

TECHNICAL NOTE

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Identification of Tear Gases in Suspect Spray Cans and Cloth Samples by Ion Mobility Spectrometry

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ABSTRACT: A handheld ion mobility spectrometer was used to characterize the vapors produced at 50°C by the active ingredients of 20 µL samples of commercially available CN and CS tear gas sprays. After separation of the active ingredients of the sprays from their carrier gases and solvents, the spectra obtained are indistinguishable from standards, and can be used as vapor phase “fingerprints” to distinguish between these tear gas agents. The evaporative method used to separate the active ingredients from propellants and solvents was simple, but very effective in removing spectral interferences. We suggest that from the perspectives of speed of response, portability, intrinsic low detection limits, and the secondary information available from ion mobility spectra, these studies illustrate the potential of mobility spectrometry to fulfill forensic requirements for a rapid screening method for suspect spray cans and clothing.

KEYWORDS: forensic science, tear gas, CN, CS, ion mobility spectrometry, portability

Acute exposure to the active ingredients of tear gas produces irritation of the skin, eyes, and mucous membranes. Severe exposure has led to fatalities (1). The ready availability of these sprays as personal protection devices has seen a concomitant increase in their use during the commission of crimes in the United Kingdom. As a result, forensic science laboratories have to be equipped to both detect trace residues on forensic samples, and to determine the contents of numerous suspect cans. Published methods for the active ingredients of tear gas sprays include thin layer chromatography (2–4), high-performance liquid chromatography (5), and gas chromatography methods (6–12).

In the present study, ion mobility spectrometry (IMS) was investigated for the identification of tear gas products. Ion mobility

spectrometers are small, truly portable devices capable of measuring concentrations of organic chemicals in the vapor phase at the µg/L level (13). Although IMS has been known as an analytical technique since the early 1970's, only a few specific applications of forensic interest have been reported. These include the detection of explosives, narcotics, and chemical warfare agents (14). In a 1997 paper we reported the characterization of lachrymatory compounds using ambient temperature IMS (15). However, considerable spectral interference was encountered when vapors from commercially available tear gas sprays were introduced into the detector. A simple evaporative method proved to be very effective at removing spectral interferences. Subsequently, a handheld ion mobility spectrometer was used to characterize the vapors produced at 50°C by the active ingredients of 20 µL samples of CN and CS tear gases. The spectra obtained were indistinguishable from standards.

Experimental

Materials—Ammonia, dichloromethane, 1,2-dichloroethane, 2-chlorobenzaldehyde and capsaicin (Aldrich Chemical Co. Ltd., Dorset, UK) were used without further purification. α -Chloroacetophenone (Lancaster Synthesis Ltd., Lancashire, UK) was recrystallized twice from hexane prior to use. 2-Chlorobenzylidenemalononitrile was prepared by the method of Corson and Stoughton (16), recrystallized three times from 2-propanol and then from hexane prior to use. Cayenne pepper (McCormick Foods, Thame, Oxon, UK) and the cotton wool pads were purchased from a local retail outlet. Denim pads were fabricated from an old, well-worn pair of jeans.

GC/MS—The contents of a range of commercially available tear gas sprays were analyzed using a programmed Carlo Erba Strumentazione gas chromatograph operating in the split mode connected to a VG Micromass 7070F mass spectrometer. Sample volume: 1 µL. Column: Carbowax 30 M (ϕ 0.32 mm; film thickness 0.25 µm). Oven programming: initial temperature 40°C; ramp 10°C/min; final temperature 250°C.

IMS System—A portable Airborne Vapour Monitor (AVM, Graseby Ionics, Bushey Road, Watford, UK). Spectra were accumulated using a Graseby Analytical ASP board controlled through a

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PC by the proprietary WASP data acquisition software (Graseby Ionics, Bushey Road, Watford, UK). Spectra could be acquired in either positive or negative ion acquisition modes (the design of IMS drift tubes does not allow both modes to be monitored simultaneously). The acetone dopant normally resident in the AVM was removed from the instrument. The reagent gas therefore was simply purified air.

