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ANALYTICAL TECHNIQUES FOR TRACE ORGANIC COMPOUNDS - II

DETECTORS FOR GAS CHROMATOGRAPHY

Prepared for publication by

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Analytical techniques for trace organic compounds II. Detectors for gas chromatography

Abstract - The principles of operation, characteristics, detection limits, and other important features are discussed for a number of gas chromatographic detectors with regard to their use in trace organic analysis. Other operating parameters which impact on trace organic analysis by GC are briefly discussed. Factors which are pertinent to selection of the proper detector for a particular analysis are pointed out. Some of the possible pitfalls of the detectors are discussed as well.

INTRODUCTION

Gas chromatographic detectors are very important in trace organic analysis for providing both universal and selective detection. A gas chromatographic detector provides measurable signals from a flow of compounds separated in time by the chromatographic column. Some ingenious approaches have produced a wide variety of useful methods of sensing the chemical flow from a gas chromatographic column. Gas chromatographic detectors can provide low limits of detection, in some cases high selectivity, and a very wide linear dynamic range. These detectors can produce both quantitative and qualitative information about compounds eluted by the chromatograph. The availability of highly responsive and selective detectors, especially in combination with modern bonded phase capillary columns, has made the technique of gas chromatography (GC) an extremely powerful tool for trace analysis in biochemical, environmental, and industrial problems. Many examples of the applicability of capillary GC for trace analysis can be found in several recent reviews (ref. 1-3).

This article is not all inclusive; however, the detectors discussed include most of those with suitable detection limits, selectivity, and reliability to be routinely used in trace organic analysis by GC, especially with capillary columns.

GENERAL CONSIDERATIONS FOR OTHER FACTORS AFFECTING OVERALL CHROMATOGRAPHIC PERFORMANCE

Although this article deals with GC detectors, it is essential to point out that, although detector characteristics are important, the performance of the entire chromatographic system determines the applicability of GC to a trace analysis problem. Dynamic range, detection limit, precision, and accuracy also depend on injection methodology, oven design, and the choice of the column. Capillary GC columns, due to the high resolution attainable, are the most widely used in trace organic analysis by GC. The ability to perform high resolution separation of complex mixtures with a minimum of coeluting interferences can enhance the overall performance of many GC detectors, preventing the occurrence of quenching and nonlinear response. The very narrow solute zones in capillary GC provide enhanced detection limits in comparison with packed GC columns. In addition, the background level observed with capillary GC columns is generally considerably lower than with packed GC columns, which provides an increase in signal-to-noise ratio. The use of capillary GC columns, however, requires a careful choice of column parameters and injection methodology since these impact on the trace analytical capabilities of the system. Injection methodology for capillary GC will not be discussed here; however, the choice among techniques such as split, splitless, or cold on-column injection must be carefully made with regard to the trace analytical problem. For example, the analysis of a mixture of compounds of high boiling point may require the use of on-column injection in order to quantitatively deliver sample components to the chromatographic column. Capillary column parameters such as the type of stationary phase and the column stationary phase film

thickness, inner diameter, and length must also be properly chosen. For example, the choice of a thin film capillary column may limit the linear dynamic range due to its limited sample capacity. The choice of a thick film capillary column will provide enhanced capacity and additional retention for highly volatile compounds; however, high boiling components may not be eluted from the column at reasonable temperatures. Several excellent discussions on the choice of the appropriate capillary column and on injection methodology are available (ref. 3-5).

Trace organic analysis using GC has often involved chemical derivatization to improve overall chromatographic performance including enhanced volatility, improved peak shape, and temperature stability. With regard to detection, derivatization enhances detection by introducing functional groups which allow the most responsive and selective GC detectors, such as the electron capture or thermionic detectors, to be used. An extensive array of chemical derivatization reactions is available for trace organic analysis.

GAS CHROMATOGRAPHY DETECTORS FOR TRACE ORGANIC ANALYSIS

In the description of GC detectors that follows, an attempt has been made to include major operational characteristics describing and affecting detector performance. The most commonly used GC detectors in trace analysis are described in individual sections. Newer detectors that show promise for trace organic analysis are combined in a separate section. Important detector characteristics are summarized in Table 1. Also included is an approximate scale indicating the complexity of operation and maintenance of the various detectors. The universal response, low cost, and other characteristics of the flame ionization detector usually make it the detector of choice for analyses where applicable. At the other extreme of cost and complexity is the mass spectrometer; however, the high degree of selectivity and low detection limits make it an extremely powerful detector for organic trace analysis. This article attempts to provide information to aid the analyst in selecting the best detector for a particular application.

