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A Comparison of Ionization Techniques for Gas Chromatography/Mass Spectroscopy Analysis of Dye and Lachrymator Residues from Exploding Bank Security Devices

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ABSTRACT: Electron impact (EI) ionization, positive ion chemical ionization (PICI), and negative ion chemical ionization (NICI) gas chromatography/mass spectroscopy (GC/MS) have been applied to the analysis of the dye and tear gases used in common bank security devices. A direct comparison of these ionization techniques showed that chemical ionization methods are more sensitive than electron impact ionization for these chemicals. The choice of NICI or PICI depends on the tear gas or dye of interest and the chemical nature of interfering substances on the evidence. We demonstrate that a procedure which uses GC/MS with one or more of these ionization techniques can provide the sensitivity and selectivity required to detect and identify submicrogram quantities of these chemicals on forensic science evidence without extensive specimen preparation.

KEYWORDS: criminalistics, chemical analysis, lachrymators, dyes, mass spectroscopy

Exploding money packets are an increasingly popular tool used to aid in the investigation of robberies. These devices are remotely activated to deflagrate or explode after the robber leaves the bank or store, rupturing the container in which the money is being held and forcibly ejecting an aerosol of red dye and tear gas. In theory, the robber and the money are stained with the red dye for easy identification while the tear gas causes abandonment of the device, money, and possibly the getaway vehicle. The laboratory examiner is often called upon to identify these chemicals on articles of clothing, upholstery from an automobile, U.S. currency, and other objects. The identification of these substances will sometimes link a suspect to a bank robbery.

This paper compares three gas chromatography/mass spectroscopy (GC/MS) techniques for the detection and identification of submicrogram quantities of 1-methylaminoanthraquinone (MAAQ), orthochlorobenzalmalononitrile (CS tear gas), and chloroacetophenone (CN tear gas) which are the commonly used red dye and lachrymators, respectively. This comparison

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indicates that negative ion chemical ionization (NICI) GC/MS can extend the lower limits of detection for both CS tear gas and MAAQ when compared with either electron impact ionization (EI) or positive ion chemical ionization (PICI) GC/MS. We demonstrate how these mass spectral techniques can be used for the examination of evidence to supplement or replace established methods of analysis [1-4] and offer the possibility of a simplified analysis procedure.

Materials

The exploding money packets were obtained from U.S. Currency Protection Corp., ICI Americas, Inc., Atlas Aerospace Division, and Protection Products Corp. A known sample of chloroacetophenone (CN tear gas) was obtained from U.S. Currency Protection Corp. and the known standards of 1-methylaminoanthraquinone (MAAQ) and orthochlorobenzalmononitrile (CS tear gas) were supplied by ICI Americas, Inc.

The helium that was used as the GC carrier gas in the EI ionization GC/MS analysis was 99.999% pure and the methane used as the GC carrier gas as the reagent makeup gas for chemical ionization GC/MS analysis was 99.97% pure. Both gases were supplied by Roberts Oxygen.

Equipment

The gas chromatograph/mass spectrometer used for this study is a Finnigan 4021 quadrupole/mass spectrometer equipped with a Finnigan INCOS 2300 data system and a Finnigan pulsed positive ion, negative ion chemical ionization (PPINICI) detector which has two dynodes at potentials of +3000 and -3000 V (for attraction of negative and positive ions, respectively) followed by a continuous dynode electron multiplier which can be operated from 0 to -3000 V.

The gas chromatograph was equipped with a 1-m by 2-mm inner diameter glass column packed with 2% OV-17 coated on Supelcoport acid washed-dimethyldichlorosilane (AW-DMCS) (100-120 mesh) for all experiments. The GC/MS interface was equipped with both a molecular jet separator for EI work and a glass-lined stainless steel direct transfer line for CI work.

Experimental Conditions

The following instrument conditions are used. The gas chromatograph is temperature programmed from 100 to 270°C at 15°C/min. The flow through the column is 35 mL/min. The carrier gas is methane in both NICI and PICI modes and helium for EI. The injector is held at 260°C and transfer line and separator are held at about 250°C. Figure 1 shows the reconstructed gas chromatogram of 100 ng each of CS tear gas, CN tear gas, and MAAQ when these conditions are observed.

