

# TECHNICAL NOTE

Jack Nowicki,<sup>1</sup> M.S.

## Analysis of Chemical Protection Sprays by Gas Chromatography/Mass Spectroscopy

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**REFERENCE:** Nowicki, J., "Analysis of Chemical Protection Sprays by Gas Chromatography/Mass Spectroscopy," *Journal of Forensic Sciences*, JFSCA, Vol. 27, No. 3, July 1982, pp. 704-709.

**ABSTRACT:** Gas chromatography/mass spectroscopy (GC/MS) is a rapid and sensitive technique for the identification of the active ingredients of commercially available chemical protection sprays. Chloroacetophenone (CN) and *o*-chlorobenzalmalononitrile (CS) are easily extracted from the liquid sprays with methanol. A basic aqueous extraction procedure is needed for sprays containing capsaicin. Residues can be further purified by preparative thin-layer chromatography. Clothing can also be analyzed for the presence of tear gas residue. The compound CN can be identified by analyzing a heated vapor headspace sample of the cloth by GC/MS. A hexane wash of the cloth is needed for identification of CS and capsaicin.

**KEYWORDS:** criminalistics, chemical analysis, tear gases

There are currently available, through both mail order and retail sale, various products being sold as chemical protection sprays or, more commonly, tear gas sprays. Although there are laws in many states prohibiting the carrying of such spray devices, placing them in the same category as concealed weapons, efforts are currently under way in several state legislatures to legalize their possession. The anticipated consequences of such legislation will be an increase in the availability and usage of these products both in the commission of crimes and as a defense against personal attack. Forensic science laboratories should be prepared to analyze both the canisters themselves and also clothing or other material for trace residues of these sprays.

Chemical protection sprays can be classified into three types, based upon their active ingredient. Sprays contain either *o*-chlorobenzalmalononitrile (CS), chloroacetophenone (CN), or capsaicin. The compounds CN and CS have been traditionally used as military tear gases. Capsaicin, extracted from the cayenne pepper, has been used as a small animal repellent. Typically, a CS or CN spray consists of 1 or 2% of active ingredient dissolved in various oils. Sprays containing capsaicin are weaker in strength, usually 0.35% active ingredient in inert oils.

Previous articles have dealt with the analysis of these liquids using ultraviolet and infrared

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<sup>1</sup>Forensic scientist, Bureau of Scientific Services, Illinois Department of Law Enforcement, Joliet.

spectroscopy [1] and gas chromatography [2]. Ultraviolet spectroscopy and gas chromatography are adequate presumptive tests, but for identification purposes, a more specific test is needed.

Infrared spectroscopy has two main drawbacks. First, it is difficult to obtain an extract of capsaicin sufficiently free of the inert oils in the spray to get a concise infrared identification. Second, there is a lack of sensitivity to trace amounts of residue found on clothing or other substances.

Gas chromatography-mass spectroscopy (GC/MS) offers much greater sensitivity than infrared spectroscopy and allows the analyst to identify capsaicin without having to go through an extensive cleanup procedure.

### Materials and Methods

Samples were analyzed with a Du Pont DP-1 GC/MS equipped with a Hewlett-Packard 1000 data system. A 1.8-m (6-ft) glass column packed with 3% OV-101 on 80-100 mesh Supelcoport was used. Injector, source, and detector temperatures were 250°C and the oven temperature was programmed from 150 to 250°C over 5 min and then held at 250°C for 5 min. Chloroacetophenone standard was obtained from Aldrich Chemical Co. Ortho-chlorobenzal-malonitrile, synthetic capsaicin, and natural capsaicin standards were obtained from K&K Laboratories. Figure 1 shows the mass spectra obtained from the standards using the above conditions.

Gag and Merck [2] discovered a difference in the infrared spectra of synthetic and natural capsaicin. Differences can also be found in their mass spectra (Figs. 1c and 1d). Synthetic capsaicin exhibits a strong mass ion at  $m/e$  of 293. Natural capsaicin exhibits a mass ion at  $m/e$  of 305, as reported by Smith [3].

