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TECHNICAL NOTE

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Processing and Interpreting Mass Spectral Data in Forensic Identification of Drugs and Explosives

Mass spectrometry has become a well-established analytical method in the forensic identification of drugs and explosives [*1,2*]. In electron impact (EI) mass spectrometry (MS) the investigated sample is ionized by an electron beam having an energy of 70 eV. Because of this high ionization energy, the ions, after their formation, will usually decompose to fragmentation products including both charged and neutral species. The complexity of the EI mass spectrum, while often an important asset because of its "fingerprint" value, is clearly a disadvantage when complex mixtures are to be analyzed. When the compound is more complex, the amount of fragment ions is larger and the chances of observing a molecular ion are smaller. Electron impact mass spectrometry can be applied to mixtures, but only after separation, usually performed by a gas chromatograph-MS combination.

In an effort to obtain simpler mass spectra various means of ionization have been developed. The most widely used is chemical ionization (CI). In CI-MS a reagent gas (methane, isobutane, ammonia, or water) is introduced into the ion source of the mass spectrometer at a pressure of 0.1 to 1 torr (13 to 133 Pa). Under these conditions a set of reagent ions is produced by ion molecule reactions in the reagent gas. The investigated sample is introduced into the ion source at normal concentrations, as in EI-MS. Consequently, as a result of a collision between a reagent ion and a sample molecule M, a protonated molecular ion MH^+ or a series of adduct ions $(M + X)^+$, or both, will be produced. These ions have relatively little excess energy, so generally only a small number of fragment ions, or none at all, is produced.

The mass spectrum, consisting of a quasi-molecular ion (M + 1), with or without the support of adduct ions, will supply information concerning the molecular mass of the investigated sample, and in the case of a multicomponent mixture it will supply information concerning the molecular masses of the various components of the sample. Only when fragmentation ions are present in the mass spectrum are we able to learn about the chemical structure of the compound.

We would like to describe and demonstrate by some examples the method used in our laboratory for mass spectral identification of drugs and explosives through the use of both EI and CI.

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Experimental Procedure

The instrument used was a DuPont 21-490 B single focusing mass spectrometer equipped with a dual CI-EI source. Source temperature was in the range of 200 to 300°C, and probe temperature was to 50 to 250°C according to the volatility of the sample. Source pressure in CI was 0.2 to 0.5 torr (26 to 66 Pa) for methane and isobutane and 0.05 to 0.1 torr (6.6 to 13 Pa) for water.

The samples were dissolved in acetone and introduced as solutions into the solid probe of the mass spectrometer. After the solvent evaporated the probe was introduced into the ion source. Salts were introduced as solids into the probe. Samples of drugs and explosives were obtained from the central laboratories of the Israeli police.

The experimental method consists of the following steps:

1. Recording a CI mass spectrum of the unknown compound. Mass spectra are recorded on an oscillographic recorder. A mass marker that produces a mass identification on the spectrum is used. Measured peak heights and mass numbers are punched on cards which are then introduced through a terminal into the central computer, an IBM 370/165. The output of the computer is a normalized line mass spectrum and a table listing of masses and normalized abundances.
2. Interpreting the mass spectrum and comparing it to a library of CI mass spectra of forensic compounds. The CI mass spectrum will normally give us the molecular weight of the compound but not necessarily its identity. The molecular weight of the unknown has to be compared to a library. This is done manually and is quite simple. We have two separate libraries of CI mass spectra of explosives and drugs that are arranged according to molecular weights and include the name and chemical structure of the compounds. These libraries also include the CI mass spectra, if available. In cases where the library includes several compounds having the same molecular weight and the CI mass spectra either do not give any clue or are not listed for all the compounds, we then go to the third step.
3. Recording the EI mass spectrum. This will give the "fingerprint" of the compound. The fragmentation pattern given by the EI mass spectrum will be matched to one of the compounds according to its chemical structure, which will provide final identification. The comparison of the EI fragmentation pattern usually has to be done for a small number of compounds having the same molecular weight. Practically, CI and EI mass spectra are recorded for every compound.

Results and Discussion

Explosives

The identification of explosives is simpler than the identification of drugs because the number of explosive compounds is much smaller than the number of potential drugs.