For EI ionization the following mass spectrometer conditions are used: mass range, 50 to 400 AMU; 27 intensity measurements per AMU at an integration time of 0.2 ms/intensity measurement (2 s/scan); ionizer 70 eV; 0.4 mA filament; -1100 V electron multiplier; and amplifier sensitivity, $\times 10^{-7}$ A/V. Source pressure before analysis is approximately 10 mPa (1×10^{-7} torr), the source temperature is 250°C, and the manifold temperature is approximately 100°C. For CI the conditions are the same as with EI ionization except that the source pressure is maintained at 39 Pa (0.29 torr) by makeup gas and the source temperature is 200°C. The mass spectrometer is used in the PPINICI mode where positive and negative ions are monitored on alternate scans of the same chromatogram for comparing the relative sensitivities of PICI and NICI. The mass spectrometer is normally used in either PICI or NICI separately for the examination of evidence.

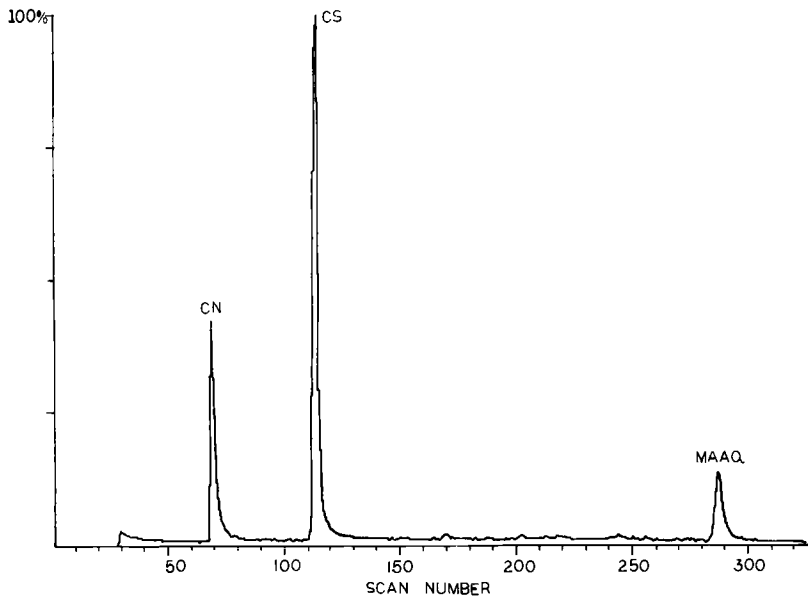


FIG. 1—Reconstructed gas chromatogram of 100 ng each of CN tear gas, CS tear gas, and MAAQ using electron impact ionization.

For the PPINICI GC/MS, the mass range is 100.0 to 400.0 AMU and 16 intensity measurements are collected per AMU with an integration time of 0.2 ms/intensity measurement (0.995 s/scan PICI, 0.995 s/scan NICI).

Comparison of Sensitivities

A solution containing 10 ng/ μ L each of MAAQ, CN tear gas, and CS tear gas was prepared in HPLC grade toluene. One run was with a 1- μ L injection of the solution with the mass spectrometer in the EI mode as is described in the previous section. A second run was made with 1- μ L injection of the solution with the mass spectrometer in the PPINICI mode as described in the previous section.

Relative intensities were determined by measuring the ion current representing the maximum intensity for a single scan which corresponded to the retention time of the dye or tear gas of interest. Both the total ion current representing a full scan (with background subtracted) and the base peak ion current were measured. The intensities were normalized by dividing the total current by the number of intensity measurements per AMU and dividing that intensity by the maximum total ion current when EI was used as the ionization technique. All intensities are reported for 10 ng for each chemical.

This comparison of EI and CI ionization modes is admittedly somewhat arbitrary and is intended only to reflect differences in sensitivity that could be expected during a laboratory analysis procedure. The efficiency of the separator and compensation for differences in the chromatograph as a result of different carrier gases and column outlet pressures have been ignored.

The signal to noise ratio (S/N) of each peak was computed by the Finnigan INCOS S/N algorithm which measured the signal as the peak height at two scan widths and computed the noise as the root mean square deviation of the intensity from the average baseline for ten

scans immediately before the peak and ten scans immediately following the peak. The S/N ratios are listed without renormalizing for differences in EI and CI conditions.

