

Chromatographic effluent detection with laser ionization mass spectrometry

By Richard B. Opsal and James P. Reilly

Open tubular column gas chromatography/mass spectrometry (GC/MS) has become one of the most versatile and powerful tools for the chemical analysis of volatile samples. The inherently high selectivity and sensitivity of the technique stems from its unique capability to separate and subsequently identify individual components of even very complex samples. Numerous instruments have been developed successfully to couple mass spectrometry with gas chromatography. Different types of mass spectrometers, ionization sources, interfaces, and gas chromatographs can comprise a GC/MS system.

The ionization source is one of the more versatile components of the mass spectrometer system. Electron impact, chemical ionization, photoionization, microwave

induced plasmas, and field ionization are some of the present sources used in GC/MS systems, although the first two are most popular. Desirable qualities of the ideal ionization source include ease of use, linear response, reproducibility, universal or selective ionization at high efficiency, control of the extent of fragmentation, and unique fragmentation patterns for each compound.

Laser ionization

Laser induced multiphoton ionization is a promising new technique, since it potentially offers high sensitivity.¹⁻³ Klimcak and Wessel demonstrated that laser ionization coupled with a proportional counter is a sensitive (approximately 10 pg for polyaromatic hydrocarbons) and selective detector for gas chromatography.² Along similar lines, a laser ionization capillary column gas chromatograph/time-of-flight mass spectrometer (TOF MS) system was developed in our laboratory.⁴

Laser ionization methods utilize stepwise or multiphoton processes. Molecules are ionized not with

a single, short wavelength photon as in conventional photoionization mass spectrometry but by absorption of two or more photons. Near ultraviolet light is then sufficiently energetic to ionize most organic compounds.

Single photon ionization with lasers would also be efficient, but at present there are no powerful lasers operating at sufficiently short wavelengths in the vacuum ultraviolet. An additional advantage of visible and ultraviolet radiation is that it is readily transmitted by air and many optical materials. Recent reviews describe laser ionization and multiphoton spectroscopy.^{1,3,5}

Our work concentrates on resonant two-photon ionization which is based on two successive single photon processes: One photon is resonantly absorbed by a molecule exciting it to an intermediate state; the excited molecule subsequently absorbs an additional photon, energetically raising it above the ionization potential. Rare gas halide excimer lasers are utilized as the light source. Some of their particularly attractive features include their high energy pulsed UV out-

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puts, energy-efficient operation and quasi-tunability. By changing the composition of the lasing medium (a halogen, rare gas mixture), a variety of output wavelengths are available. The results described here in were obtained with Lumonics KrF ($\lambda = 249$ nm) and ArF ($\lambda = 193$ nm) excimer lasers.

Gas chromatography/mass spectrometry

Because laser ionization studies generally utilize pulsed, low-duty-cycle lasers, obtaining a complete mass spectrum from each laser pulse is imperative for efficient detection. A limited number of mass spectrometers satisfy this multi-channel requirement. These include mass spectrographs with array detection, Fourier transform mass spectrometers, and time-of-flight mass spectrometers. Only the latter two have been used with laser ionization GC/MS.^{4,6} Time-of-flight mass spectrometers are also relatively inexpensive, and their simplicity allows easy fabrication. The laser pulse provides a natural time zero for time-of-flight analysis, and commercially available electronics enable facile data collection and signal averaging.⁷ Finally, TOF instruments have high ion transmission and a theoretically unlimited mass range. The mass spectrometer utilized in this work is a home-built reflectron TOF MS which has been described in detail elsewhere.⁷

Their high chromatographic resolution and low gas flow rates make capillary column gas chromatographs particularly suitable for GC/MS applications. This work utilizes a commercial capillary column GC (Varian 3700 with capillary on-column injector) with little modification. Figure 1 is a schematic drawing of the apparatus. The capillary column is interfaced

directly to the ion source of the TOF MS, and laser radiation enters the spectrometer perpendicular to the plane of the picture.

Experiments

A comparison of chromatograms obtained with a conventional flame ionization detector and with the laser GC/MS system is presented in Fig. 2. It is well known that flame ionization detectors have approximately unit mass re-

sponse for hydrocarbons.⁸ Similarly, electron impact ionization exhibits nearly constant ionization probabilities for different molecules. However, with laser ionization, ion yield varies due to differences in each molecule's spectroscopy and photophysics.