The flame ionization detector (FID)

Since its introduction by McWilliam and Dewer (ref. 6), the FID has become the most widely used detector in GC due to its low detection limits, wide dynamic range, reliability, and general utility for a variety of problems in trace organic analysis. Most commercial detectors are similar in the important aspects of detector design.

In the FID the GC effluent is premixed with hydrogen and flows through a burner top jet where it is burned in a surrounding laminar air flow. A suitable potential (300-400 V) applied to two electrodes, the flame jet and collector electrode, allows ions formed in the flame to be collected with high efficiency. The current generated is measured and amplified with a standard electrometer. Normally the background ionization is low, providing a minimal baseline current. When an organic sample containing $-CH_X$ groups is introduced into the flame, a large increase in current is observed. The response of the FID to an organic compound is due to the generation of ions via the chemiionization process shown below.

$$CH\cdot + O\cdot \rightarrow CHO^+ + e^-$$

This flame process generates ions in proportion to the number of oxidizable carbon atoms in the eluting compound. The FID responds only to those compounds that produce charged species when burned in a hydrogen/air flame. The detector does not respond to inorganic gases and carrier gas impurities, which results in a stable baseline. For trace organic analysis the FID is considered to be a universal detector with several advantages. Almost all organic compounds have low detection limits and have response factors that usually do not vary as much as other GC detectors. For example, the relative response factors are very similar for a variety of hydrocarbons regardless of compound type or molecular weight. Therefore, quantitative analysis of hydrocarbon mixtures is possible using relative response factors. The low detection limits, stable baseline, and nearly universal response of the FID provide excellent compatibility with the new generation of bonded phase fused silica capillary GC columns. In addition, the FID response shows minimal effects due to changes in carrier gas flow, pressure, and temperature changes. However, the response of the detector is dependent on the hydrogen/air ratio, which must be carefully controlled. The near universal response of the FID can, however, be problematic in targeted

compound analysis, where interferences can occur in analyzing complex mixtures. In these cases a more selective GC detector should be chosen as appropriate. The FID response depends on mass flow and it has a detection limit of 2×10^{-12} g/sec.

The thermal conductivity detector (TCD)

One of the early detectors used for GC (ref. 7) was based on thermal conductivity. The TCD has the advantages of almost universal response and also response factors for most compounds which are nearly the same. However, the TCD has relatively high detection limits and so it is usually not the detector of choice for trace organic analysis.

The TCD is based on measurement of the difference in thermal conductivity that results when a GC peak enters a measurement cell. The cell normally has a cylindrical configuration with a heated wire in the middle; the detector circuitry measures the thermal conductivity between the filament and the cell wall. The TCD is very susceptible to environmental fluctuation, and so usually a reference cell is used to provide a more stable baseline. More complex configurations are also used to achieve lower detection limits and better stability (see ref. 8 for a more complete discussion). Another design uses a single cell in which the flow is rapidly switched (on the order of 10 Hz) between the GC carrier gas and a reference gas (ref. 9). This design minimizes detector drift and provides baseline stability. Normally either hydrogen or helium are used as the carrier gas with the TCD due to their high thermal conductivity. Both of these gases have similar properties with respect to operation of the detector; however, helium would be preferred for inertness.

The linear dynamic range for the TCD is about 1×10^5 and the detection limit is about 4×10^{-10} g/mL (for propane). Capillary GC requires fast response times and small detector volumes, but detectors designed for use with capillary GC are available. The detection limits of the TCD are compound dependent but are, in general, more than an order of magnitude higher than the FID. Quantitative analysis is relatively easy since TCD response factors are generally about the same.

The photoionization detector (PID)

The PID is a versatile detector which provides low detection limits for a wide variety of organic and inorganic species. A commercial version which uses ultraviolet lamp sources is currently available (ref. 10).