### Extraction of Contents of Spray Canisters

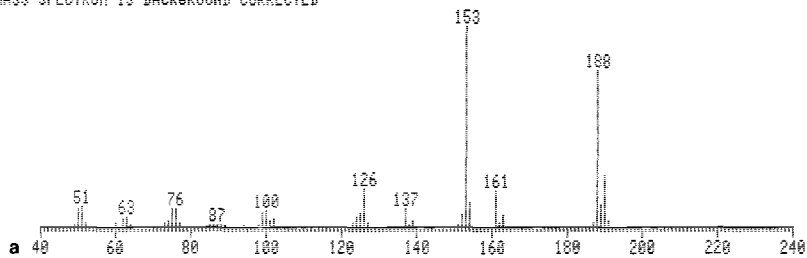
Sprays containing CS or CN can contain oils that are miscible with methanol (for example, Chemical Shield brand) or immiscible with methanol (Paralyzer brand). In the latter case, 5 mL of liquid is extracted with 5 mL of methanol. The methanol is concentrated down to 1 mL. With the alcohol-miscible sprays, 5 mL of liquid is evaporated to dryness with a stream of air and gentle warming. The residue is taken up in methanol.

A simple methanol extraction of capsaicin-containing sprays does not yield a sufficiently clean product for analysis. Thornton [4] has proposed an alkali-methanol extraction procedure with subsequent identification by thin-layer chromatography (TLC). An alternative is to use an aqueous sodium hydroxide extraction [3].

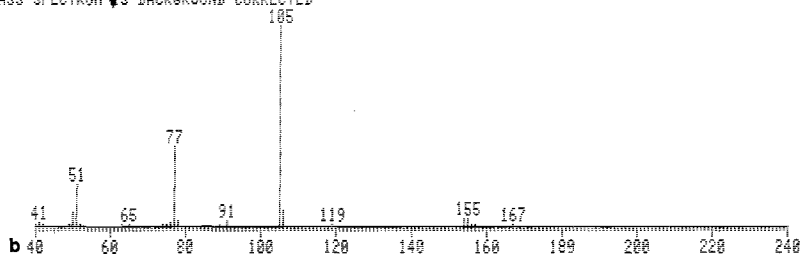
Five milliliters of liquid from the canister is extracted with 5 mL of a 5% aqueous sodium hydroxide solution. The aqueous extract is washed two times with hexane, then acidified with hydrochloric acid and extracted with chloroform. The chloroform layer is evaporated to dryness and the residue dissolved in methanol.

The methanol solutions, containing some residual impurities, can then be analyzed by GC/MS. The samples can be further purified by preparative TLC. The methanol solutions are spotted or streaked on a glass TLC plate coated with silica gel 60, 0.25-mm thickness with fluorescent indicator, and developed in a solvent system consisting of cyclohexane/chloroform/acetic acid (70:20:10). The compounds CS and CN have  $R_f$  values of approximately 0.5 and capsaicin has an  $R_f$  of approximately 0.2. The spot or band is scraped from the plate. The CS and CN can be extracted with methanol. Capsaicin must be extracted with a 5% aqueous sodium carbonate solution. The aqueous extract is then acidified and extracted with chloroform, and the chloroform layer evaporated to obtain an oily residue that is dissolved in methanol. The methanol solutions are then introduced into the GC/MS. Figure 2 shows the total ion chromatograms for CS, CN, and capsaicin extracted by these methods.

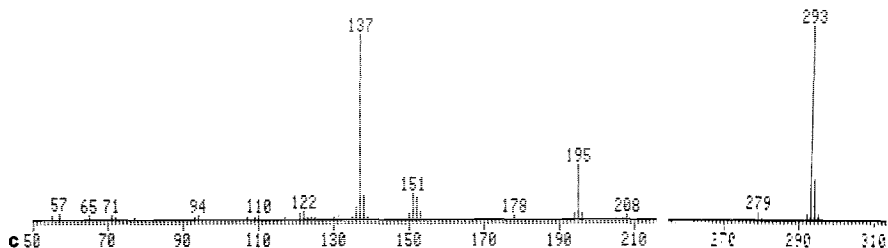
PEAK # 1 BASE 3196685 SCALE 1.00 RT 2.61 %TI 22.62 SCAN # 39 TEMP 176C  
 MASS SPECTRUM IS BACKGROUND CORRECTED