General Operation—The AVM recycles air through an internal filter system. Some ionization of moisture and oxygen takes place in the ionization chamber. In purified air, the positive reactant ions are generally held to be $H^+(H_2O)_2$ and $H^+(H_2O)_3$, with the O_2^- ion commonly seen as the major negative reactant ion (13). These ions give rise to a single peak known as the reactant ion peak (RIP). The introduction of a volatile component into the spectrometer produces additional negative and positive product ions through reactant ion-sample vapor molecule interactions. These ions give rise to spectral peaks at characteristic drift times relative to the RIP. The spectra thus obtained are essentially the vapor phase fingerprints of the target molecules.

General Method—Denim produces significant but variable IMS spectra at temperatures above approximately 75°C. Clean cotton does not. Although both fabrics depressed the RIP signal in both ion acquisition modes at 50°C, they did not produce spectra at this temperature. They were, therefore, considered acceptable for use as models of swabs or contaminated clothing nondestructively heated to assist contaminant identification.

Tear gas sprays available at retail outlets or by mail order typically contain 1 to 5% w/v active ingredient. Analytical standards (0.5% to 10% w/v) were prepared in dichloromethane and 1,2-dichloroethane, solvents with strong IMS responses in the negative ion acquisition mode. Tear gas canisters were vented into glass containers from which samples were drawn. A 20 μ L aliquot of sample was placed on a pad in the “vaporization chamber”—a 500 mL round-bottomed flask. The flasks were evacuated at 50°C/10 to 20 mm Hg (water pump pressure) for 20 min. The atmospheres inside the flask were then sampled by introducing the nozzle of the AVM into the neck of the flask.

Results and Discussion

The negative ion acquisition mode (negative polarity) spectrum produced after evaporation of a 20 μ L aliquot of 5% w/v solution of α -chloroacetophenone (CN, Fig. 1, I) is shown in Fig. 2a. The signals at 5.1 may be due to chloride ion (Cl^-), and that at 8.8 ms due to a molecular adduct of the form MCl^- (13). The spectrum shown is typical of the saturated instrument response produced by the high vapor phase concentrations of this compound seen in this study. The linear dynamic range of the AVM is small, typically only two orders of magnitude for the compounds studied herein (15). Quantitative data can be obtained provided the response is within the linear dynamic range. In this case, the response is outside the linear dynamic range. As a result, the spectra may be used to characterize the presence of a target molecule and initiate an alarm response, but not for quantification. The negative polarity spectrum produced after evaporation of a similar volume of a 5% w/v solution of 2-chlorobenzylidenemalononitrile (CS, Fig. 1, II) is shown in Fig. 2b. The CS spectrum is relatively straightforward, consisting as it does of a broad peak, possibly due to (MCl^-) , at 8.9 ms, and a second intense signal, possibly due to a cluster ion of the form $(M.O_2^-)$ at 10.5 ms (13). Again the spectrum shown is typical

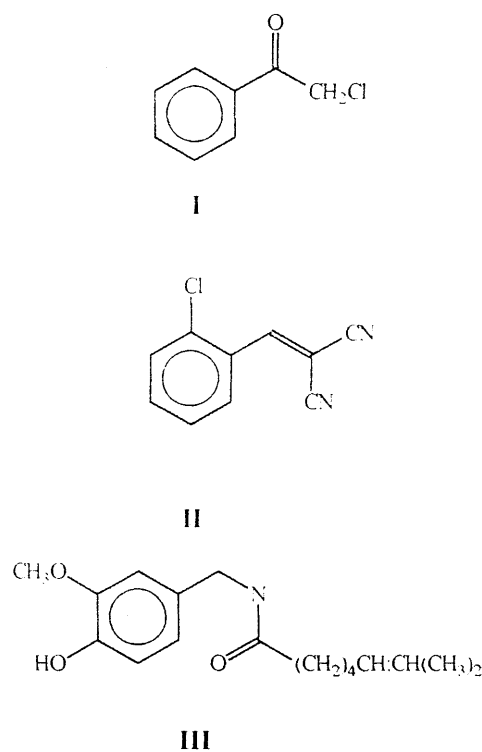


FIG. 1—Chemical structures of target molecules: I α -chloroacetophenone, CN; II 2-chlorobenzylidenemalononitrile, CS; III capsaicin.

