas chromatograph (Porapak Q column). At this bath temperature the head gas contained only one component as shown by a single peak (retention time 1.4 min) on the GC trace. Direct gas syringe transfer of a head-gas sample (3 × 20 ml) from the chilled tube (−40°) to the minimum-volume infrared gas cell provided a simple method of procuring a



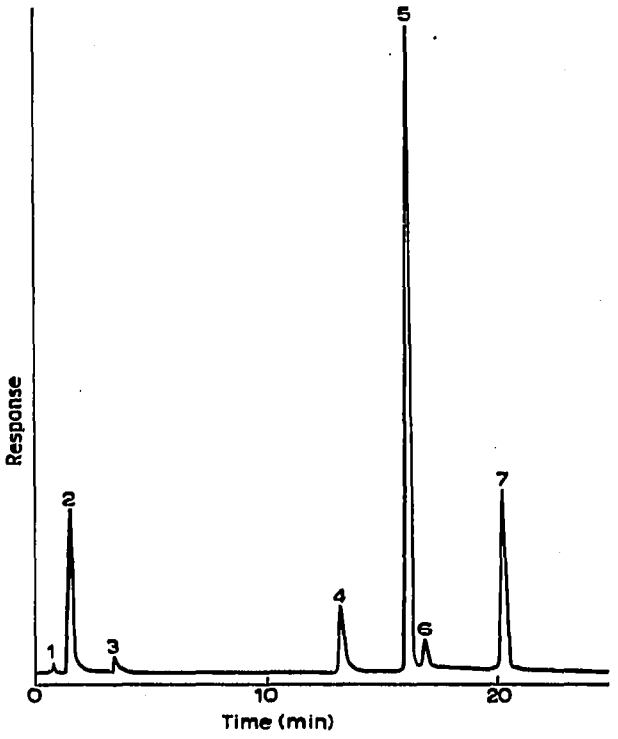


Fig. 1. Pyrex bomb assembly. 1 = Adapter (stainless steel); 2 = silicone rubber septum; 3 = neoprene gasket; 4 = thrust ring (stainless steel); 5 = 3.5-mm capillary tubing; 6 = gland nut (stainless steel); 7 = Pyrex carius tubing, wall thickness 3 mm.

Fig. 2. Chromatogram of the residual oil left from an aerosol tear gas sample. 1 = Dichlorodifluoromethane; 2 = trichlorofluoromethane; 3 = acetone; 4 = chloroacetone; 5 = bromoacetone; 6 = 1,1-dichloroacetone; 7 = 1,1-dibromoacetone.

sample of a low-boiling component (propellent) for IR examination. A hypodermic needle (26 gauge) was then permanently inserted through the septum seal as a pressure-release device and the temperature of the stock sample was slowly raised to −8°. GC (Porapak Q column) of another head-gas sample at this temperature revealed the presence of a second low-boiling component (retention time 4.2 min). This substance was collected, subsequent to separation by GC, in a liquid nitrogen-cooled glass capillary. After collection, the capillary was maintained at liquid nitrogen temperature, flame-sealed and the contents were subjected to IR analysis in the minimum-volume gas cell.

The stock sample was further warmed to room temperature while the needle pressure release allowed equilibration to atmospheric conditions. The difference in weight between the original sample and that at room temperature was assumed to be due to loss of propellent.

Samples (0.6 μl) of the residual oil were then injected into the coupled gas chromatograph (Carbowax 20M column)–mass spectrometer to provide a qualitative analysis of the individual components by their mass spectra. The composition of peaks

TABLE I

RETENTION TIMES AND ANALYSIS OF THE RESIDUAL OIL FROM AN AEROSOL SAMPLE

*Peak No.**	*Retention time (min)*	*Compound identified*	*% of total*
1	0.8	dichlorodifluoromethane	0.4
2	1.6	trichlorofluoromethane	8.3
3	3.4	acetone	1.3
4	13.2	chloroacetone	7.1
5	16.0	bromoacetone	63.5**
6	16.8	1,1-dichloroacetone	2.9
7	20.1	1,1-dibromoacetone	16.5

* See Fig. 2.
**Bromoacetone represents 1.5% of the initial aerosol sample.

