

TECHNICAL NOTE

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Spectral Differentiation and Gas Chromatographic/ Mass Spectrometric Analysis of the Lacrimators 2-Chloroacetophenone and *o*-Chlorobenzylidene Malononitrile

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ABSTRACT: 2-Chloroacetophenone (CN) and *o*-chlorobenzylidene malononitrile (CS) are the most common chemical agents used as lacrimators in the United States. There is a lack of complete spectral data on these compounds in the literature. Spectral data (ultraviolet, fluorescence, proton nuclear magnetic resonance, and infrared) and a gas-liquid chromatographic/mass spectrometric method are presented that differentiate and identify CN and CS. These methods and data were used to identify a forensic science specimen from an accidental intoxication.

KEYWORDS: toxicology, lacrimators, tear gases, chemical analyses

2-Chloroacetophenone (CN) and *o*-chlorobenzylidene malononitrile (CS) are the common chemical agents used as lacrimators by the U.S. military and law enforcement agencies [1]. Numerous personal protection gas devices also contain CN or CS [2]. Acute exposure to these compounds produces lacrimation, burning of the skin and eyes, rhinorrhea, coughing, dyspnea, dizziness, nausea, and vomiting [3]. Recent findings indicate that long-term toxicities of these compounds appear unlikely [4], although fatalities have been reported as a result of excessive exposures to CN and CS [5,6].

Identification of these compounds by a forensic science laboratory may require separation or purification and spectral determination by various methods of analysis. There is a lack of complete spectral data on these compounds in the literature. Ultraviolet and infrared spectral analysis [2], thin-layer chromatographic methods [7], and gas-liquid chromatographic

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methods [8-10] have been developed. There are yet other analytical methods (such as fluorescence, nuclear magnetic resonance, and gas-liquid chromatography/mass spectroscopy) commonly available to the forensic toxicologist for positive identification of these compounds. Spectral data (ultraviolet, fluorescence, nuclear magnetic resonance, infrared, and mass) and a capillary gas-liquid chromatographic/mass spectrometric method that differentiate and identify CN and CS are presented in this technical note. These methods were used to identify a forensic science specimen from an accidental intoxication.

Methods and Materials

Chemicals

CN was obtained as a pure chemical standard (95%, Aldrich Chemical Co. Inc., Milwaukee, WI). CS was procured in a powder form from a police riot grenade (assayed 97% pure by gas-liquid chromatography). Methanol was distilled in glass (99.9%, Burdick and Jackson, Muskegan, MI). Deuteriochloroform (99.8% deuterated) and tetramethylsilane were

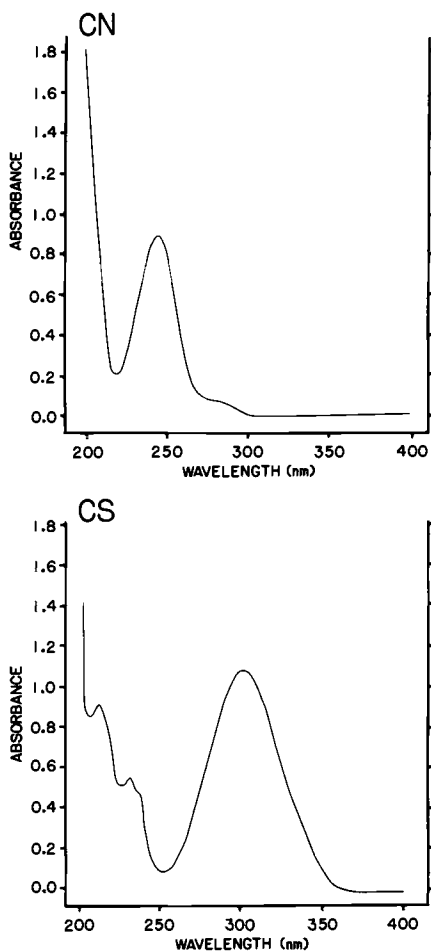


FIG. 1—Ultraviolet spectra of CN and CS.