of the saturated instrument response produced by high vapor phase concentrations of this compound. The negative polarity spectrum produced after evaporation of 20 μ L of a 5% w/v suspension of cayenne pepper is shown in Fig. 2c. Given that capsaicin produces no consistent spectra in either positive or negative polarity (the lack of instrument sensitivity to a molecule otherwise containing functionality of high proton affinity and electronegativity may be explained if capsaicin, although having a relatively low melting point (65°C), has an extremely low vapor pressure), in this case it is not capsaicin that is being monitored but some unknown volatile components of the pepper. The exact nature of these components must be determined by IMS/MS.

The positive polarity spectrum produced after evaporation of a 20 μ L aliquot of 5% w/v solution of α -chloroacetophenone is shown in Fig. 3a. This spectrum is typical of the saturated positive polarity response to high vapor phase concentrations of this compound. The peak dominating the spectrum may be a cluster ion of the form $(MH^+ \cdot L_n)$, a dimeric ion (M_2H^+) or possibly even a clustered dimer $(M_2H^+ \cdot L_n)$ (13). The positive polarity spectrum produced after evaporation of a 20 μ L aliquot of 0.32% w/v aqueous solution of ammonia (often used in the UK as a substitute for commercial tear gas sprays since it is cheap and readily available from retail outlets) is shown in Fig. 3b. Again, this spectrum is typical of the saturated instrument response produced by high vapor phase concentrations of this compound.

The evaporative method used to separate the active ingredients from solvents was simple, but very effective. The spectra obtained were essentially the vapor phase fingerprints of the target molecules. CS and cayenne pepper did not give a positive ion acquisition

