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Chemical Ionization Mass Spectrometry

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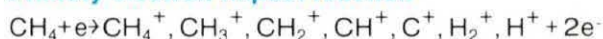
Introduction

One of the exciting new techniques in mass spectrometry has been the development of the chemical ionization source¹. In comparison to the electron impact source, chemical ionization offers the advantages of simpler cracking patterns, intense quasi-molecular ions and easy-to-interpret spectra.

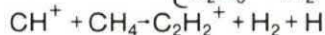
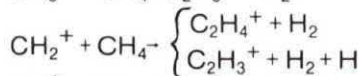
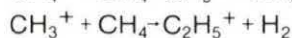
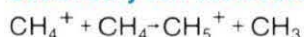
Principle of Operation

Chemical ionization (CI) is a form of high pressure mass spectrometry (0.5-1.5 torr) where the compound of interest is reacted with reactant ions. The reactant ions are formed from one substance by a combination of electron impact and ion-molecule reactions. The reaction of these ions with the material to be chemically ionized occurs by ion-molecule reactions. In most of the work done to date, methane has been the source of reactant ions. The reactant ions formed from methane are shown below:

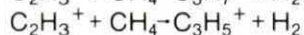
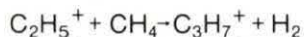
Primary electron impact reaction



Secondary ion-molecule reactions



Tertiary ion-molecule reactions



The ions which predominate in the above reactions are CH_5^+ (47% of the total), C_2H_5^+ (41% of the total) and C_3H_5^+ (6% of the total). For these ions the chemical ionization processes involve the transfer of massive entities such as protons (H^+), hydride ions (H^-) and alkyl carbonium ions (R-CH_2^+).

Thus, CI spectra are quite different from electron impact (EI) spectra, which are governed by Franck-Condon considerations. Furthermore, the nature of the CI process is such that the product ions formed

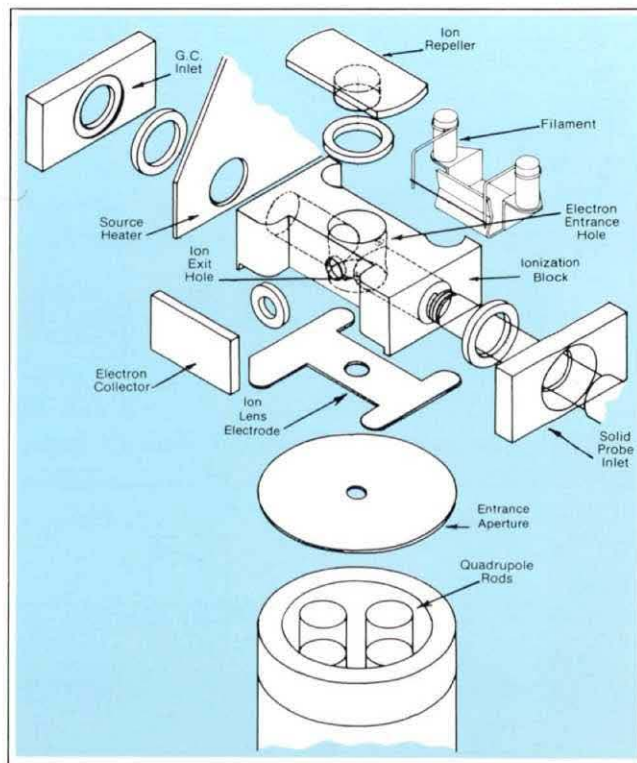


Figure 1: Exploded view of chemical ionization source.

contain even numbers of electrons. This is in contrast to the odd-electron ions formed by EI and field ionization processes. Also, the amount of energy involved in CI reactions tends to be low, depending on the identity of the reactant material used; this accounts for the simpler cracking patterns and generally high intensity of the quasi-molecular ion.

It is possible to use many different gases as reactants and thus produce spectra from reactant ions of different energies. Other reactant gases used in CI (major reactant ion in parenthesis) are n-propane ($i\text{-C}_3\text{H}_7^+$), hydrogen (H_3^+), isobutane ($t\text{-C}_4\text{H}_9^+$), nitrogen (N_2^+), water (H_3O^+ , H_5O_2^+), rare gases (R^+), methanol (CH_3OH_2^+ , $(\text{CH}_3\text{OH})_2\text{H}^+$) and ammonia (NH_4^+ , N_2H_7^+).

Component Description

A chemical ionization source (Fig. 1) used in a multipurpose gas chromatograph/mass spectrometer system must allow entrance of the GC effluent and solid probe sample. In addition, it is desirable to have the source operable in the EI mode.