NMR grade (Norell Inc., Landisville, NJ). Potassium bromide was IR grade (Fisher Scientific, Norcross, GA). Butabarbital (BB) was an analytical standard (Applied Science Laboratories Inc., State College, PA).

Instrumentation

Spectral analyses were performed with the following instrumentation: ultraviolet spectrophotometry with a Cary Spectrophotometer (Model 21, Varian Instruments, Palo Alto, CA), fluorescence spectrophotometry with an Aminco-Bowman Spectrophotofluorometer (Model J4-8960, American Instrument Co., Silver Spring, MD), infrared spectrophotometry with a Perkin Elmer Grating Infrared Spectrophotometer (Model 521, Perkin Elmer, Norwalk, CT), nuclear magnetic resonance spectrometry with a JEOL Nuclear Magnetic Resonance Spectrometer (Model FX-90Q, JEOL, Peabody, MA), and gas-liquid chromatography/mass spectrometry with a Finnigan Gas Chromatograph/Mass Spectrometer (Model 4000, Finnigan Corp., Sunnyvale, CA) equipped with a 15-m by 0.25-mm inside diameter, DB-5 bonded phase fused silica capillary column with a 1.0- μ m film (J & W Scientific, Rancho Cordova, CA). Fluorometric quartz cells (Model 3-H-10, Markson Science, Phoenix, AZ) were used for ultraviolet and fluorescence spectral analysis.

Procedures

Ultraviolet spectra were obtained using 0.01% solutions of CN and CS in methanol and fluorescence spectra were from 0.0005% solutions in methanol. Infrared spectra were of 1% mixtures of CN and CS in potassium bromide wafers. Nuclear magnetic resonance spectra

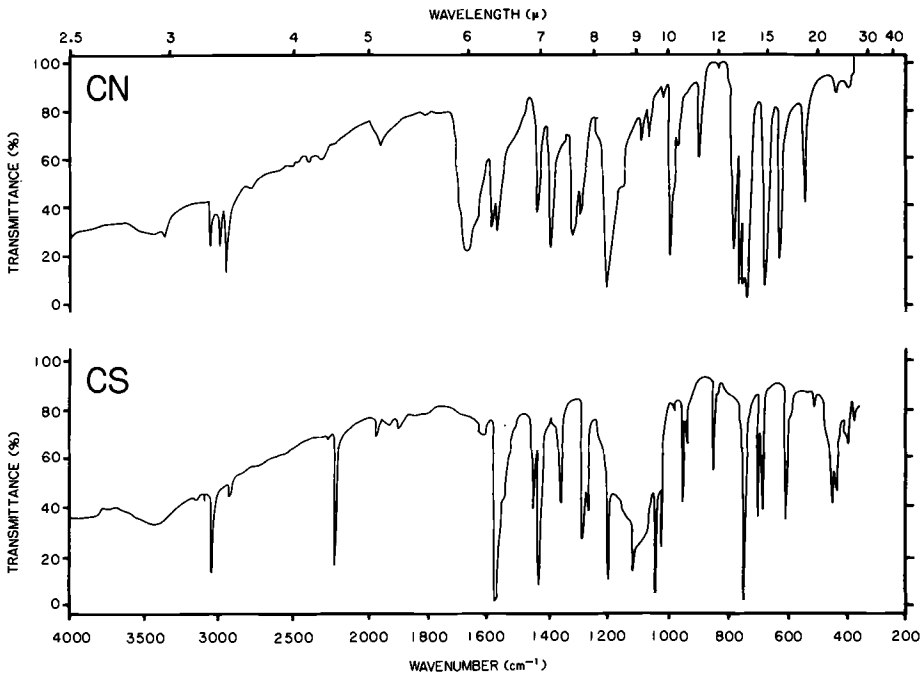


FIG. 2—Infrared spectra of CN and CS.