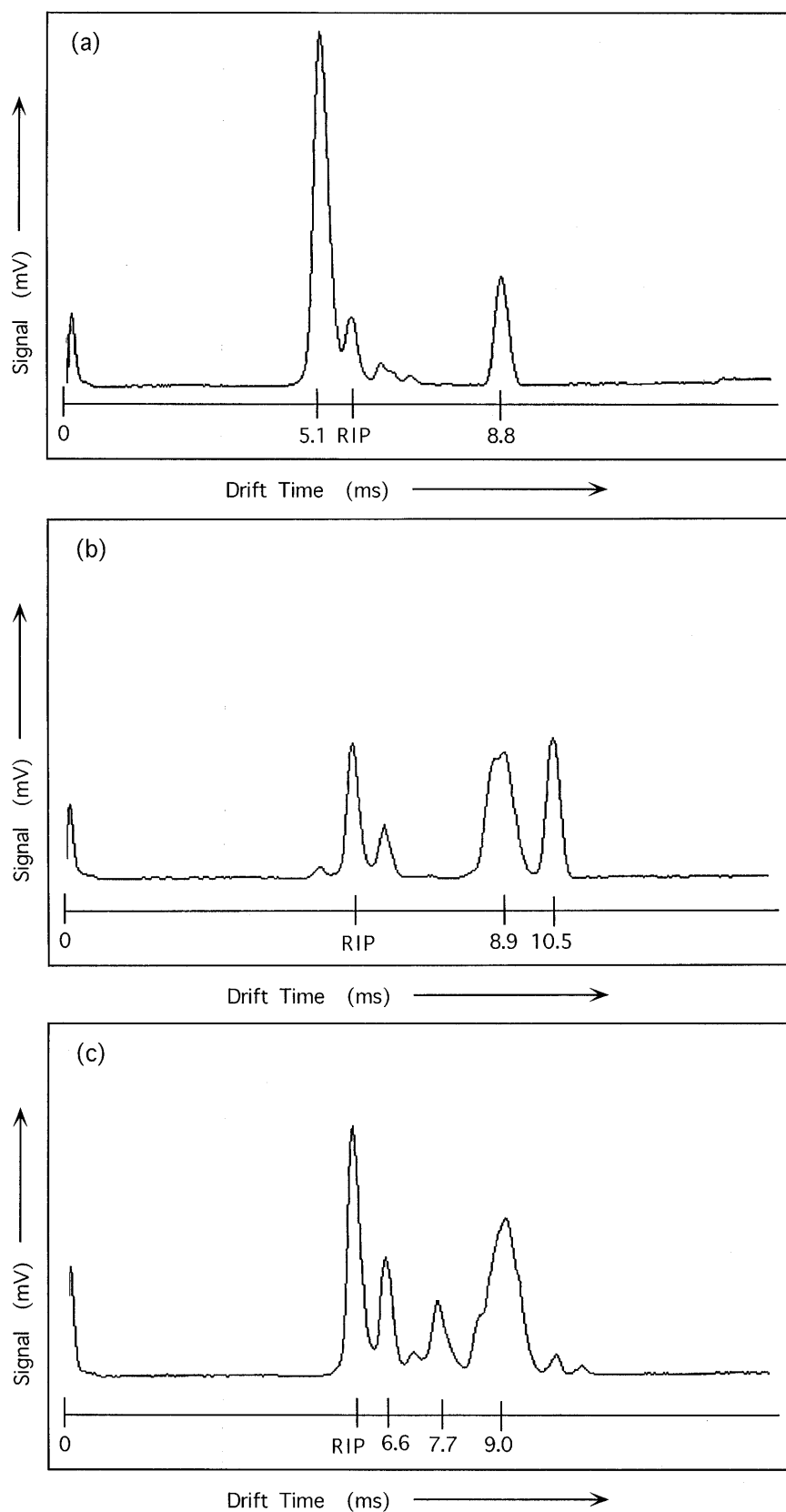


FIG. 2—Typical negative ion acquisition mode spectra produced after evaporation of 5% w/v halocarbon solutions of (a) α -chloroacetophenone, (b) 2-chlorobenzylidenemalononitrile, and (c) a 5% w/v suspension of cayenne pepper.

