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GAS CHROMATOGRAPHIC DETECTION BY ELECTRON IMPACT-INDUCED FLUORESCENCE SPECTROMETRY OF MOLECULAR FRAGMENTS

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SUMMARY

Detection in gas chromatography (GC) via measurement of fluorescence of fragment species formed by 100-eV electron impact (EI) of compounds as they elute from the column is described. The detector is both selective (generating fragment species diagnostic of functional groups present in the parent molecule) and universal (producing a signal for all analytes). Figures of merit (limits of detection, linearity and precision) for EI-induced fragment fluorescence detection in GC are reported.

INTRODUCTION

Molecular fluorescence spectrometry exhibits two important characteristics (the ability to detect very small quantities of compounds and the generation of information useful for compound identification) that cause the technique to be of considerable potential utility for detection in gas chromatography (GC)[1]. Numerous detection systems for GC based on the measurement of molecular fluorescence have been described[2–13], some of which use supersonic expansion or matrix isolation techniques[7,9,11–13].

A major shortcoming of molecular fluorescence in chromatographic detection is that most molecules do not exhibit sufficiently high fluorescence quantum yields to be detectable at realistic concentrations. This difficulty has been surmounted in liquid chromatography by the widespread application of derivatization reactions that convert non-fluorescent analytes to fluorescent products[14]. Analogous procedures for GC detection have been much slower to develop.

Virtually any non-fluorescent molecule in the gas phase can be fragmented to form fluorescent species; such common molecular fragments as OH, NH, CN, CH and SH (as well as many atomic fragments) are intensely fluorescent, and their spectroscopic characteristics are well known[15]. The most common techniques for converting non-fluorescent molecules to fluorescent fragments are photolysis[16–21] and electron impact (EI)[19,22–25]. With the use of electronic array detectors, fluorescence spectra of fragments formed from compounds eluting from a GC column are measurable "on-the-fly".

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In 1984, Gierczak *et al.*[24] discussed the characteristics of EI-induced fragmentation as a means of generating emissive fragments from a variety of non-fluorescent organic molecules and considered its potential advantages as a technique for detection in GC. However, these investigators did not interface their EI-fluorescence apparatus to a gas chromatograph, and were thus unable directly to assess its performance as a GC detector. The present report describes techniques for interfacing electron impact-fragmentation fluorescence spectrometry (EI-FFS) to a gas chromatograph and the characteristics of EI-FFS as a GC detector.

EXPERIMENTAL

Instrumentation

A schematic diagram of the apparatus is shown in Fig. 1. A gas chromatograph (Perkin-Elmer Sigma 3) is equipped with a glass capillary column (30 m × 0.5 mm O.D.). The end of the column is connected, via a union fitting, to a glass capillary tube of the same diameter as the column, which is threaded through a heated glass-lined stainless-steel transfer line (15 cm × 0.6 cm O.D.) that passes the column eluent into a vacuum chamber. No splitters or other interface devices are used; the entire GC eluent is transferred through the glass capillary tube to the vacuum chamber. The chamber comprises a two-compartment stainless-steel cross, having a total volume of 4 l, differentially pumped by two Balzers TSU 331 turbomolecular pumps (pumping speeds: 330 l/s for helium). The pressure in the chamber is $3 \cdot 10^{-8}$ Torr or less in the absence of sample.

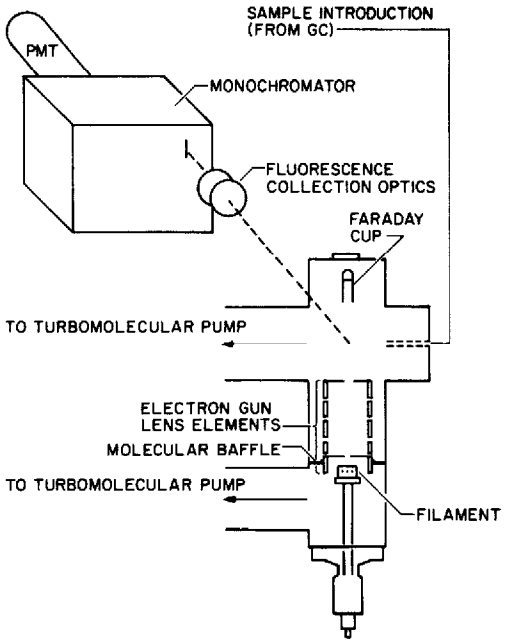

Fig. 1. Schematic diagram of EI-FFS detector, using a photomultiplier tube (PMT) to detect fluorescence.