Figure 1 shows the EI and CI mass spectra of pure trinitro-*m*-xylene (TNX). The CI mass spectrum has mainly one peak at *m/e* 242 (M + 1), which gives the molecular weight of the compound. Only the EI mass spectrum will provide information about the chemical structure of the compound. The EI spectrum has a base peak at *m/e* 224, which is M-OH, resulting from an "ortho effect" known to occur in *o*-nitroaromatic compounds having a hydrogen-containing substituent such as CH_3, OH, and NH_2 ortho to a nitro group [*3*]. There is also a double ortho effect leading to M-2OH at *m/e* 207 and a triple ortho effect leading to M-3OH at *m/e* 190. The peak at *m/e* 149 was found by high resolution MS [*4*] to be $(M\text{-}CO\text{-}2OH\text{-}NO)^+$. A high abundant peak is observed at *m/e* 103 from the $(M\text{-}3NO_2)^+$ ion, which is the diagnostic ion of the 2,4,6-trinitroaromatic system. An abundant

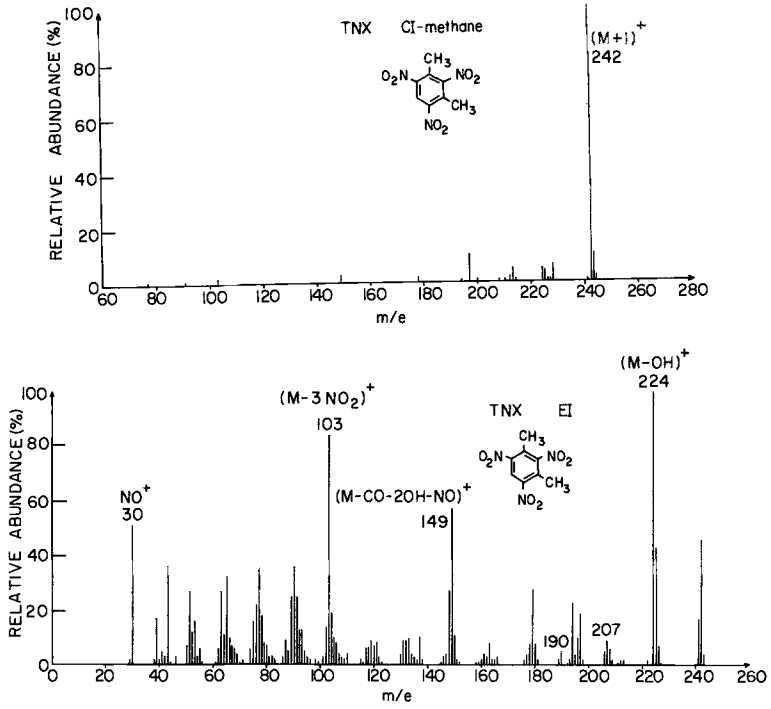

FIG. 1—*Electron impact and CI mass spectra of trinitro*-m-*xylene.*

NO^+ ion peak and a low abundant NO_2^+ ion peak are present, both of them characteristic of the 2,4,6-trinitroaromatic system.

A sample taken from the debris of an explosion site produced the CI mass spectrum shown in Fig. 2. The debris was extracted with acetone, and after evaporation of the solvent the residue was introduced with the solid probe into the mass spectrometer. The peak at *m/e* 228 can be clearly identified as the M + 1 ion peak of trinitrotoluene (TNT). Abundant phthalate-ester ion peaks are observed at *m/e* 363 and 391 caused by diheptyl phthalate and dioctyl phthalate originating from the plastic garbage container in which the explosive was placed. The mass spectrum also contains some adduct ion peaks and some peaks caused by impurities from the debris. The identification of TNT in this case was confirmed by thin-layer and gas chromatography.

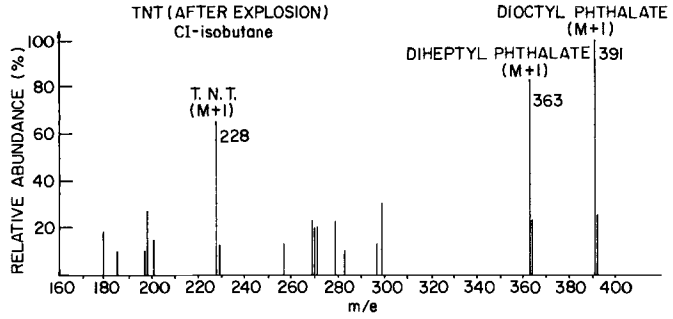

FIG. 2—*Chemical ionization mass spectrum of trinitrotoluene* (TNT) *in a sample from an after-explosion site.*

Drugs

In the case of drugs it is necessary to deal with a much larger number of compounds. We have catalogued the drugs according to molecular weight. The catalogue includes the name of the compound, its chemical structure, and the CI mass spectrum, if available.