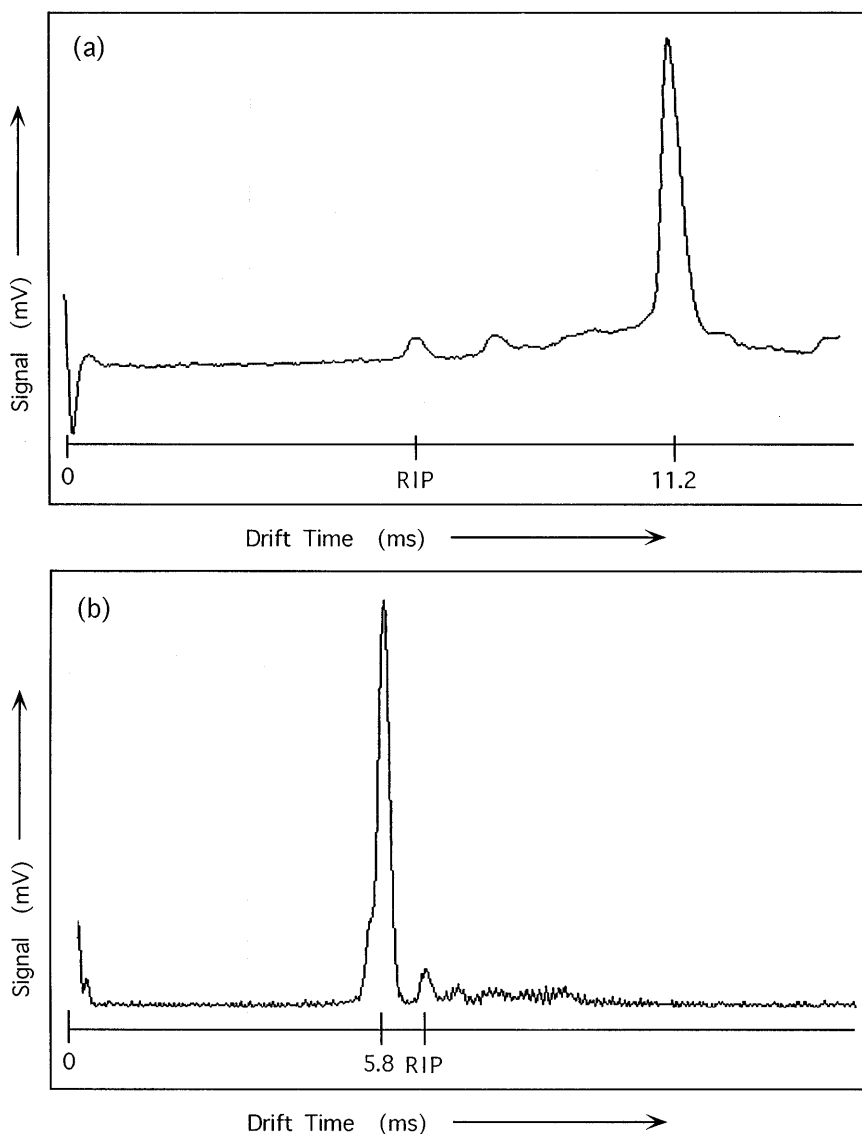


FIG. 3—Typical positive ion acquisition mode spectra produced after evaporation of (a) 5% w/v halocarbon solutions of α -chloroacetophenone; (b) 0.32% w/v aqueous solutions of ammonia.

mode response, ammonia did not give a negative ion mode response, and capsaicin (Fig. 1, III) did not produce a consistent IMS response in either mode (15).

GC/MS studies identified a wide range of compounds in the tear gas sprays (Table 1). Almost all the contents identified are volatile IMS interferences. To assess the efficacy of our evaporative

method, ten randomly selected tear gas canisters of known active ingredient were tested. Of these ten samples, four were CN, three CS, and three capsaicin/pepper sprays (Table 2). The evaporative method quickly and simply removed the bulk of propellants and solvents found in the spray. However, even traces of solvents such as acetone or ethanol cause significant spectral interference in the positive ion acquisition mode as a result of their high proton affinity. Such interference was sufficient to swamp the response produced by CN, but not that of ammonia. As a result, positive ion acquisition mode spectra were not reliable as indicators of the active ingredient of the sprays, except for those containing ammonia. Halocarbons likely to interfere with the acquisition of negative ion acquisition mode spectra are not highly electronegative compared to CN and CS. Once the bulk of these molecules have been removed from the sample, the negative ion mode responses of CN and CS dominated the spectra, and could be used to characterize

TABLE 1—Twelve most common propellants and solvents found in commercial tear gas canisters confiscated at UK ports-of-entry.

chlorofluoromethane	nitromethane
trichlorofluoromethane	<i>n</i> -butane
dichloromethane	iso-butane
1,1,1-trichloroethane	dodecane
trichloroethylene	acetone
ethanol	isopropylalcohol

TABLE 2—Analysis of tear gas sprays by IMS and GC/MS.

Canister	Contents		
	Label	GC/MS	IMS
CN1	'10-4' Chemical Billy	CN	CN
CN2	Chemical Mace	CN	CN
CN3	The Black Belt	CN	CN
CN4	Phaser	CN	CN
CS1	N/A	CS	CS
CS2	N/A	CS	CS
CS3	N/A	CS	CS
P1	Stop	capsaicin	inconclusive
P2	Pepper Box	capsaicin	inconclusive
P3	6% Pepper Defense	capsaicin	inconclusive

the tear gases containing those substances. Results for the pepper sprays were inconclusive. Capsaicin does not produce a consistent IMS response in either mode. For complete coverage of the most commonly encountered lachrymators, putative capsaicin sprays may have to be chemically treated to produce volatile derivatives that produce strong, characterizable IMS responses.

Conclusions

We have shown that IMS is sensitive to the ionizable vapors produced by small quantities of commercial ammonia, CN, and CS solutions once potential interferences have been removed. This can be done expediently by evaporation. We suggest that from the perspective of speed of response, portability, and low detection limits, and the secondary information available from IMS spectra, these studies illustrate the potential of mobility spectrometry to fulfill forensic requirements for a rapid screening method for suspect spray cans and clothing.

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