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Concise Identifications of Commonly Encountered Tear Gases

This laboratory recently received two submissions on unrelated matters, each containing a tear gas canister. The offenses were aggravated assault and aggravated robbery. Our effort to identify conclusively the chemical composition was delayed because we had little prior experience with the compounds and we found relatively little published material that dealt with the specific problems of separation of the primary constituent from the typical carriers [1,2].

Minnesota statutes prohibit the sale and, under certain conditions, the possession of "any substance composed of a mixture of tear gas and chemicals which has or is designed to have a disabling effect upon any person," except by police and military personnel. It can be illustrated historically that chloroacetophenone (CN) and *ortho*-chlorobenzalmalononitrile (CS) were "designed to have a disabling effect upon any person." The designed purpose of capsaicin (cayenne pepper) is not so clear, but it was included in this study because these three compounds comprise the commonly encountered tear gases.

Experimental Procedure

Chloroacetophenone (CN) $C_6H_5COCH_2Cl$ was identified in an aerosol canister marketed as Federal Streamer by Federal Laboratories, Inc., Saltsburg, Pa. The canister produces a volatile, low-viscosity spray. Minimal exposure to the spray results in a sweet, fruit-like odor. Chloroacetophenone was separated from the balance of the spray components by evaporating under a mild stream of air without heating to minimize the loss and recrystallizing from hexane. No further purification was found to be necessary. The resultant crystals were identified with a Beckman IR 20 infrared spectrometer (Fig. 1).

Ortho-chlorobenzalmalononitrile (CS) $ClC_6H_4CHC(CN)_2$ was identified in an aerosol canister marketed as Paralyzer Model X621 by Defense Products Manufacturing Corp., St. Louis, Mo. The spray is a viscous, oily foam. Sensation upon minimal exposure is not an odor but rather a burning irritation. *Ortho*-chlorobenzalmalononitrile was separated from the balance of the spray components by extracting it from its oily carrier with ethanol. The ethanol is evaporated with an air stream to near dryness without heat. The residue is filtered and washed with cold hexane. The crystals were identified by infrared spectrometry (Fig. 2).

In each of the above cases, an approximately 5-s discharge of the aerosol canisters produced extracted yields adequate for identification by these methods.

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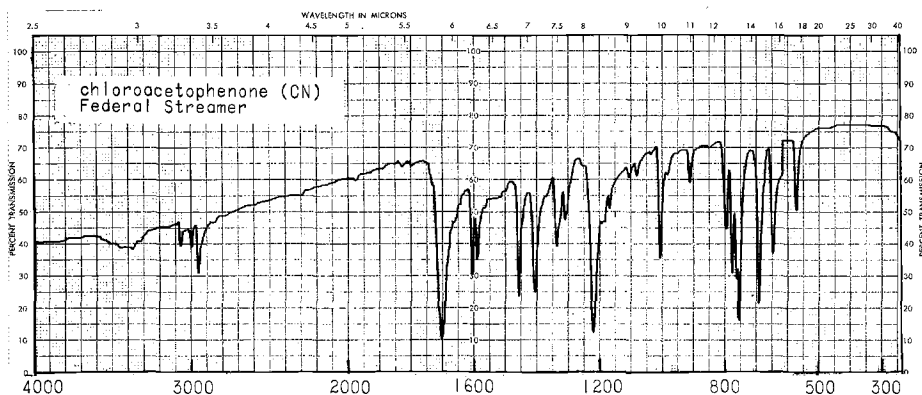


FIG. 1—Infrared spectra of CN (KBr pellet).