Examination of Evidence

Samples suitable for analysis by GC/MS are prepared by first visually examining the evidence for any sign of a red dye. Suitable areas of the specimen are then extracted with a minimum volume of a high purity intermediate polarity solvent such as chloroform or acetone. The resulting solution can be concentrated by blowing a stream of dry nitrogen over the surface of the solution at room temperature. This procedure results in little or no loss of the chemicals of interest if the sample is not taken completely to dryness. Approximately 1.0 μL of the resulting solution is then injected into the GC/MS without further preparation. The samples are generally analyzed with separate runs using the EI ionization mode or separately with methane PICI or NICI. In this way the mass spectrometer sensitivity can be optimized for each technique.

It should be noted that while Rhodamine-B is frequently used as a component of exploding dye packages, this laboratory makes no attempt to identify this chemical in trace quantities. This chemical is a widely used dyestuff which is found in a number of consumer items

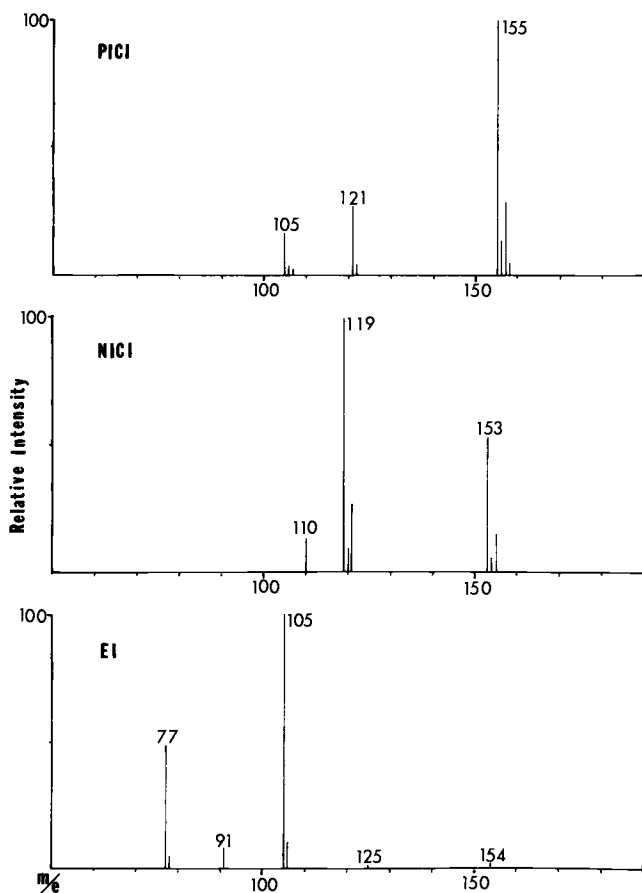


FIG. 2—Mass spectra of chloroacetophenone (CN tear gas) using PICI, NICI, and EI ionization.

and can frequently be identified in trace quantities on normally circulated U.S. currency. A recognizable mass spectrum can be obtained for the dye, but a different procedure than that described in this paper must be used.

Results

Figures 2, 3, and 4 show the mass spectra for CN tear gas, CS tear gas, and MAAQ, respectively, which result when PICI, NICI and EI ionization are used. The EI mass spectrum shown here for CN tear gas matches the spectrum found in the literature [5]. The mass spectra of CS tear gas and MAAQ have not been reported previously. Both CS and CN tear gas appear to undergo simple fragmentation; however, the EI spectrum of MAAQ is complicated by a McLafferty rearrangement. The spectra for all three chemicals obtained with PICI are predictable showing the predominate ($M+1$) ion. The NICI mass spectrum of both CS tear gas and MAAQ show a predominate M^- ion with little fragmentation indicating ionization by the classic resonance electron capture mechanism [6, 7]. The NICI mass spec-