The two compartments of the chamber are separated by the lens assembly of an electron gun constructed to the design of Erdman and Zipf[26]. The gun comprises a nickel grid, three gold-plated copper electron lenses (separated from one another by an assembly of sapphire balls), and a filament that serves as the electron source. From among the various filament materials available, 1% thoriated tungsten (Scientific Instrument Services, Ringoes, NJ, U.S.A.) appears least susceptible to corrosion in the presence of a wide variety of organic compounds. The filament is operated at 2.5 A and −100 V. The electron lens elements direct the 100-eV electron beam to its point of intersection with the GC eluent, where its current is approximately 1 mA ($6 \cdot 10^{15}$ electrons/s) and its diameter is 1 cm.

Fluorescence exits the chamber through a quartz viewport and is focused by two fused-silica lenses (focal lengths: 15 and 20 cm) onto either of two detection systems. For acquisition of fragment fluorescence spectra "on-the-fly", an EGG PAR OMA-II system, consisting of a Model 1420 intensified silicon diode array mounted to a Model 1225 0.25-m polychromator, is used. With 0.25-mm entrance and exit slits, a total spectral range of 130 nm is dispersed across the 700 intensified elements in the diode array, giving rise to an effective spectral resolution of 0.2 nm. The diode array is cooled to a temperature of 258 K. In all cases, any fluorescence background contributed by the carrier gas is subtracted.

For fluorescence measurements at fixed wavelength, an RCA 8850 photomultiplier tube mounted on a 0.25-m monochromator (Kratos GM-250), is used as a photon counter with EGG ORTEC modular photon-counting electronics. The photomultiplier tube is operated at room temperature at 1750 V. Using 0.70-mm entrance and exit slits, the spectral bandpass of the monochromator is 2 nm. Fluorescence spectra or gas chromatograms are plotted by an X–Y recorder.

Chromatographic techniques

The GC column is a 30 m × 0.32 mm I.D. glass capillary using, as bonded stationary phase, methyl-3,3,3-trifluoropropyl polysiloxane (J&W Scientific). Helium is used as carrier gas. The column can be operated isothermally or can be temperature programmed. Both for isothermal and temperature-programmed operation, the range of column temperatures used in this work was 300–365 K.

RESULTS AND DISCUSSION

Fragment fluorescence spectra

EI-FFS spectra for a large number of compounds have been obtained; representative example spectra are shown in Fig. 2. Table I lists the most intense fragment emissions, and their wavelength maxima, for a number of monofunctional organic compounds. As noted previously by Gierczak *et al.*[24], EI-FFS spectra of organic molecules tend to be very rich in hydrogen atomic emission lines. Other prominent fluorescent fragments include CN (from nitriles and amines), OH (from alcohols), SH^+ (from thiols), CO (from carbonyl compounds and ethers) and Cl^+ (from chlorinated compounds). In Table II are compiled the most intense fragment emissions produced by EI of a series of bifunctional organic compounds. In most cases, fragment emissions diagnostic of both functional groups are observed (*e.g.*, OH and SH^+ from 2-mercaptoethanol).