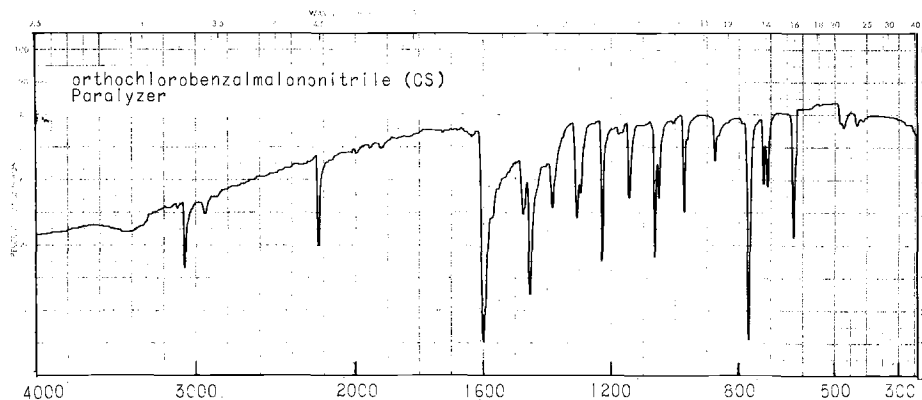


FIG. 2—Infrared spectra of OS (KBr pellet).

Capsaicin was identified in an aerosol marketed as Halt Dog Repellant by Animal Repellants, Inc., Griffin, Ga. Capsaicin is the pungent principle component in various species of *Capsicum*, *Solanaceae*. The spray is a viscous, oily, amber foam. Capsaicin was separated from many of the spray components by spraying into ethanol. The ethanol fraction was "washed" several times with mineral oil. The ethanol fraction was evaporated to near dryness. Capsaicin was identified on two commonly available gas chromatography columns. The instrument was a Hewlett-Packard 5830A with flame ionization detectors. The columns were 6-ft (1.8-m) glass, with 3% OV-17 on 80-100 mesh Chromosorb W-HP and 3% OV-1 on 80-100 mesh Chromosorb W-HP. The operating parameters are displayed on the chromatograms (Figs. 3 and 4).

In an effort to acquire a known capsaicin, two compounds represented as capsaicin were examined. They were purchased from ICN Life Sciences Group, Cleveland, Ohio, and identified as natural capsaicin, catalog number 2757, and synthetic capsaicin, catalog number 18746. The infrared spectra and the gas chromatograms of the two ICN products are distinguishable (Figs. 5-10). The product identified as natural capsaicin yielded retention times compatible with Halt capsaicin. The synthetic capsaicin is of questionable composition and was not used as a known.

TEMP1 275 275
 TIME1 10.0
 INJ TEMP 275 275
 FID TEMP 350 350
 OVEN MAX 300

CHT SPD 1.00
 ATTN 2↑ 8
 FID SGNL A
 SLP SENS 1.00
 AREA REJ 1
 FLOW A 45
 FLOW B 44
 OPTN 0

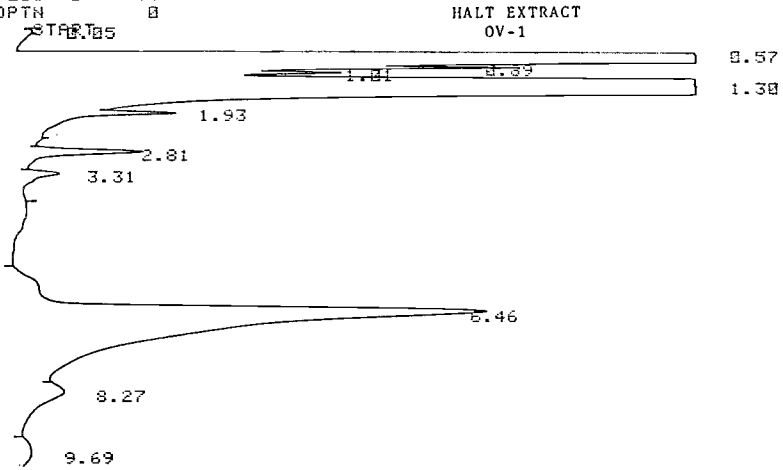


FIG. 3—Gas chromatogram of Halt extract (OV-1).