The gas flow conductance out of the source must be low so that the filament and the rest of the spectrometer are not under excessive pressure. The electron entrance and ion exit holes should be as large as possible to optimize sensitivity, but not so large as to raise the pressure over 10^{-4} torr in the rest of the system when the source interior pressure is at 1 torr. There also must be additional lines to the source to bring in the sample and the reagent gases.

The source consists of a filament, ionization block, electron collector, ion repeller, ion lens and quadrupole entrance aperture. When used in the CI mode, the source parameters generally used are 100 microamp emission, 100 volts electron energy, 5 volts ion acceleration voltage, 1 to 5 volts ion repeller and 10-50 volts of lens voltage. The entrance aperture is at ground potential. When used in the EI mode, the source parameters are the same except the repeller is raised to 20-40 volts. Because of the closed nature of such a source, it is necessary to provide heating to reduce background. An internal heater capable of raising the temperature of the source to 250°C in ten minutes is incorporated.

CI In GC/MS Systems

In general, the interfacing of a GC to a MS has two problems which must be overcome; high gas flow rates and low sample to carrier gas ratio (or low system dynamic range). Both problems have been solved to some extent by the use of separators.² However, if a separator is not used the low sample to carrier (reactant) gas ratio actually becomes an asset since with CI the reactant gas to sample gas ratio must be at least 100:1. However the ion source diffusion pump must be still capable of handling the entire GC effluent.

Figure 2 shows the arrangement of a GC/MS system utilizing an EI-CI source. The ion source is differentially pumped by a 1200 liter/sec diffusion pump with a water cooled cold cap. The main chamber is pumped by a 300 liter/sec pump with a liquid nitrogen baffle. The two chambers are separated by a vacuum baffle. With this arrangement 5-10 ml/min of methane can be run into the source from the gas chromatograph without the use of a separator.

When solid probe samples are to be analyzed in the EI mode, the reagent gas is simply turned off. With no separator in the system EI spectra on GC samples cannot be run. However, if helium is used as the carrier-reagent gas the resulting spectra from charge exchange reactions shows remarkable resemblance to EI spectra^{3,4,5}, and higher flow rates can be used. A controller module with flow switching valves is provided to regulate gas flow into the solid probe. It also will allow any one of three reagent gases to be routed to either the solid probe or GC. Evacuation of gas lines is also provided.

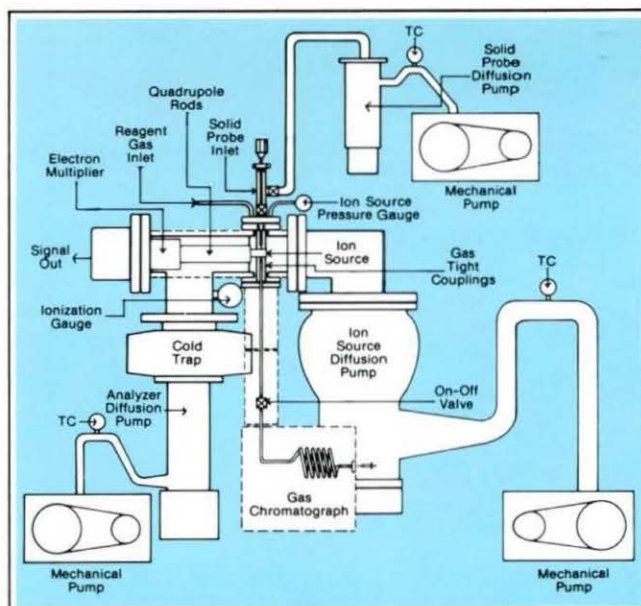
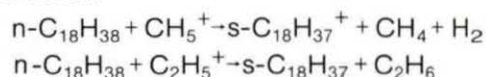


Figure 2: Vacuum diagram of Finnigan Model 1015C or 3100 with chemical ionization system.

Applications—Hydrocarbons

Hydrocarbons are characterized by the formation of the $(M-1)^+$ quasi-molecular ion (i.e. molecular ion minus one) which occurs by H^- abstraction. This can occur as a direct hydride ion abstraction with C_2H_5^+ or a dissociative proton transfer from CH_5^+ . Using $n\text{-C}_{18}\text{H}_{38}$ as an example, the following can occur:



The reactions above which produce the secondary octadecyl ion are exothermic. The formation of the primary octadecyl ion would be slightly endothermic and thus relatively improbable.