Figure 3 shows the CI-isobutane mass spectrum of a drug found to be trihexyphenidyl (benzhexol). The $(M + 1)^+$ peak at *m/e* 302 provides the information that the molecular weight of this compound is 301. The peak at *m/e* 98 is an EI contribution.

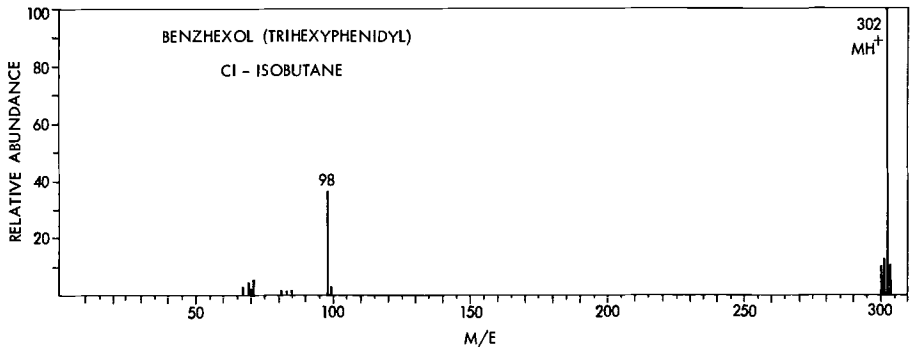

FIG. 3—*Chemical ionization mass spectrum of trihexyphenidyl.*

Our library included four compounds having a molecular weight of 301: trihexyphenidyl, oxymorphone, isoxsuprine, and dihydrocodeine. Chemical ionization mass spectra of all four compounds were included. The CI mass spectra of isoxsuprine and dihydrocodeine have besides the M + 1 peak two more abundant peaks, while the CI mass spectra of trihexyphenidyl and oxymorphone have only an M + 1 ion peak. To obtain a positive and unambiguous identification the EI mass spectrum of the suspected drug was recorded and is shown in Fig. 4. From the EI fragmentation pattern it was found that the compound was trihexyphenidyl.

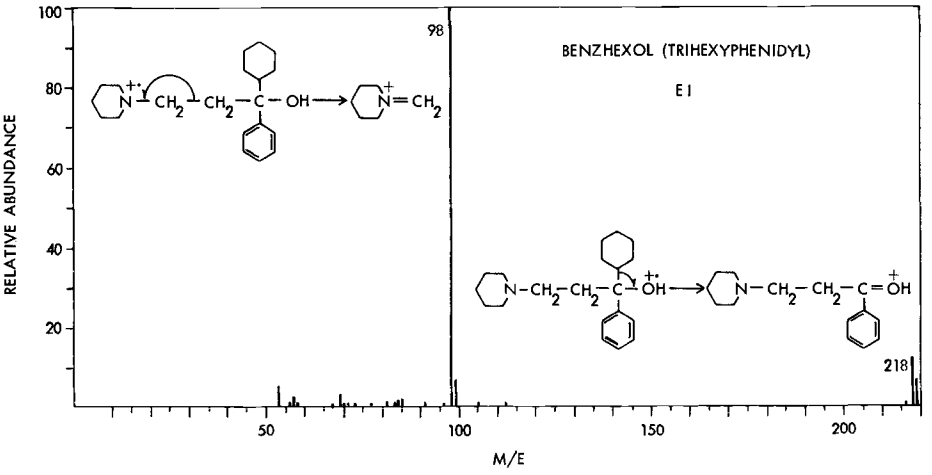

FIG. 4—*Electron impact mass spectrum of trihexyphenidyl.*

Another example is the identification of a drug suspected to be Scophedal®. Figure 5 shows the CI mass spectra of this drug with isobutane and water as reagents. Scophedal