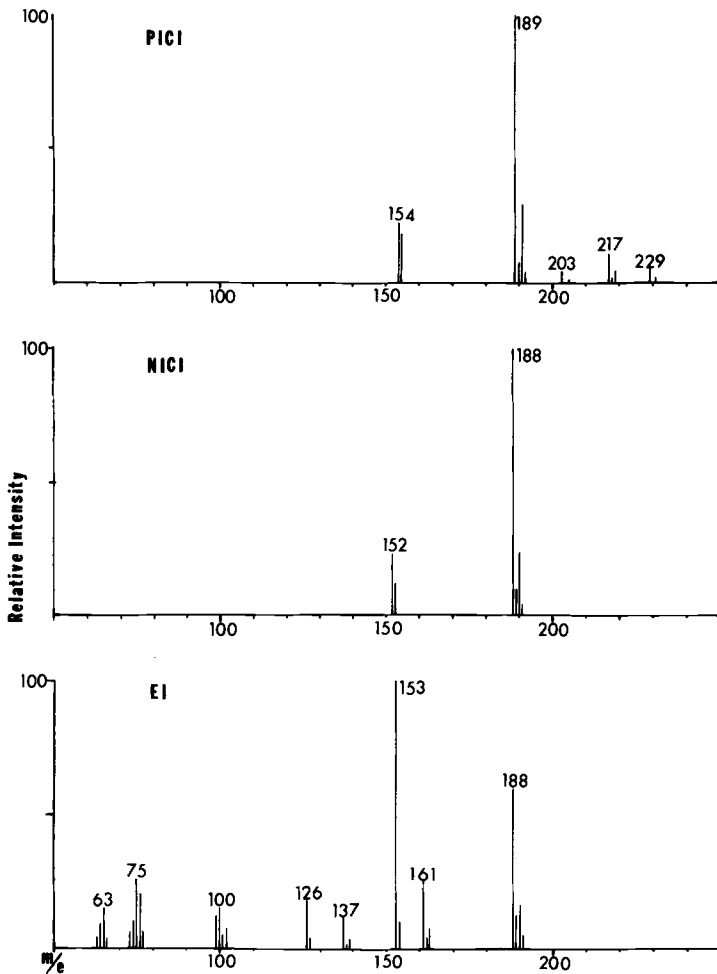


FIG. 3—Mass spectra of orthochlorobenzalmalononitrile (CS tear gas) using PICI, NICI, and EI ionization.

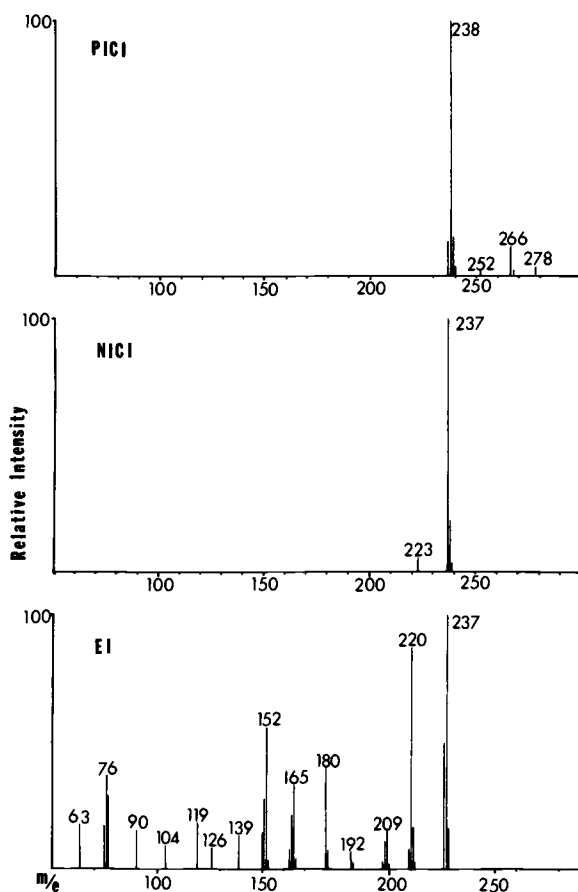


FIG. 4—Mass spectra of 1-methylaminoanthraquinone (MAAQ) using PICI, NICI, and EI ionization.

trum of CN tear gas is significantly different showing predominate $(M-1)^-$ and $(M-35)^-$ ions as is customary for chlorinated compounds [6].

The comparisons of sensitivities for CS tear gas, CN tear gas, and MAAQ are summarized in Tables 1, 2, and 3, respectively. Clearly NICI can provide greater sensitivity for both MAAQ and CS tear gas than either PICI or EI ionization. Because CN tear gas does not undergo resonance electron capture ionization, but instead appears to be ionized by the loss of a hydrogen or chlorine atom, NICI GC/MS would rarely be the most favorable technique.

Discussion

The usefulness of any analytical technique for the examination of evidence ultimately depends on both the sensitivity and selectivity of the method. While the results listed in the previous section form a foundation which may aid in choosing the most sensitive ionization method for GC/MS analysis of these materials, the method that gives the lowest minimum detectable limit will vary with the method of extraction and cleanup and the type and amount of interfering substances. Specimens that are badly contaminated with hydrocarbons will generally be best analyzed by NICI, whereas pliable plastics or other evidence that

TABLE 1—Comparison of relative sensitivities and signal-to-noise ratios (*S/N*) for *o*-chlorobenzal-malonitrile (CS) as a function of ionization mode.