The PID operates on the principle that a species can absorb ultraviolet light of a suitable frequency with resultant dissociation into an ion and electron:

$$A + h\nu \rightarrow A^+ + e^-$$

where A^+ is the ionized molecule and $h\nu$ is a photon of energy greater than the ionization energy. The detector consists of a sealed ultraviolet lamp adjacent to a chamber containing a pair of electrodes. A potential applied to an accelerating electrode allows the electronic measurement of the ions formed by the absorption of ultraviolet light at a collector electrode. Lamps with energies ranging between 9.5-11.7 electron volts are available, which can provide some selectivity in detection based on lamp ionizing energy. Of importance is the fact that the detector is virtually nondestructive, allowing its use in series with other GC detectors. For instance, the detector has been utilized in series with an FID for the qualitative determination of hydrocarbon classes based on relative molar responses (ref. 11). Current commercial PID units optimized for capillary GC columns have all glass inlet lines, low internal cell volume, and the ability to perform high temperature analysis (up to 300°C). Because the response of the PID depends on concentration, these improvements have resulted in 100-fold lower detection limits with capillary GC columns. Operation at higher temperatures has expanded applications to the analysis of high molecular weight, nonvolatile compounds such as drugs and pesticides.

Difficulties can sometimes be encountered with contaminated optical windows. In addition the detector response varies with structure, which can limit its application as a universal detector for quantitative analysis of complex mixtures. The selectivity of the PID, which is based upon differences in ionization energy, is not as high as other selective GC detectors.

TABLE 1. Summary of detector characteristics

DETECTOR	TYPE	APPROXIMATE DETECTION LIMIT	SELECTIVITY	LINEAR RANGE	TEMP. LIMIT °C	RELATIVE COMPLEXITY[a]
Flame Ionization (FID)	Universal (organic carbon compound)	2×10^{-12} g/sec	N/A	$>10^7$	420	1
Thermionic Emission (TID)	Selective (organic nitrogen and phosphorus)	1×10^{-13} g/sec N 5×10^{-14} g/sec P	N/P 1:5 N/C 5×10^4:1 P/C 10^5:1	10^5	420	2
Flame Photometric (FPD)	Selective (sulfur and phosphorus)	$<1 \times 10^{-11}$ g/sec S $<1 \times 10^{-12}$ g/sec P	S/C 10^3-10^6:1 P/C $>10^5$:1	$\geq 10^3$ (S) (square law) $\geq 10^4$ (P)	420	2
^{63}Ni Electron Capture (^{63}Ni ECD)	Selective (halogens and other electron capturing groups)	highly variable, as low as 5×10^{-15} g	N/A	10^4	420	2
Photoionization (PID)	Universal	2×10^{-13} g/sec	Based upon ionization energy	$>10^7$	350	2
Thermal Conductivity (TCD)	Universal	4×10^{-10} g/mL (propane)	N/A	$>10^5$	400	1
Hall Electrolytic Conductivity (HECD)	Selective (halogen, sulfur, nitrogen, and ester-containing compounds)	5×10^{-13} g/sec Cl $2\text{-}4 \times 10^{-12}$ g/sec N $2\text{-}4 \times 10^{-12}$ g/sec S	Cl/C $>10^6$:1 N/C $>10^6$:1 S/C $>5 \times 10^4$:1 NO/N $>10^2$:1	10^6 (Cl) 10^4 (N) 10^4 (S)	400	2
Thermal Energy Analyzer (TEA)	Selective (nitrosamines)	100 pg (dimethyl nitrosamine)	N-NO/C ∞ N-NO/NO 1-4:1	10^6	Above GC column limit	3
Fourier Transform Infrared (FTIR)	Universal or Selective	200 pg-40 ng	Variable	10^4	280-375	4
Mass Spectrometer (MS)	Universal or Selective	EI: 10-100 pg NICI: Variable; as low as 25 fg	Variable	10^5	350	Low Resolution 4 High Resolution 5

[a]The detectors are rated in terms of complexity of operation and maintenance, ranging from simple (1) to complex (5).

The PID response can be as much as 10-50 times higher for organics than an FID. Detection limits in the low picogram range are possible for organic and inorganic species. The stated detection limit of the PID is 2×10^{-13} g/sec and the linear dynamic range is 1×10^{7}.