Figure 3 provides examples of the sensitivity obtained with laser ionization. Selected ion monitoring is necessary for these high-sensitivity measurements, due to the highly efficient ionization of cer-

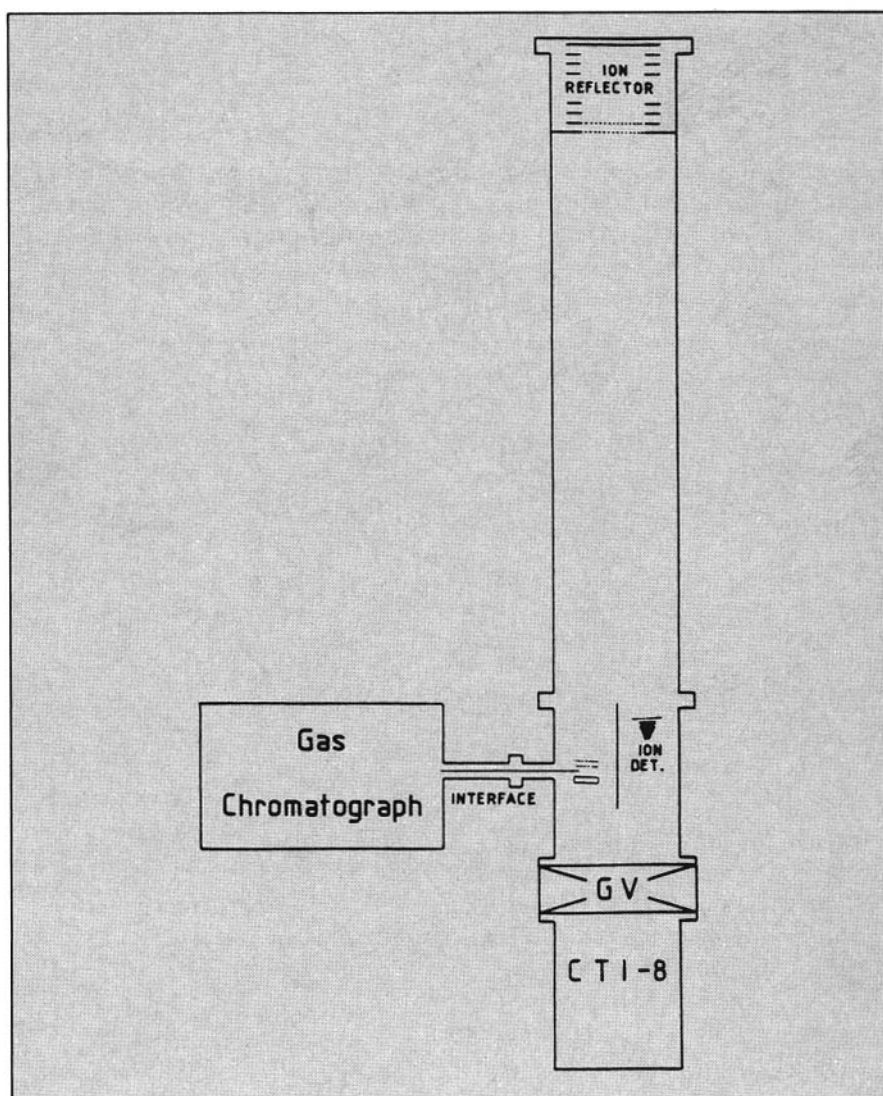


FIGURE 1. Gas chromatograph interfaced reflectron mass spectrometer used to record laser ionization mass spectra and chromatograms, GV = gate valve; CTI-8 = vacuum cryopump.