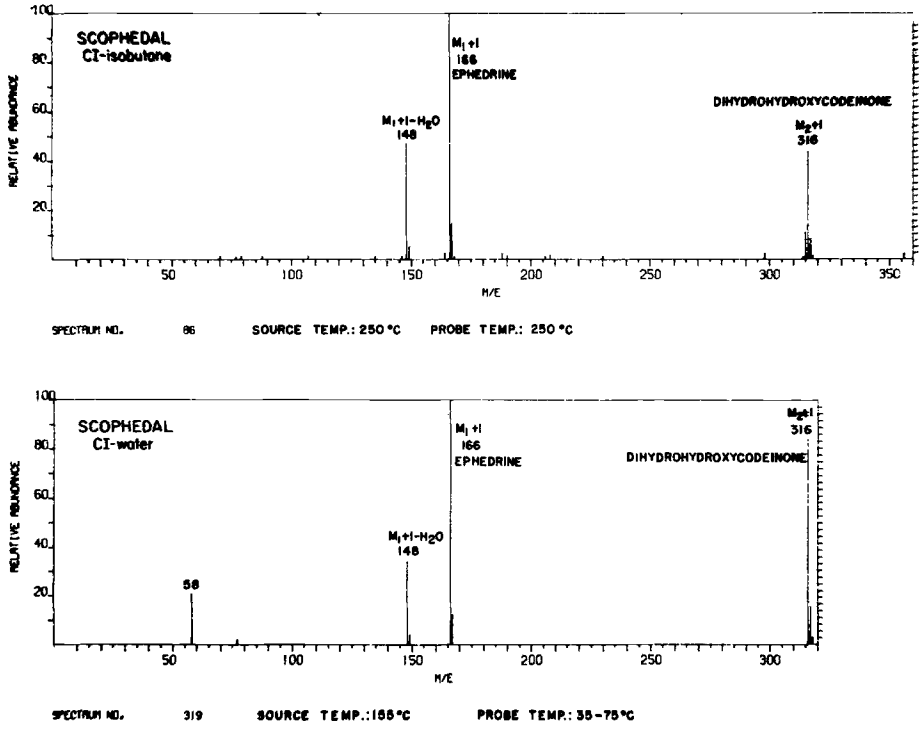

FIG. 5—*Chemical ionization mass spectrum of Scophedal.*

has three components: oxycodone (dihydrohydroxycodeinone), ephedrine, and a very small amount of scopolamine. In the CI mass spectra no detectable peaks gave evidence of the presence of scopolamine. However, the peak at *m/e* 316 could be the M + 1 ion of oxycodone and the peak at *m/e* 166 could be the M + 1 ion of ephedrine.

Our library included one other compound having a molecular weight of 315, chlorprothixene, but the CI mass spectrum of this compound produces, besides the M + 1 base peak, a 30% abundant isotopic peak at *m/e* 318 owing to chlorine. Other compounds having a molecular weight of 165 are 4-hydroxyphenylisopropylmethylamine, benzocaine, *p*-methoxyamphetamine and *m*-methoxyamphetamine. Although the CI mass spectra of these compounds differ from the CI mass spectrum of ephedrine, an EI spectrum was recorded and is shown in Fig. 6. Ephedrine is characterized by a molecular ion peak at

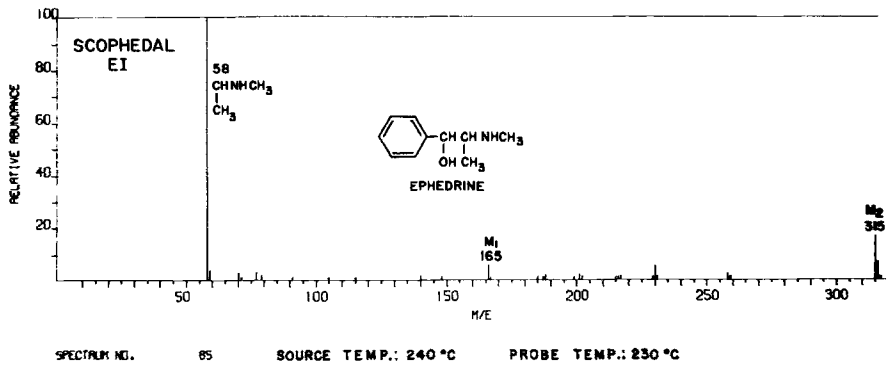

FIG. 6—*Electron impact mass spectrum of Scophedal.*

m/e 165 and a characteristic fragmentation peak at *m/e* 58. The same peak at *m/e* 58 is also observed as an EI contribution in the CI mass spectrum when using water as a reagent because of the lower water pressure.

Summary

The value of CI-MS in combination with EI-MS has been demonstrated as an analytical method for the identification of forensic compounds. Data acquisition consists of converting the recorded mass spectra into plotted and tabulated normalized mass spectra by using a central computer. Chemical ionization mass spectral library comparison and identification are done manually.

A system based on a microprocessor is planned to replace the manual conversion to plotted and tabulated mass spectra, and CI library comparison will be performed by the central computer.

Acknowledgment

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