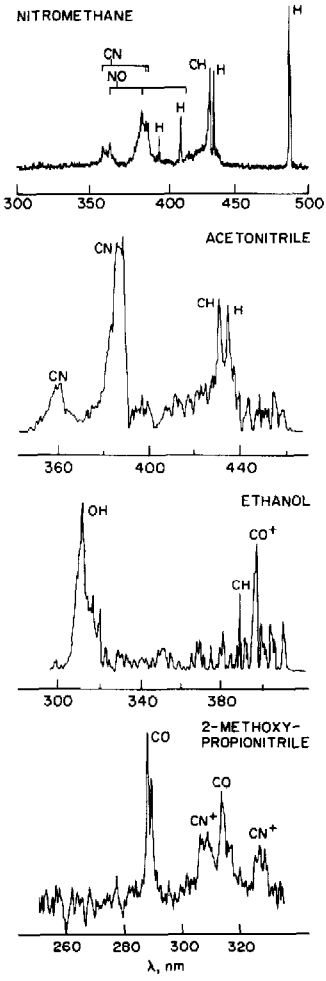

Fig. 2. EI-FFS spectra at 100 eV of nitromethane, acetonitrile, ethanol and 2-methoxypropionitrile. Major fragment emissions are identified in each case.

Using the definitions of Ettre[27], EI-FFS is a "selective" detector; *i.e.*, it identifies classes of compounds, but cannot be expected generally to produce conclusive identification of specific molecules. For example, the EI-FFS spectrum of an unknown aliphatic amine provides unambiguous identification of the compound class, but fails to identify the specific compound.

Unlike most "selective" detectors, EI-FFS can be used either in "selective" or "universal" modes, depending on whether single- or multiple-wavelength detection of fluorescence is utilized. If fixed-wavelength detection is used (*e.g.*, a monochromator or filter plus a photomultiplier tube), element- or compound-class selective detection is achieved by measuring the fluorescence of a single fragment as compounds elute from the column. For example, if fluorescence is monitored only at 337 nm (the wavelength of NH $A^3\Pi \rightarrow X^3\Sigma$ fluorescence), the EI-FFS detector is selective for primary amines;

TABLE I

FRAGMENTS OBSERVED IN THE EI-FFS SPECTRA OF MONOFUNCTONAL ORGANIC COMPOUNDS

Parent compound	*Fragments (positions of emission lines, nm)*[a]
Acetone	H(486,434,410,397), CH(431,389), CO(314)
Acetonitrile	CN(388), H(486,434,410), CH(431)
Carbon tetrachloride	Cl^+(439,460), CCl(460c,278)[b]
Chloroform-*d*	C^2H(431), ^2H(436,434), Cl^+(439)
Dichloromethane	CH(431,388), H(486,434,410), Cl(439,359)
Diethylamine	H(486,434), CH(431), CN(388)
Ethanethiol	H(486,434,410,397), CH(431, 388), SH^+(360)
Ethanol	H(486,434,410), OH(306), CH(431,389), CO^+(397)
n-Hexane	H(486,434,410), CH(431,388)
Nitrobenzene	H(486,434,410,397), CH(431), CN(388,359), NO(386)
Nitromethane	H(486,434,410,397), CH(431), NO(386,364,354), CN(388,359)
Tetrahydrofuran	H(486,434,410), CO(389,438), CH(431), CO^+(397,395)

[a] Fragments listed in decreasing order of their intensity in EI-FFS spectrum.
[b] c denotes a broad continuum in the EI-FFS spectrum.

if fluorescence is monitored at 388 nm (CN $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ fluorescence), the EI-FFS detector responds to any organic molecule containing a C–N bond. The detector also responds selectively to organometallics; metal atom fluorescence is usually produced[28].

On the other hand, if fluorescence is monitored simultaneously at many wavelengths (using a diode array detector), the EI-FFS detector generates a signal for all compounds, and the individual fragment fluorescences can be used to identify the principal functional groups present in each eluting compound.