Ionization Mode	Total Ion Current		Base Peak Ion Current	
	Relative Response ^a	<i>S/N</i> ^b	Relative Response ^a	<i>S/N</i> ^b
EI	1.00	38	0.183 ^c	230
PICI	3.51	95	1.41 ^d	650
NICI	67.9	310	39.9 ^e	340

^aAll responses were normalized to the EI total ion current as is described in the text.

^bSee test.

^c(a) *m/z* = 153.

^d(b) *m/z* = 189.

^e(c) *m/z* = -188.

TABLE 2—Comparison of relative sensitivities and signal-to-noise ratios (*S/N*) for chloracetophenone (CN) as a function of ionization mode.

Ionization Mode	Total Ion Current		Base Peak Ion Current	
	Relative Response ^a	<i>S/N</i> ^b	Relative Response ^a	<i>S/N</i> ^b
EI	1.00	7	0.269 ^c	35
PICI	1.45	15	0.456 ^d	63
NICI	0.274	2	0.100 ^e	20

^aAll responses were normalized to the EI total ion current as is described in the text.

^bSee test.

^c(a) *m/z* = 105.

^d(b) *m/z* = 155.

^e(c) *m/z* = -119.

TABLE 3—Comparison of relative sensitivities and signal-to-noise ratios (*S/N*) for 1-methylaminoanthraquinone (MAAQ) as a function of ionization mode.

Ionization Mode	Total Ion Current		Base Peak Ion Current	
	Relative Response ^a	<i>S/N</i> ^b	Relative Response ^a	<i>S/N</i> ^b
EI	1.00	15	0.073 ^c	35
PICI	0.906	6	0.113 ^d	20
NICI	39.6	99	31.6 ^e	132

^aAll responses were normalized to the EI total ion current as is described in the text.

^bSee test.

^c(a) *m/z* = 237.

^d(b) *m/z* = 238.

^e(c) *m/z* = -237.

are heavily contaminated by phthalates will generally be best analyzed by PICI or EI GC/MS.

By using the greatly different selectivities and sensitivities of these three ionization techniques to their advantage, this laboratory has greatly improved its ability to examine this type of evidence. In one case, NICI GC/MS provided a positive identification of CS tear gas on the shoe of a suspect who was arrested three months after the robbery for which he ultimately plead guilty. Both EI and PICI GC/MS have been used previously to analyze the same evidence and both gave negative results for CS. The practical advantages that are gained by using the greatly differing selectivities of these ionization techniques can also be used to simplify analysis. This laboratory has not encountered any case in which the sample extract contained a level of interfering substances which required any cleanup procedure such as thin-layer chromatography or high pressure liquid chromatography if the most favorable GC/MS technique was used.

References

- [1] Gay, J. A. and Merick, N. F., "Concise Identification of Commonly Encountered Tear Gases," *Journal of Forensic Sciences*, Vol. 22, No. 2, April 1977, pp. 358-364.
- [2] Stahl, C. J., Young, B. C., Brown, R. J., and Ainsworth, A. A., "Forensic Aspects of Tear-Gas Pen Guns," *Journal of Forensic Sciences*, Vol. 13, No. 4, 1968, pp. 442-469.
- [3] Sreenivasan, V. R. and Boese, R. A., "Identification of Lachrymators," *Journal of Forensic Sciences*, Vol. 15, No. 3, July 1970, pp. 433-442.
- [4] "Procedure for the Qualitative Identification of Security Pac Dye (1-Methylaminoanthraquinone) on Paper Currency by Visible Spectrometry or GC/Mass Spectrometry," Report, ICI United States Inc., Valley Forge, PA, June 1977.
- [5] *EPA/NIH Mass Spectral Data Base*, U.S. Department of Commerce/National Bureau of Standards, Washington, DC, 1978 Spectra No. 532-274, p. 507.
- [6] Large, R. and Knof, H., "A Comparison of Negative and Positive Ion Mass Spectrometry," *Organic Mass Spectrometry*, Vol. 11, 1976, pp. 582-598.
- [7] Hunt, D. F., Stafford, G. C., Jr., Crow, F. W., and Russell, J. W., in *Analytical Chemistry*, Vol. 48, No. 14, Dec. 1976, pp. 2098-2105.

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