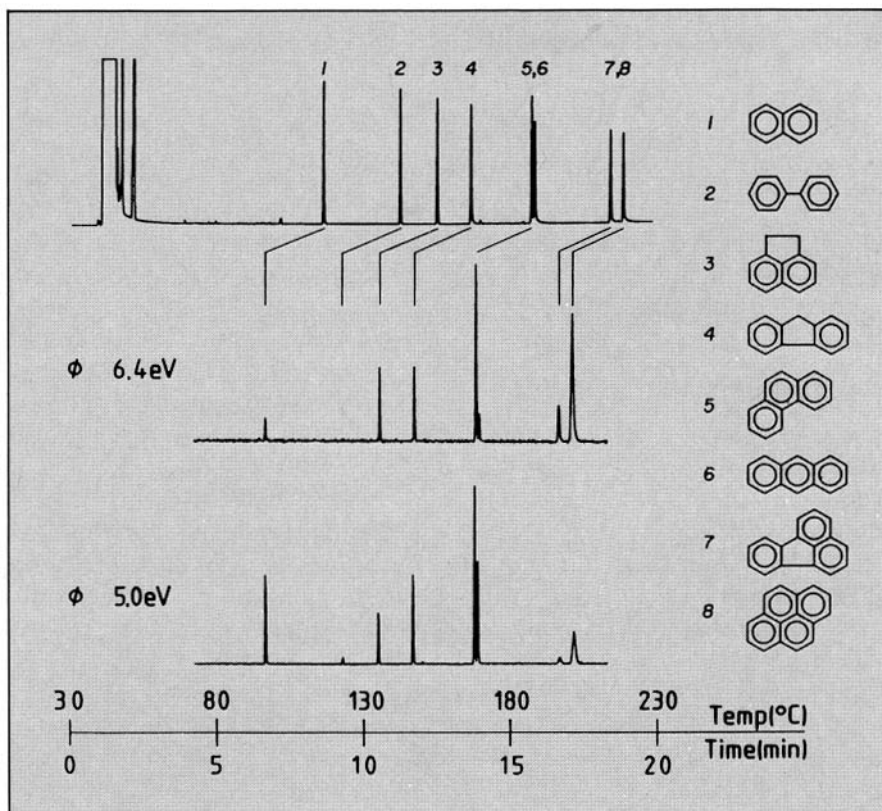


FIGURE 2. Capillary column gas chromatograms of a mixture of the eight polycyclic aromatic hydrocarbons depicted in the figure. Flame ionization detection, 5 ng per component. ArF laser ionization, mass integrated ion yield, 0.5 ng per component. KrF laser ionization, mass integrated ion yield, 0.5 ng per component.

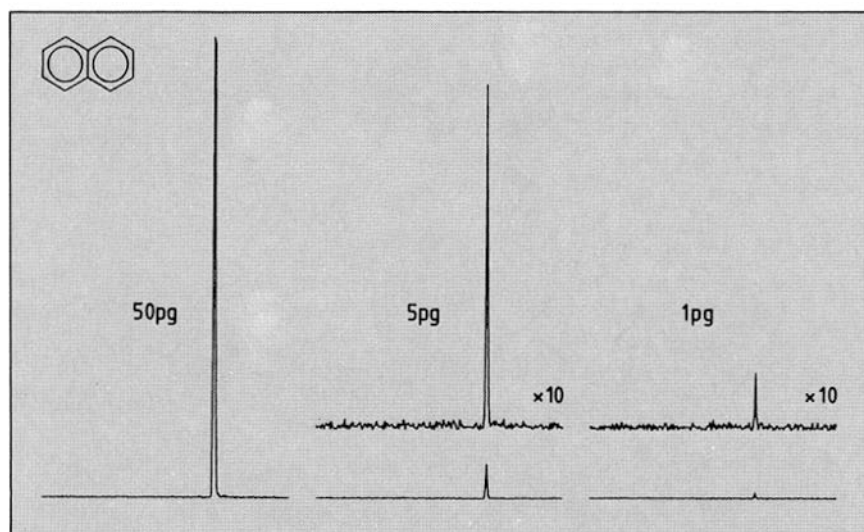


FIGURE 3. Selected ion chromatograms demonstrating detection sensitivity for naphthalene with KrF laser ionization and selected ion monitoring.

tain background molecules. Selected ion chromatograms are displayed for 50 pg, 5 pg and 1 pg of injected naphthalene monitoring only the ion current for m/z 128.

The detection limit for naphthalene, at a signal-to-noise ratio of 2, is approximately 400 fg.

While detection sensitivity is high, selectivity is even more re-

markable. This is of particular interest in the chemical analysis of complex mixtures. Gasoline, for example, contains hundreds of components.⁹ Most of these are alkanes and olefins. However, a number of alkylbenzenes and polycyclic aromatic hydrocarbons are also present. Laser ionization selectively ionizes these latter compounds.

Figure 4(a) is a flame ionization detected (FID) chromatogram of a gasoline sample. Readily visible are the major components of gasoline. (Minor components are evident when the scale of this figure is expanded). Within the first five minutes after sample injection, compounds corresponding to the light aliphatic fraction of gasoline elute. Figures 4(b) and 4(c) are ion yield chromatograms with ArF and KrF laser ionization, respectively. The components that are detected with laser ionization are alkylbenzenes, naphthalene, and various alkylnaphthalenes that appear relatively late in time. An analogous study utilizing 266-nm laser radiation yielded similar selectivity.⁶ The aliphatic components are absent in both of these chromatograms, due to their high ionization potentials (IP's > 10.0 eV) and weak ultraviolet absorptions at the laser wavelengths.

Figure 5 exhibits mass spectra of ethylbenzene and o-xylene that were obtained while the chromatogram in Fig. 4 was being recorded. Ionization of the two isomeric compounds with the KrF excimer laser yields quite analogous spectra. This result is similar to that obtained with conventional electron impact mass spectrometry. The molecular ion (at m/z = 106) is easily identified. Ionization of the compounds with ArF laser radiation yields mass spectra that are more fragmented and that exhibit substantially lower molecular ion abundance. Most importantly,

the two ArF laser-induced mass spectra are quite dissimilar; this enables unambiguous differentiation and "fingerprinting" of the two isomers.