Limits of detection

The limit of detection is defined as the minimum quantity of analyte, injected into the chromatograph, required to produce a fluorescence signal twice that of the

TABLE II

FRAGMENTS OBSERVED IN THE EI-FFS SPECTRA OF DIFUNCTIONAL ORGANIC COMPOUNDS

Parent compound	*Fragments (positions of emission lines, nm)*[a]
1-Bromo-3-chloropropane	H(486), CH(431,388), Cl^+(386)
3-Chloro-1-propanol	H(486), OH(306), CH(431), Cl^+(386)
Chlorodifluoromethane	CH(431), H(486,434,410,397), HCl^+(351,359)
2-Mercaptoethanol	H(486,434,410,397), CH(431), OH(306), SH^+(335,360), CS (280,260)
Methoxyacetone	H(486,434), CH(431,388), CO(438)
2-Methoxyethylamine	H(486,434,410), CH(431), CN(388), NH(337), CO(292,313,302)
2-Methoxypropionitrile	H(486,434,410), CH(431), CN(388,359), CO(292,313,302), CN^+(306,318,295)
4-Nitrobutyronitrile	H(486,434), CN(388), CH(431)
2-Nitro-1-propanol	H(486,434,410,397), OH(306), CH(431), CN(388)

[a] Fragments listed in decreasing order of their intensity in EI-FFS spectrum.

TABLE III
LIMITS OF DETECTION FOR EI-FFS DETECTION OF ORGANIC COMPOUNDS

Compound	*Limit of detection (μg)*	*Optical detector*
Acetonitrile	0.8	Photomultiplier tube
	10	Intensified diode array
Chloroform	2	Photomultiplier tube
	45	Intensified diode array
Dichloromethane	0.9	Photomultiplier tube
Nitromethane	1	Photomultiplier tube
	10	Intensified diode array
1-Nitropropane	2	Photomultiplier tube
	25	Intensified diode array
2-Nitropropane	2	Photomultiplier tube
	25	Intensified diode array

background noise observed in the presence only of carrier gas; in each case, the fluorescence measurement is made at the wavelength maximum of the EI-FFS spectrum (usually H_β fluorescence, 486 nm). The results are compiled in Table III, wherein it is noted that the limits of detection obtained using the photomultiplier tube as detector are invariably superior to those obtained using the diode array detector. These results are indicative of the relative detectivities of our diode array and photomultiplier systems, and cannot be generalized to conclude that photomultiplier detection is invariably superior to use of an array detector.

Linearity

EI-FFS measurements are generally linear in the partial pressure of parent compound in the vacuum chamber from the limit of detection (typically *ca.* 10^{6} Torr) to an upper pressure limit (*ca.* 10^{-3} Torr) which exceeds that ever reached using a capillary GC column[19]. It is therefore expected that the analytical calibration curve for GC detection by EI-FFS should be linear over at least three decades in quantity of analyte. This prediction was verified for nitromethane (measuring the H emission at 486 nm), for which the calibration plot was linear over the range 1 μg 2 mg. Accordingly, quantitative calibration techniques for which linear analytical curves are desirable (*e.g.*, standard addition) should be readily applicable to GC using EI-FFS detection.

Precision

One of the major advantages of EI is that beam currents from heated-filament electron guns can be regulated with much higher precision than the outputs of most photon sources used in conventional fluorescence spectrometry. Typical relative standard deviations for repetitive measurements of fragment intensities in EI spectra of pure compounds introduced into the vacuum chamber by bulb (rather than GC) are 1.0% or less[19]. Hence, for EI-FFS in GC detection, the precision is determined by the reproducibility with which samples are injected onto the column, rather than that of fragment production and fluorescence detection.

Dead volume

An important characteristic of a chromatographic detector is the extent to which its dead volume degrades the apparent efficiency of the chromatographic column. Obviously, the vacuum chamber used in EI-FFS detection has a much greater volume than many conventional GC detectors. However, the total volume of the capillary tube used to transport the column eluent to the vacuum chamber is very small, and the flow-rate of gas through the vacuum chamber is such that the residence times of eluent molecules in the observation region are very short. For capillary column GC, the base widths of chromatographic peaks increased by an average factor of 1.012 when EI-FFS detection was used, compared with those obtained using a conventional flame ionization detector. The largest increase in peak base width observed for EI-FFS detection, relative to that obtained using the flame ionization detector, was a factor of 1.02. Hence, despite the relatively large volume of the EI-FFS detector, only minor peak broading is introduced. An example chromatogram of a eight-component mixture, using H atom fluorescence at 486 nm, is shown in Fig. 3.