The electron capture detector (ECD)

The ECD, introduced by Lovelock and Lipsky (ref. 12), has extremely high selectivity and low detection limits for compounds which capture thermal electrons efficiently. Due to these features, the ECD has been widely used in trace organic analysis, especially in environmental and biochemical applications (ref. 13).

The ECD consists of a chamber containing two electrodes and a radioactive source which emits electrons (or beta rays) as it decays. The emission produces a significant amount of low energy thermal electrons in the GC carrier gas effluent. The application of a suitable potential provides for the collection of the available electrons in the cell which gives rise to a standing baseline current. Elution of a component capable of capturing electrons results in reactions which decrease the observed standing current, thus providing a measurable signal. Due to improvements in design and operating characteristics, current detectors use a coaxial cylinder or pincup design rather than plane parallel geometry. The direct current mode of operation, which exhibited nonlinear and anomalous behavior due to space charge effects and contact potentials, has been replaced by pulse sampling modes of operation in which pulses of appropriate amplitude and duration are applied to sample the instantaneous cell current. Most commercial detectors currently available utilize the variable frequency constant-current principle. In this mode of operation, the cell current is held at a constant reference value by electrical feedback circuitry which adjusts the frequency of the applied voltage pulse. When a compound capable of capturing electrons enters the detector cell, the applied frequency increases to maintain a constant cell current. The frequency of the applied pulse is converted to an output voltage which is directly proportional to the concentration of the eluting substance. Due to the elimination of space charge and contact potentials and the achievement of thermal equilibrium, the variable frequency constant-current ECD has a linear dynamic range of 1×10^{4}. The detection limit of the ECD can be as low as 5×10^{-15} g/sec. In addition, current commercial versions of the detector are well adapted for routine use with capillary GC columns. ^{63}Ni and ^{3}H are typically used as the ionizing radioactive source; ^{63}Ni has the advantage of operation at a higher temperature and is less subject to variation from contamination problems. The cell gas used is either nitrogen or an argon/methane gas mixture.

The ECD response depends critically on temperature and this parameter must be carefully controlled. Additionally, response factors for different compounds may vary widely, which complicates the use of the detector for quantitative mixture analysis. The detector is susceptible to general background contamination; the chromatographic system should be leak tight, and the carrier and cell gas should be highly pure (oxygen free). Contamination of the detector by column bleed and compounds eluting from the column at high temperature should be minimized. The pneumatic system should be free of background contamination, such as compounds desorbed from elastomeric parts of pressure and flow controllers. The sensitivity of the ECD to these physical operating conditions make it more complicated to operate routinely.

The ECD has been widely used in the detection of polyhalogenated compounds such as pesticides and polychlorinated biphenyls, polyaromatic hydrocarbons, nitriles, nitro compounds, organometallic compounds, and sulfur containing compounds. The detector has also been widely used for trace analysis in biochemistry, in many cases with suitably derivatized compounds. Interestingly, research using selected dopants in the cell gas, such as oxygen or nitrous oxide, has demonstrated sensitization of the ECD to increase the ability to detect compounds that normally have a minimal response (ref. 14,15).

The thermionic detector (TID)

The TID can detect nitrogen and phosphorus containing compounds with high selectivity and low detection limits. The TID was reported first by Karmen and Guiffrida for phosphorus detection (ref. 16), and by Wells for selective nitrogen detection (ref. 17). Design improvements have reduced early detector difficulties of variable response and poor reliability. Current versions of this detector use an electrically heated alkali (rubidium) coated ceramic cylinder or alkali doped glass bead suspended in the center of a collection electrode. The gas stream of hydrogen, air, and carrier gas

from the detector jet forms a low temperature plasma inside the hot cylinder (ref. 18). Although the detailed mechanism of operation is still under investigation, it is believed that ion current is generated by thermionic emission of negatively-charged particles from the surface of the hot bead (ref. 19). Highly electronegative CN radical and PO radical, found in the plasma, are the probable species forming negative ions for nitrogen and phosphorus containing compounds, respectively. Ion current is collected and measured with a standard differential electrometer.