Demonstrations of laser ionization selectively have not been limited to molecules as different as the alkanes and aromatic hydrocarbons. Some of the more impressive selectivity studies involve isomers of polyaromatic hydrocarbons. We have demonstrated selective ionization of chrysene (IP = 7.8 eV) over triphenylene (IP = 8.1 eV) with a XeCl excimer laser ($\lambda = 308$ nm, $h\nu = 4.0$ eV).⁴ Two photons from this laser simply do not exceed the ionization potential of triphenylene.

Selective ionization of the anthracene/phenanthrene isomers has also been demonstrated.² Recent studies in which internally cold molecules in supersonic beams are ionized by tunable dye lasers¹⁰ represent a further exciting extension of this method.

Laser ionization of molecules, which has been made possible by the advent of modern coherent light sources, is an ultrasensitive, highly selective new method of chemical analysis that should have a significant impact on analytical science in the near future.

Acknowledgment

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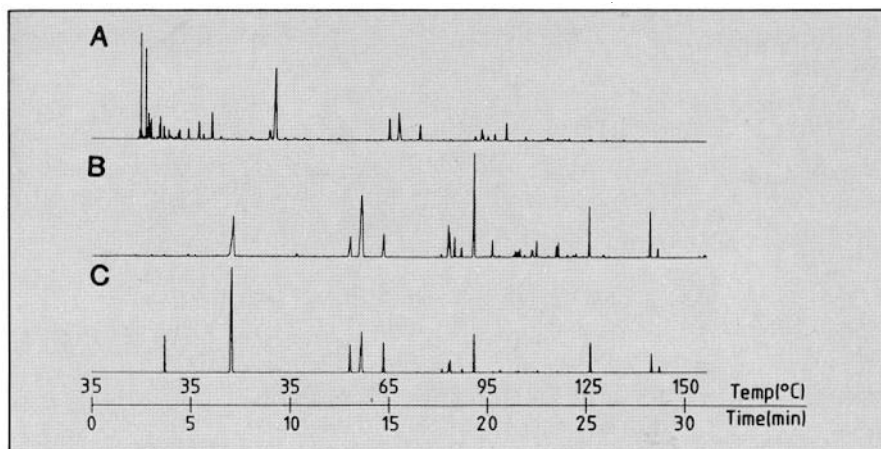


FIGURE 4. Capillary column gas chromatograms of a 0.2 μ L gasoline sample. (a) Flame ionization detection (FID). (b) ArF laser ionization, mass integrated ion yield. (c) KrF laser ionization, mass integrated ion yield.

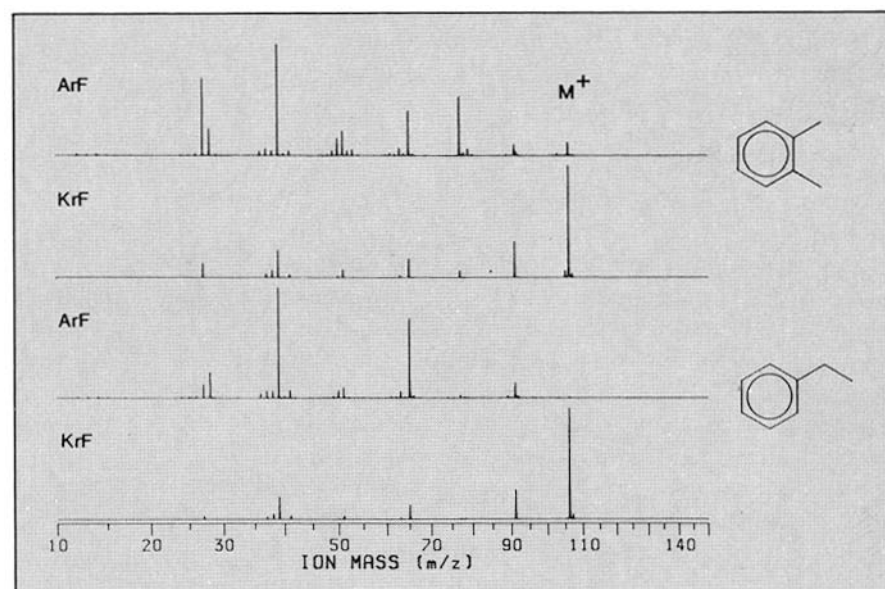


FIGURE 5. Laser ionization TOF mass spectra of a pair of C₈H₁₀ isomers demonstrating the wavelength selective nature of mass spectral fingerprinting possible with this method.