Branched alkanes give spectra similar to normal alkanes but there are generally less $(M-1)^+$ ions

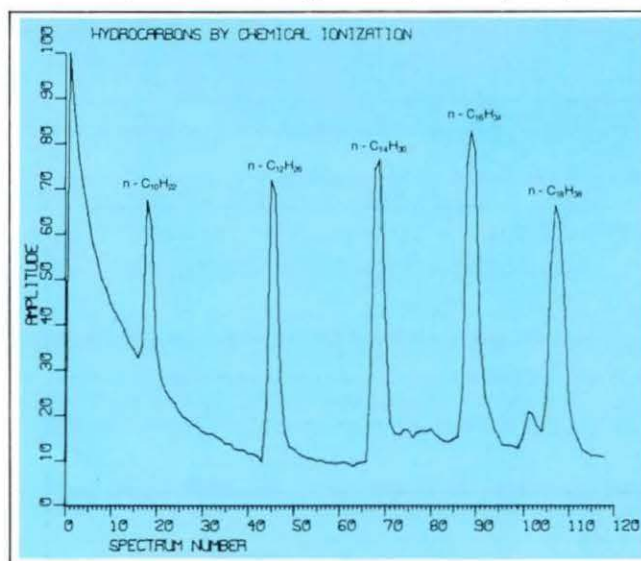


Figure 3: Hydrocarbons by GC/CIMS: $10' \times 1/8''$ S.S., 3% SE-30 on 80/100 Chromosorb W (HP); carrier gas, methane, to give 900μ pressure in the ion source (direct connection); sample size, $1 \mu\text{l}$ ($5 \mu\text{g}$ per component in hexane); injector 225°C ; crossover 230°C ; column $85^{\circ}\text{C} - 250^{\circ}\text{C}$ @ $15^{\circ}\text{C}/\text{min}$; ion source 100°C ; filament current $500 \mu\text{a}$ @ 100eV .

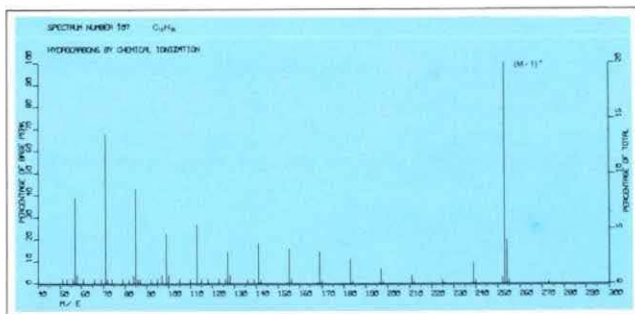


Figure 4: Chemical ionization mass spectrum of n-octadecane.

and more fragment ions with branched alkanes. Figure 3 is a GC/CIMS analysis of a normal hydrocarbon mixture. A spectrum of n-octadecane is shown in Figure 4. Note the $(M+19)^+$ peak present in the spectrum; this may be due to the addition of H_3O^+ from the H_2O impurity in the spectrometer or methane carrier gas.

Barbiturates

The mass spectrum of barbiturates is characterized by $(M+29)^+$ and $(M+41)^+$ which indicates the attachment of $C_2H_5^+$ and $C_3H_5^+$ to the parent ion. Figure 5 is a computer reconstructed chromatogram of a GC/CIMS analysis of a barbiturate mixture (5 μ g per component). Figure 6 is a mass spectrum of phenobarbital. Note that the $(M+1)^+$ ion represents 50% of the total ionization of the mass spectrum.

The technique of chemical ionization is still fairly new. However, it has been applied to the analysis of several classes of compounds: prostaglandins⁶, barbiturates⁷, esters⁸, alkaloids⁹, peptides¹⁰, amino acids¹¹, various hydrocarbons^{12,13,14}, and dangerous drugs¹⁵.

A combined EI-CI source has been described by Arsenault et al¹⁶ which allows alternate EI and CI