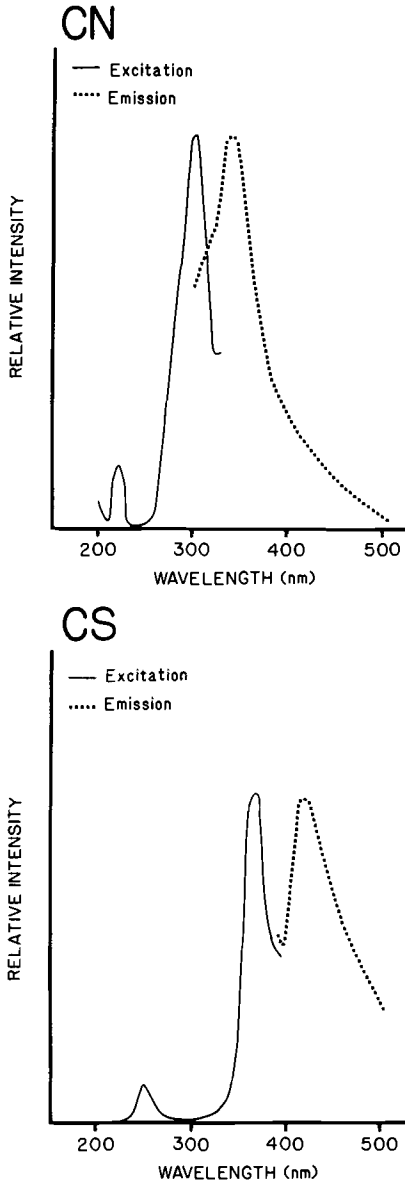


FIG. 3—Fluorescence spectra of CN and CS.

were obtained on 20% solutions of the lacrimators in deuteriochloroform with a radiation frequency of 90 MHz. Scanning rates and sensitivities were set for maximum resolution.

CN and CS were separated on the capillary column using splitless injection under the following conditions: helium carrier at a flow rate of 24 cm/s, injector 200°C, column 100°C for 1.5 min then programmed at 20°C/min to 250°C. At 30-s postinjection, the injector was vented with helium at a flow rate of 32 mL/min to eliminate excess solvent vapors and the septum was swept with 13 mL/min of helium. Mass spectrometer data were acquired using electron ionization (ion source temperature 250°C, emission current 0.30 mA, electron multiplier voltage 1490 V, electron energy 70 V) and multiple ion detection with an instrument dwell time of 0.1 s/mass unit. CN and CS were 0.01% solutions in methanol, and butabarbital, the internal standard, was a 0.1% solution in methanol.

Results and Discussion

The aromatic portions of CN and CS displayed UV absorptions in the 230- to 300-nm range. CN had a UV maximum at 245 nm while CS had a UV maximum at 295 nm with minor absorbances at 211 and 230 nm (Fig. 1). The infrared spectrum of CN had intense

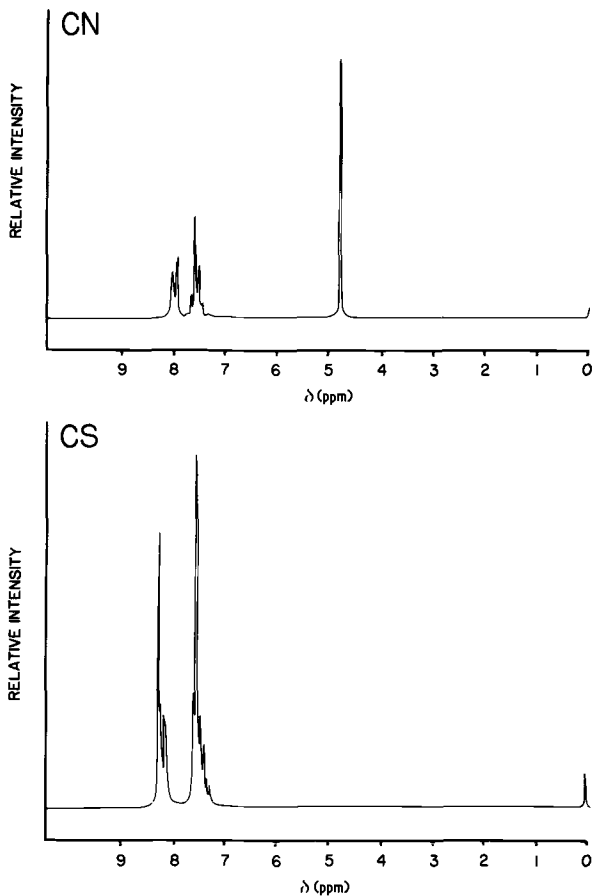


FIG. 4.—¹H Nuclear magnetic resonance spectra of CN and CS.