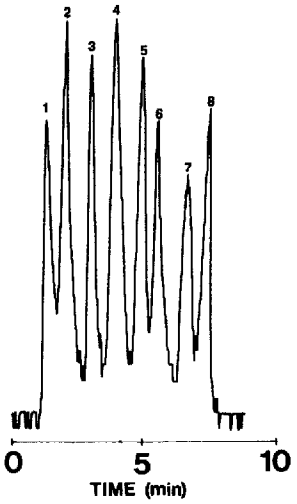

Fig. 3. EI-FFS chromatogram of eight-component mixture measured at 486 nm (H_β fluorescence). Compounds: 1 = methanol; 2 = 2-propanol; 3 = acetone; 4 = acetonitrile; 5 = nitromethane; 6 = 2-pentanone; 7 = 2-nitropropane; 8 = 1-nitropropane. Conditions: isothermal at 25°C for 3 min, then programmed at 18°/min to a final temperature of 80°C.

Universality and choice of carrier gas

EI is a universal fragmentation technique; any compound eluting from a GC generates an EI-FFS spectrum. Unfortunately, the carrier gas also generates fluorescence; for example, the EI-induced fluorescence of N_2^+ can serve as the basis of a sensitive technique for detection of N_2[29]. Because bombardment with 100-eV electrons causes electronic excitation[22], even an atomic carrier gas, such as helium, generates background emission. The EI-induced spectrum of helium contains many atomic emission lines. Nonetheless, for single-wavelength detection using a mono-

chromator–photomultiplier system, a wavelength can be found for any common fragment at which the background emission produced by helium is small (< 700 counts/s in the photon-counting mode). In the case of "on-the-fly" acquisition of spectra using an array detector, it is necessary to subtract the helium fluorescence background (as was done routinely in this work, including the spectra shown in Fig. 2), causing some degradation in the signal-to-noise ratio (S/N). This problem could be alleviated by interposing an interface device, analogous to those used in GC mass spectrometric systems[30], between the column exit and vacuum chamber (at the cost of additional instrumental complexity and loss of some analyte in the interface).

Possible improvements of EI-FFS detector

The relative simplicity of the EI-FFS detector is an attractive feature. At the cost of increasing complexity, two strategies could be used to improve limits of detection. First, use of a pulsed-electron gun coupled with gated detection (analogous to use of a pulsed laser[31]) should improve S/N; very high instantaneous currents (analogous to the very high peak powers of pulsed laser) can be produced using pulsed-electron guns[32]. Second, not all fragments generated by 100-eV EI of a parent molecule are formed in emissive excited states. Those fragments formed in the ground state by EI can subsequently be excited by a pulsed laser, generating enhanced fragment fluorescence signals[33].

CONCLUSION

As previously emphasized by Gierczak *et al.*,[24] a GC detector based on EI-FFS can be operated as either a universal or a selective detector. Any organic or organometallic compound containing hydrogen produces hydrogen atomic fragment emission at 486 nm; use of a single-wavelength detector (*e.g.*, an interference filter–photomultiplier combination) would enable operation as a universal detector. At the same time, different classes of compounds produce different major fragments (Tables I and II), endowing the EI-FFS detector with substantial selectivity and ability to identify functional groups present in unknown compounds. Interference by co-eluting compounds of dissimilar chemical nature[27] can accordingly be circumvented. Spectra generated by EI-FFS are considerably less useful for identification of specific compounds than those produced by a mass spectrometer; the molecular mass, for example, cannot be obtained from an EI-FFS spectrum. On the other hand, the EI-FFS system described here is less expensive and easier to use than a mass spectrometer.

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