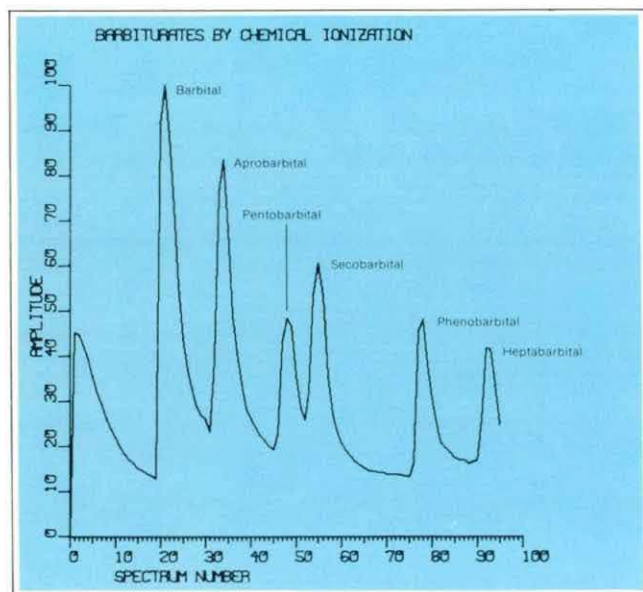


Figure 5: Barbiturates by chemical ionization: 10' x 1/8" S.S., 3% SE-30 on 80/100 Chromosorb W (HP); carrier gas methane to give 700 μ pressure in the ion source (direct connection); injector 225 $^\circ$ C; crossover 230 $^\circ$ C; column 170 $^\circ$ C-230 $^\circ$ C @ 10 $^\circ$ /min; ion source 100 $^\circ$ C; filament current 500 μ a @ 100eV.

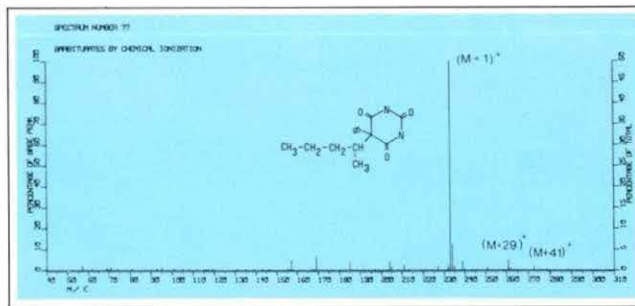


Figure 6: Chemical ionization mass spectrum of phenobarbital.

mass spectrometry of a gas chromatographic effluent.

For further details on chemical ionization, the reader is referred to an excellent article by Munson⁵.

REFERENCES

- Munson, M.S.B. and Field, F.H., *Journal of the American Chemical Society*, 88, 2621 (1966).
- Junk, G.A., "Gas Chromatograph-Mass Spectrometer Combinations and Their Applications," *Int. J. Mass Spec and Ion Physics*, in press (1971)
- Schoengold, D.M. and Munson, B., *Analytical Chemistry* 42, #14, 1811, December 1970.
- Foltz, R., Private Communication
- Munson, M.S.B., *Analytical Chemistry* 43, 29A-43A, November 1971.
- Desiderio, D.M., Burgus, R., Dunn, T.F., Vale, W., Guillemin, R. and Ward, D.N., *Organic Mass Spectrometry* 5, 221 (1971).
- Fales, H.M., Milne, G.W.A., and Axenrod, T., *Analytical Chemistry* 42, 1432-1435 (October 1970).
- Munson, M.S.B. and Field, F.H., *Journal of the American Chemical Society*, 88, 4337 (1966)
- Fales, H.M., Lloyd, H.A. and Milne, G.W.A., *Journal of the American Chemical Society*, 92, 1590 (1970)
- Kiryushkin, A.A., Fales, H.M., Axenrod, T., Gilbert, E.J., and Milne, G.W.A., *Organic Mass Spectrometry*, 5, 19 (1971)
- Milne, G.W.A., Axenrod, T. and Fales H.M., *Journal of the American Chemical Society*, 92, 5170 (1970).
- Munson, M.S.B. and Field, F.H., *Journal of the American Chemical Society*, 89, 1047 (1967).
- Field, F.H. and Munson, M.S.B., *Journal of the American Chemical Society*, 89, 4272 (1967).
- Field, F.H., Munson, M.S.B. and Becker, D.A., *Advances in Chemistry Series*, Number 58, 167-192 (1966).
- Milne, G.W.A., Fales, H.M. and Axenrod, T., *Analytical Chemistry* 43, 1815-1820, (November 1970).
- Arsenault, G.P. and Dolhun, J.J., 18th Annual Conference on Mass Spectrometry, San Francisco, June 1970.

Circle Reader Service Number 1

Analysis Of A Kraft Paper Mill Effluent By Electron Impact And Chemical Ionization GC/MS

by J. B. Knight, E. J. Bonelli and R. E. Finnigan

The current emphasis on a cleaner environment is responsible for a myriad of innovations, ranging from recycling cans to ecological political platforms. The U.S. Government has, in fact, created a major organization, the Environmental Protection Agency, to study and hopefully control air pollution, water pollution, noise, thermal pollution and solid waste disposal problems.

One of the major sources of water pollution is disposal of industrial waste products such as the effluent of kraft pulp mills. While many of the organic compounds occurring naturally in wood and some