TEMP1 275 275
 TIME1 10.0
 INJ TEMP 275 275
 FID TEMP 350 350
 OVEN MAX 300

CHT SPD 1.00
 ATTN 2↑ 9
 FID SGNL +B
 SLP SENS 1.00
 AREA REJ 1
 FLOW A 45
 FLOW B 44
 OPTN 0

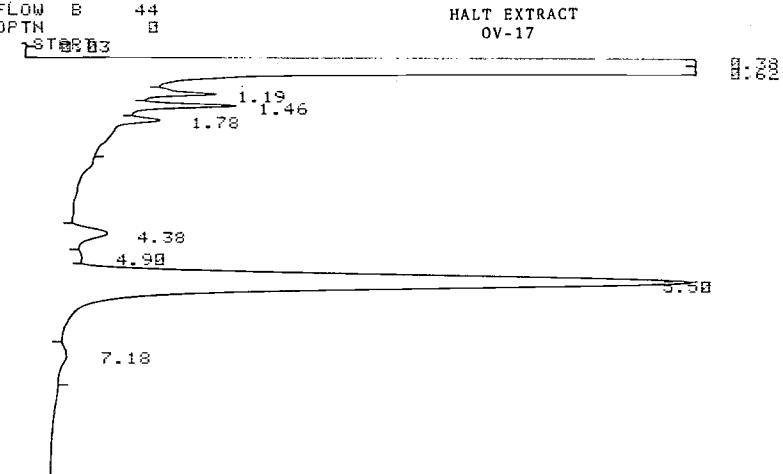


FIG. 4—Gas chromatogram of Halt extract (OV-17).

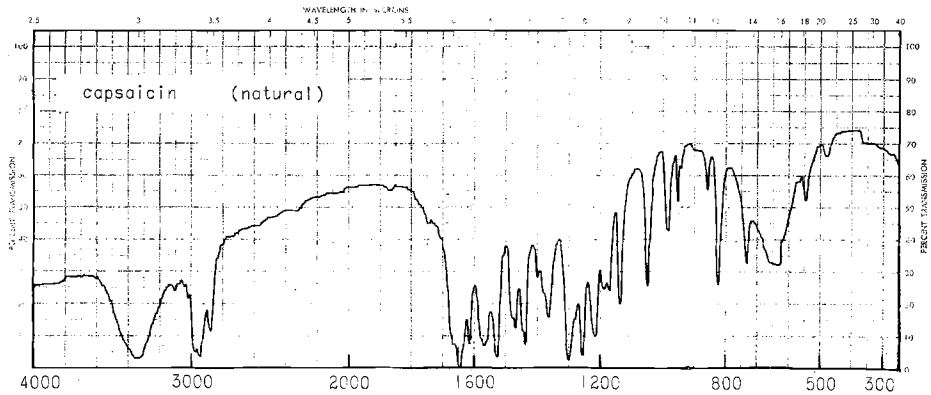


FIG. 5—Infrared spectra of natural capsaicin (KBr pellet).

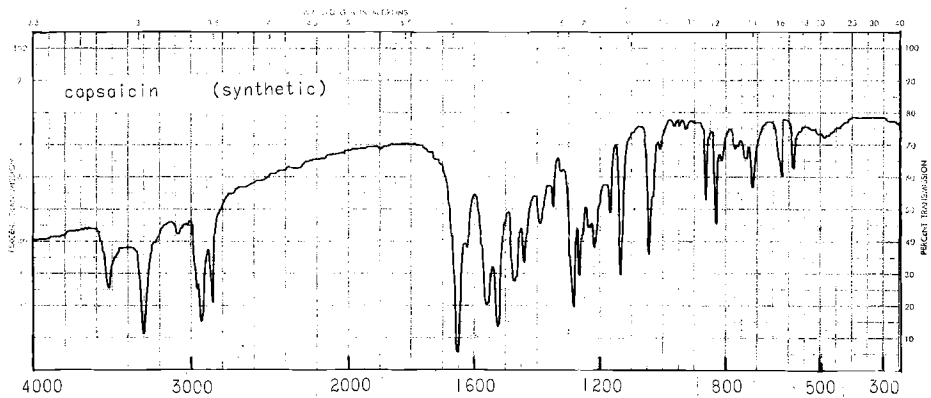


FIG. 6—Infrared spectra of synthetic capsaicin (KBr pellet).