absorptions at frequencies of 2950, 1670, 985, and 730 cm^{-1} , while that of CS had absorptions at frequencies of 3050, 2230, 1580, and 1045 cm^{-1} (Fig. 2). Although both compounds are aromatic and demonstrate representative absorptions in the 2900- to 3150- cm^{-1} , 1400- to 1700- cm^{-1} , and 900 to 1200- cm^{-1} ranges, the absorption at 2230 cm^{-1} is representative of a nitrile moiety and clearly differentiates CS. The UV and IR spectra are comparable to those reported by Sreenivasan and Boese [2].

Fluorescence spectral analysis revealed that CN had an excitation maximum at 300 nm and an emission maximum at 340 nm (Fig. 3). The spectrum of CS had an excitation maximum of 370 nm and an emission maximum of 420 nm. The nitrile and chlorine substituents produced bathochromic shifts in the aromatic fluorescence spectra of these compounds.

The ^1H NMR spectra of CN and CS are illustrated in Fig. 4. CN had absorptions at chemical shifts of 7.88, 7.54, and 4.71 ppm while CS had absorptions at chemical shifts of 8.26, 7.54, and 7.52 ppm referenced to tetramethylsilane. Absorptions at chemical shifts in the range of 7.0 to 8.5 ppm are representative of the aryl hydrogen that both molecules contain, whereas CN has aliphatic hydrogen on its methyl moiety, which produced the upfield absorption at 4.71 ppm. The alkene hydrogen peak of CS has been shifted to the aryl region.

A reconstructed total ion chromatogram of a 1- μL aliquot of a 10:5:1 mixture of CN:CS:BB is illustrated in Fig. 5. Relative retention times to BB, the internal standard, were 0.600 for CN and 0.876 for CS. The chemical structures and mass spectra for CN and CS are illustrated in Fig. 6. Major ions for CN were 105, 77, and 51 m/e and for CS were 153, 188, and 161 m/e . The base peak of CS represents an ion with the loss of the chlorine (153) while the base peak of CN has the loss of CH_2Cl (105).

Spectral analysis of CN and CS by each of the methods described clearly differentiated the compounds. The data presented should prove useful to the toxicology laboratory having any of the instrumentation above available for analysis of forensic science specimens. The combination of these spectroscopic techniques can provide significant structural information for identification of these chemicals.

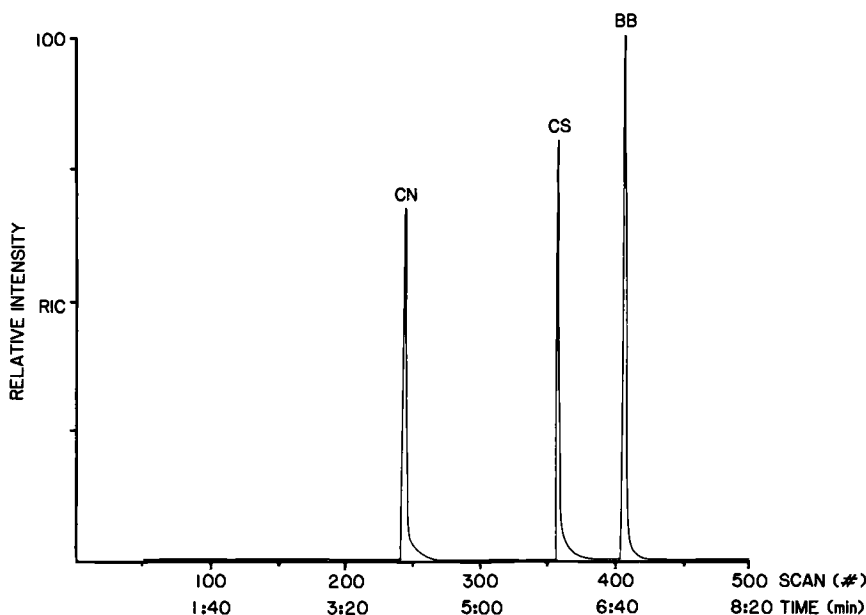


FIG. 5—Reconstructed total ion chromatogram of 1- μL aliquot of CN:CS:BB (10:5:1).