PEAK # 1 BASE 2247821 SCALE 1.00 RT 1.09 %TI 43.47 SCAN # 12 TEMP 166C  
 MASS SPECTRUM IS BACKGROUND CORRECTED



PEAK # 1 BASE 601672 SCALE 1.00 RT 7.52 %TI 25.41 SCAN # 123  
 MASS SPECTRUM IS BACKGROUND CORRECTED



PEAK # 1 BASE 48012 SCALE 1.00 RT 6.80 %TI 38.84 SCAN # 110 TEMP 252C  
 MASS SPECTRUM IS BACKGROUND CORRECTED

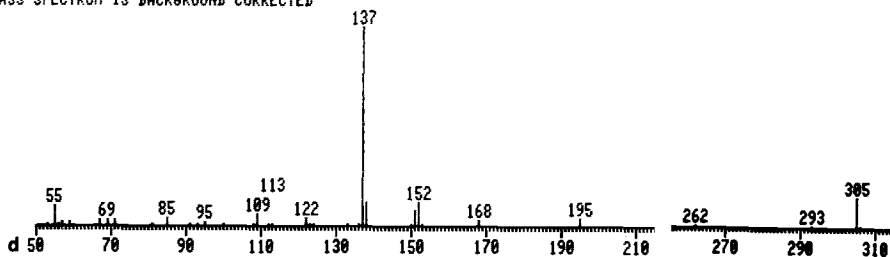


FIG. 1—Mass spectra of (a) *o*-chlorobenzalmalononitrile, (b) chloroacetophenone, (c) synthetic capsaicin, and (d) natural capsaicin.

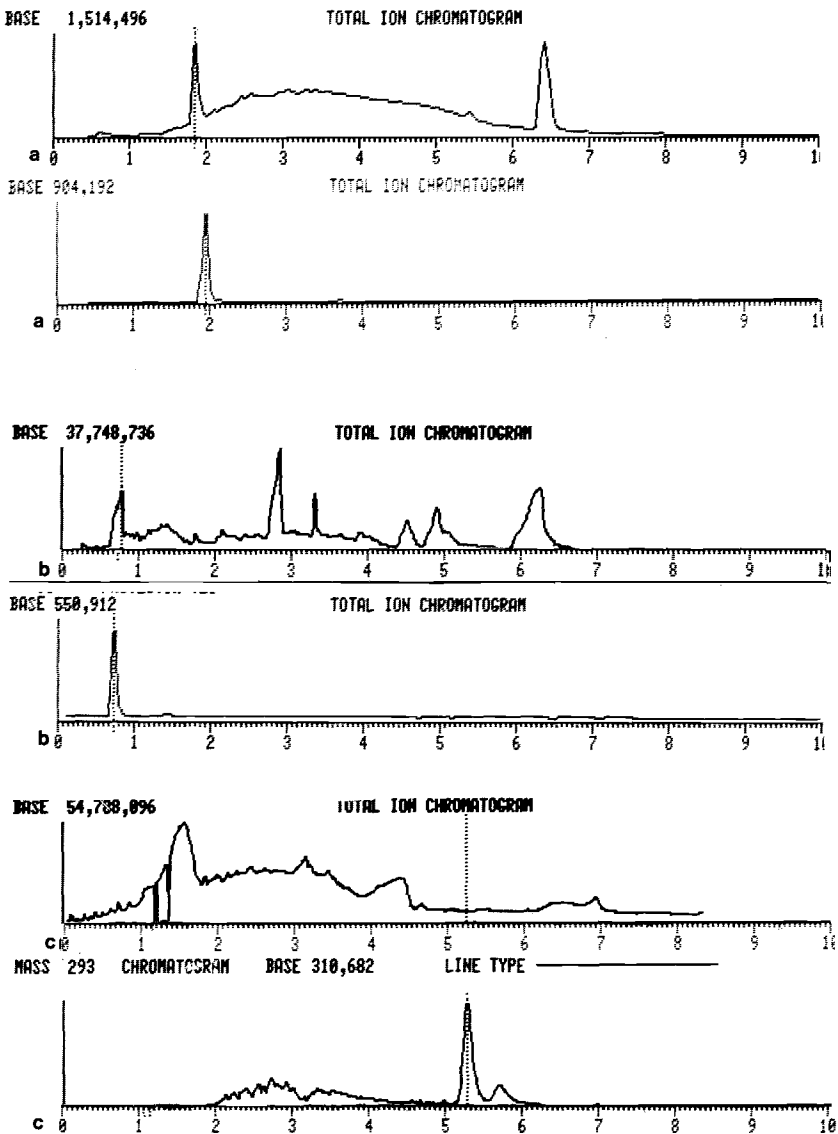


FIG. 2—(a) Total ion chromatograms of extract of CS canister before (top) and after (bottom) TLC. (b) Total ion chromatograms of extract of CN canister before (top) and after (bottom) TLC. (c) Total ion chromatogram (top) and mass 293 chromatogram (bottom) of extract from capsaicin canister prior to TLC.