A tangent effort to provide an independent primary known capsaicin by extracting it from cayenne pepper and Tabasco® sauce was unsuccessful. Gas chromatographic data was not adequately diagnostic, likely because of the low concentration.

Discussion

The identification of chloroacetophenone after a simple extraction from the commercial CN products is accomplished by infrared spectrometry. The resultant spectrogram is compatible with published spectrograms [4]. No significant spectral differences should be expected.

The infrared identification of *ortho*-chlorobenzalmalononitrile in CS tear gas products is successful after the proposed extraction method. Confirmation is again made with published literature [4]. Some previously published spectra [2] of CS appear to contain a contaminant which is virtually eliminated by the proposed extraction.

Efforts to adequately purify capsaicin for infrared spectral identification were fruitless. Preparative gas chromatography would likely be successful but is beyond the forensic laboratory's requirements given the proposed two-system gas chromatographic identifica-

TEMP1 275 275
 TIME1 10.0
 INJ TEMP 275 275
 FID TEMP 350 350
 OVEN MAX 300

CHT SPD 1.00
 ATTN 2† 8
 FID SGNL A
 SLP SENS 1.00
 AREA REJ 1
 FLOW A 44
 FLOW B 44
 OPTN 0

CAPSAICIN, NATURAL
 OV-1

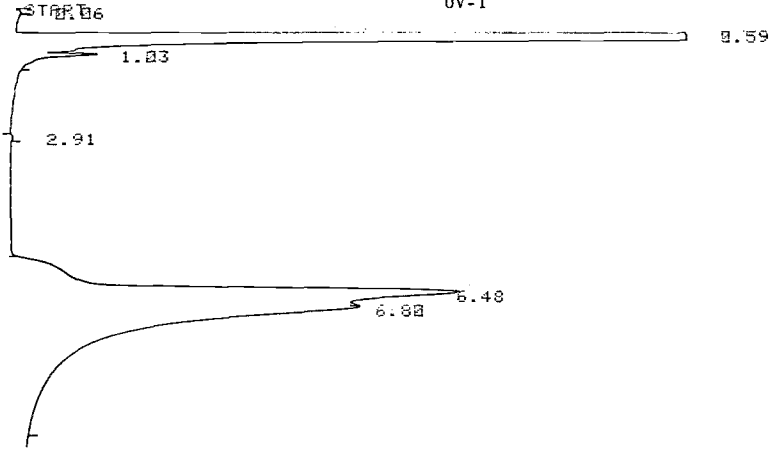


FIG. 7—Gas chromatogram of natural capsaicin (OV-1).

TEMP1 275 275
 TIME1 10.0
 INJ TEMP 275 275
 FID TEMP 350 350
 OVEN MAX 300

CHT SPD 1.00
 ATTN 2† 9
 FID SGNL +B
 SLP SENS 1.00
 AREA REJ 1
 FLOW A 44
 FLOW B 44
 OPTN 0

CAPSAICIN, NATURAL
 OV-17

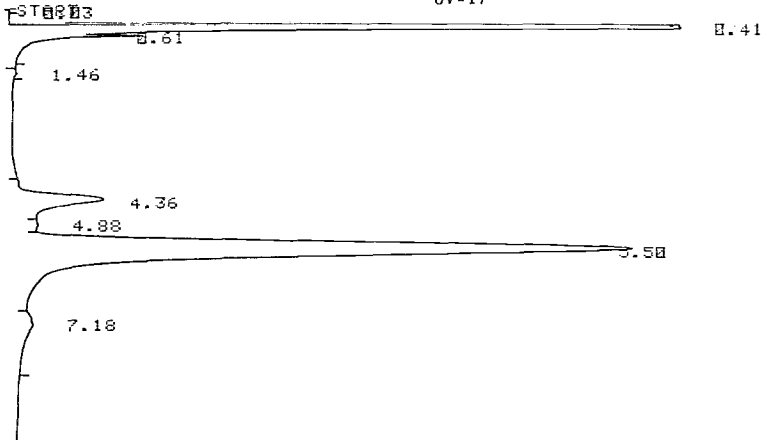


FIG. 8—Gas chromatogram of natural capsaicin (OV-17).