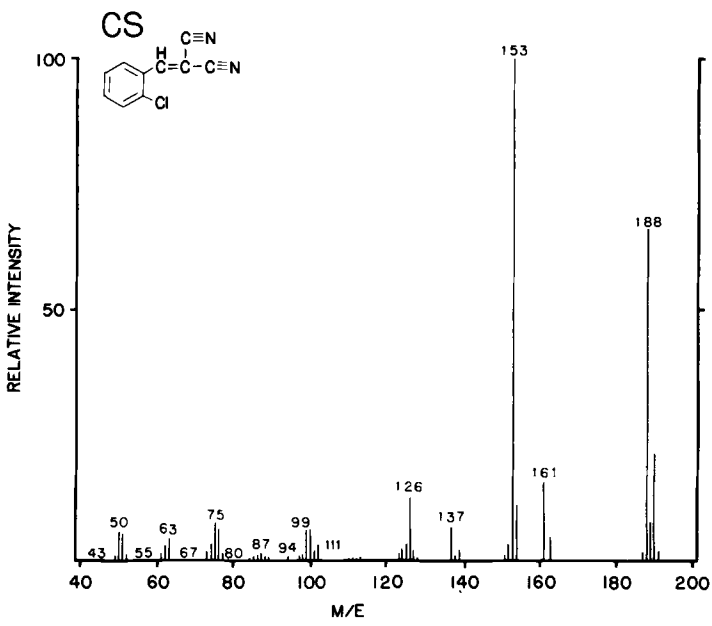
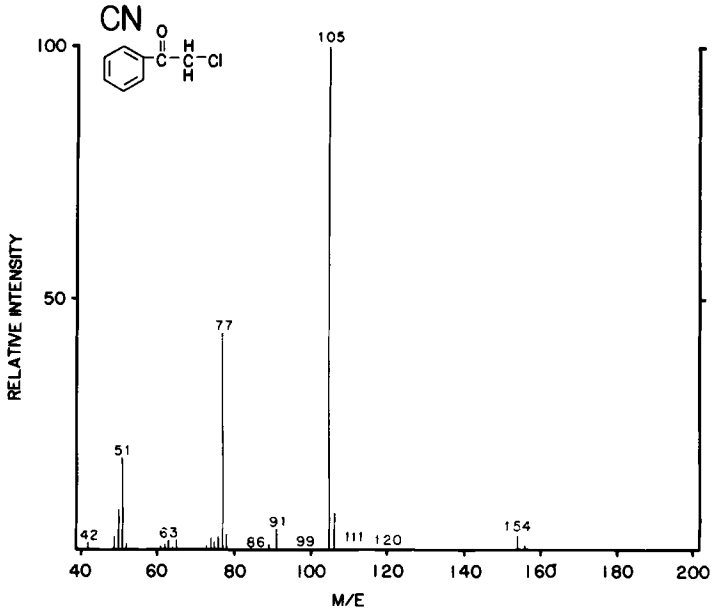


FIG. 6—Mass spectra of CN and CS.

Case Report

A (0.1-L [4-oz]) baby food jar of a yellowish-white powder was found by police officers scattered over a downtown mall area. Police exhibited signs of an acute exposure to lacrimatory agents (lacrimation, burning of skin and eyes, rhinorrhea, coughing, and dyspnea). Because of severe eye irritation, the contaminated personnel were treated at a local eye hospital where nursing staff performing the decontamination were also intoxicated. Spectra of the powder for each of the methods described were indistinguishable from those obtained from the CS standard. Local law enforcement agencies determined that the CS had been illegally obtained from a military reserve unit in an adjacent state.

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