1, 2, 3, and 4 was verified by reference spectra from the compilation of Cornu and Massot[5]. Interpretation of the mass spectra of the remaining peaks was relatively straightforward, and was based on the masses and relative intensities of the molecular and fragment ions. Quantitative results were obtained by cutting out and weighing the peaks from the chromatogram. Fig. 2 illustrates the chromatographic separation achieved and Table I lists the quantities and identities of each component found.

RESULTS AND DISCUSSION

Several workers[6–9] have been successful in the GC separation of various lachrymators. It was determined, however, by comparison of GC retention times that the usual irritants such as α-chloroacetophenone (CN) and *o*-chlorobenzylidenemalonitrile (CS) were not present in the aerosol projector being examined. For this reason, the method of spraying a burst from the aerosol container into a beaker[9] was not employed for fear of losing some or all of a given component, thus leading to a false quantitative analysis. To obviate this possibility the Pyrex pressure bomb shown in Fig. 1 was used and provided a stock sample tube with an excellent pressure seal and a convenient means of entry for the introduction or removal of samples.

The technique of prechilling (dry ice–acetone bath) the Pyrex bomb prior to sample introduction lowered the vapour pressure of the propellents and helped to avoid losses. GC monitoring (Porapak Q column) of the head gas as the sample was warmed from dry ice–acetone temperature to −40° revealed only one component (retention time 1.4 min). The IR spectrum of a head-gas sample taken at −40° indicates this component to be dichlorodifluoromethane. A second component which became evident when the sample temperature had risen to −8° (retention time 4.2 min) was collected from the chromatograph and identified (IR) as trichlorofluoromethane. These two halogenated compounds accounted for 97.7% of the weight of the sample as sprayed from the aerosol dispenser. Since the propellent represents such a major portion of the aerosol it is advisable to remove it, especially if there is a concern about minor components as they may otherwise be of too low

a concentration to be detected. The propellent may also mask the lachrymator peaks by giving strong detector response[9].

The residual oil (at room temperature) was seen to contain five components in addition to the two propellents when chromatographed on the Carbowax 20M column. The chromatogram is shown in Fig. 2 and illustrates the excellent peak shape and separation achieved. This separation facilitated the identification of the components when the mass spectrometer was coupled to the gas chromatograph. Table I shows bromoacetone to be the major component (63.5%) of the residual oil, after the evaporation of the two halogenated propellents, and that it was the most active irritant present. For an overall analysis, the propellents dichlorodifluoromethane and trichlorofluoromethane accounted for 97.7% of the original mixture. The main lachrymator, bromoacetone, was present to the extent of 1.5%, and the remaining 0.8% of the mixture consisted of acetone, chloroacetone, 1,1-dibromoacetone, and 1,1-dichloroacetone. The 1,1-dichloroacetone and 1,1-dibromoacetone may be deliberate additives or may be present as impurities from the corresponding monohalogenated compounds. The analysis reported here was for samples collected when the aerosol canister was relatively full and might change as the contents were exhausted.

The peak pattern shown in Fig. 2 and the relative proportions of components listed in Table I did not change when elevated injection port temperatures or glass columns were used. Differences might have been expected since metal-catalyzed decomposition of some halogenated irritants has been reported[7,8].

The Porapak Q column[10] was used for the separation and identification of the two propellents due to the excellent separation which it afforded of these rather similar compounds. The Carbowax 20M column, if carefully controlled, could be used for the entire analysis, and when coupled with the mass spectrometer eliminates the need for the IR spectrophotometer. The Pyrex pressure tube sampling device was very satisfactory for the analysis of a single aerosol projector and could be adapted for routine analysis. In an extensive analytical program, however, such as the routine inspection of aerosol containers following manufacture, it might be profitable to investigate other more direct sampling techniques[11–13].

The interest in non-lethal weapons in general and chemical irritants in particular has greatly increased in recent years because of their widespread use[1,2] and occasional reports of serious consequences[3] from exposure to the more common agents such as CS and CN. Bromoacetone, the active ingredient in the aerosol projector reported here, although not as widely used or as potent as other irritants, nevertheless carries a class A poison label[14]. The propellent employed is one of the more popular types and possesses an intrinsic potential hazard at close quarters in that it can cause frostbite injuries[2]. As a result of these facts, the need for quality control and the use of unreliable manufacturers' labels[1] would seem to require a rapid and reliable method of analysis for these devices. The coupled gas chromatograph and mass spectrometer technique reported here could be readily adapted to satisfy this requirement.

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