TEMP1 275 275
 TIME1 15.0
 INJ TEMP 250 250
 FID TEMP 350 350
 OVEN MAX 300

CHT SPD 1.00
 ATTN 2↑ 10
 FID SGNL A
 SLP SENS 1.00
 AREA REJ 1
 FLOW A 44
 FLOW B 44
 OPTN 0

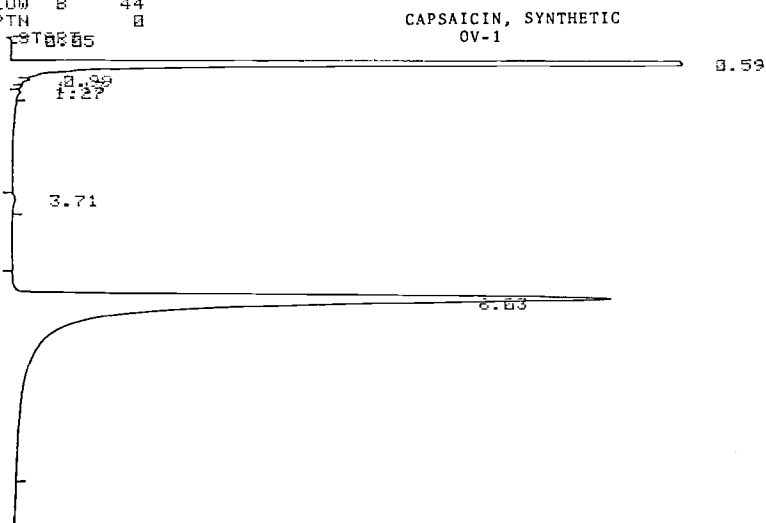


FIG. 9—Gas chromatogram of synthetic capsaicin (OV-1).

TEMP1 275 275
 TIME1 8.0
 INJ TEMP 250 250
 FID TEMP 350 350
 OVEN MAX 300

CHT SPD 1.00
 ATTN 2↑ 10
 FID SGNL +B
 SLP SENS 1.00
 AREA REJ 1
 FLOW A 44
 FLOW B 45
 OPTN 0

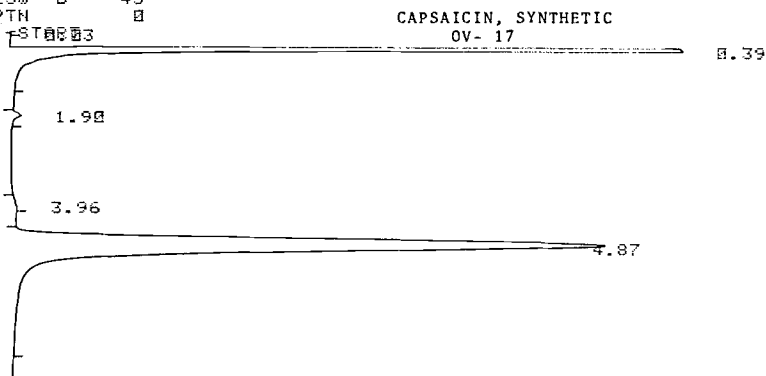


FIG. 10—Gas chromatogram of synthetic capsaicin (OV-17).

tion. The "known synthetic capsaicin" used in these analyses is obviously of dubious composition, as illustrated by both the infrared spectra and the gas chromatograms.

This laboratory has often received inquiries from persons using CS and CN tear gases, either legitimately or illegitimately, as to how it can be removed from clothing, furniture, auto interiors, and similar materials. Ethanol with dish soap are readily available household products which have been proven effective.

Summary

There is a yet-unrealized potential for the illegal use of tear gas products. Identification of the active component is necessary for the thorough prosecution of such crimes. Instrumental techniques are proposed which will enable the identification of the most commonly encountered tear gases.

References

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- [4] *Sadtler Standard Spectra*, Sadtler Research Laboratories, Inc., Philadelphia, Pa.

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