### Extraction of Cloth

On occasion, it might be necessary to examine the clothing of a suspect for residue of a tear gas spray used by his victim to ward off an attack. Usually, the type of spray used is known and the analysis can proceed accordingly; however, this might not always be the case. On such occasions, a systematic analysis of the clothing for all three types of sprays is needed.

The compound CN has a very high vapor pressure and will readily dissipate into the at-

mosphere. For this reason, clothing suspected of containing CN should be sealed in an airtight container, such as a friction-top paint can or screw-top glass jar. The can containing the clothing is to be heated for 10 min in a 70°C oven and a sample of the headspace vapor analyzed by GC/MS (Fig. 3). The GC oven temperature should be programmed from 50 to 100°C over 10 min.

Capsaicin and CS can be identified by first extracting the cloth with hexane. One portion of the hexane wash can be analyzed for CS by evaporating off the hexane and redissolving the residue in methanol. A second portion of the hexane wash can be analyzed for capsaicin by extracting with 5% aqueous sodium hydroxide and following the same procedure as with the spray canisters.

The white linen cloth used in the experiment did not interfere with any of these analyses. Although it is not anticipated that other types of cloth, such as a synthetic like polyester, would interfere, it would still be good practice to use control samples whenever possible.

#### Acknowledgments

I would like to thank Mr. George Dabdoub and Dr. Donald Plautz for their contributions to the procedures presented here.

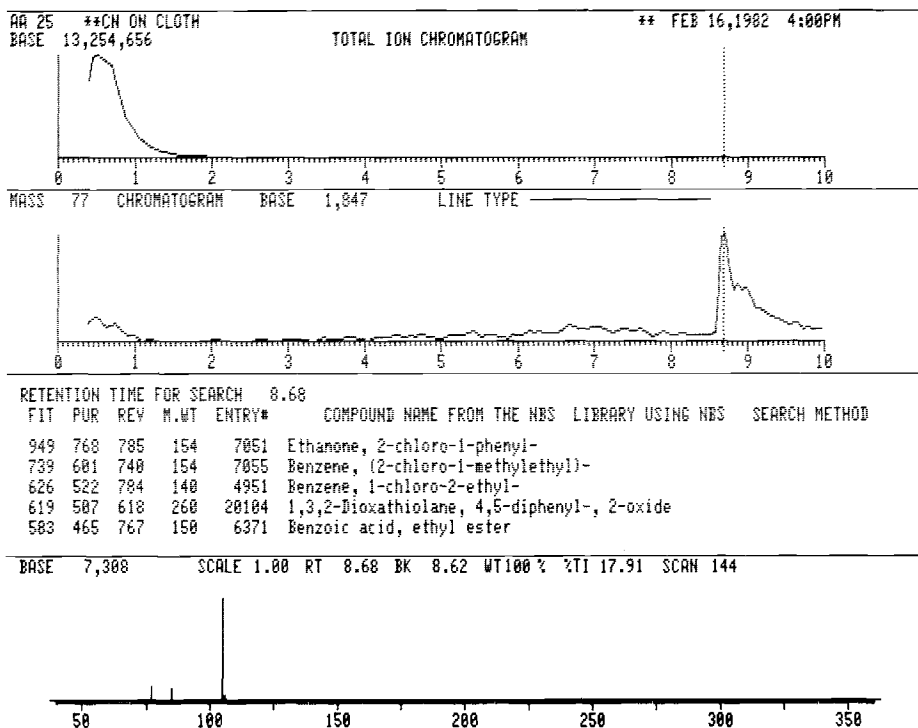


FIG. 3—Total ion chromatogram of headspace of cloth impregnated with CN spray (top); mass chromatogram of the cloth (second from top); computer search and fit to standards library (third from top); and mass spectra at retention time of 8.68 min (bottom).

**References**

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Address requests for reprints or additional information to  
Jack Nowicki  
Bureau of Scientific Services  
Illinois Department of Law Enforcement  
515 E. Woodruff Rd.  
Joliet, IL 60432