The TID has detection limits close to those of the ECD. The limit of detection for phosphorus and nitrogen is 5×10^{-14} and 1×10^{-13} g/sec, respectively. The TID has a response to nitrogen approximately 50 times greater than that for the FID while phosphorus response is about 500 times higher. The linear dynamic range of the detector is 1×10^5. The selectivity of the TID for nitrogen and phosphorus over carbon is approximately 10^4-10^5:1.

Experimentally, several operational parameters must be carefully controlled including the temperature of the alkali source and the flow rate of hydrogen gas. Adjustments for source aging and contamination may be necessary.

Consideration must also be given to the possibility of interferences and poor quantitation in the determination of low concentrations of nitrogen containing molecules due to quenching from coeluting solvent or high levels of hydrocarbons in the mixture. The use of capillary GC columns minimizes potential interferences and quenching effects. The TID has been applied to problems in environmental, pesticide, biochemical, and drug analyses.

The flame photometric detector (FPD)

The FPD, originally described by Brody and Chaney (ref. 20), is a highly selective detector with low detection limits for the determination of analytes containing sulfur and phosphorus, with almost no response to those which do not. The FPD is basically a flame emission photometer; the compounds to be determined are burned in a hydrogen rich flame which, acting as a low temperature plasma, provides sufficient energy to produce atoms and simple molecular species and excite them to higher electronic states. Excited species return to the ground state with the characteristic emission of light. Bandpass filters isolate the appropriate analytical wavelengths which are detected and amplified by a photomultiplier tube. The selective sulfur emission at 394 nm is due to S_2^*. Emission from phosphorus is detected at 526 nm. Detector response is linear with phosphorus concentration while sulfur concentration is proportional to the square root of detector response. The linear dynamic range in the phosphorus mode is 1×10^4. In the sulfur mode, the linear dynamic range is 1×10^3 on a log-log scale.

The selectivity of response for phosphorus to hydrocarbons is 10^5:1, while that for sulfur to hydrocarbons can range from 10^3-10^6:1. The detection limit of the FPD is 1×10^{-11} g/sec for sulfur and 1×10^{-12} g/sec for phosphorus, which provides subnanogram detection capabilities. Recent work has indicated that detector response to sulfur and phosphorus is strongly dependent on operating conditions, requiring the gas flow rates and temperature to be precisely controlled.

Several characteristics of the FPD are potentially troublesome. Due to overlap of band spectra, the detector selectivity of phosphorus to sulfur can be as low as 5:1, making sulfur interference possible in the phosphorus mode. However, sulfur to phosphorus selectivity is 10^4:1, allowing potential interferences in the phosphorus mode to be cross checked against response for sulfur. The potential for quenching of sulfur emission by coeluting organic impurities must be considered, although the recently introduced dual flame detectors overcome quenching problems to some extent (ref. 21).

The FPD has been applied in the detection of pesticides and pesticide residues, mercaptans, thiophenes, and chemical warfare agents. The detector has also been widely used in petrochemical analysis and in the analysis of flavors and foods.

The Hall electrolytic conductivity detector (HECD)

The HECD (ref. 22) is an improved version of the conductivity detector described initially by Coulson (ref. 23). It is a selective detector for the analysis of compounds containing nitrogen, halogen, or sulfur, and may also be used for nitrosamine analysis.

The HECD is based upon the catalytic oxidation or reduction of sulfur, nitrogen, and chlorine to stable inorganic species which can be measured by electrical conductivity following dissolution in a stream of water. The selectivity of the HECD depends upon the specificity of the reactions producing the conducting species of interest.

Nitrogen and chlorine containing compounds are measured by their conversion to ammonia and hydrogen chloride, respectively. Hydrogen gas is added to the gas chromatographic effluent which is then hydrogenated over a nickel catalyst in a reaction furnace. After passage through a scrubber to remove other combustion products, ammonia or hydrogen chloride pass into the detector cell in which they are readily ionized in a flowing water stream and detected with low detection limits by electrical conductivity. The circulating closed water system in the cell allows for the removal of generated ions by an ion exchange resin, which provides a differential output signal.

Sulfur containing compounds are detected by combustion in an oxygen atmosphere to form sulfur dioxide and sulfur trioxide. Dissolution of these inorganic species in water results in a high degree of ionization from sulfurous or sulfuric acid. Interferences from organic compounds, which form carbon dioxide on combustion producing carbonic acid in the detector cell, can be troublesome in the sulfur mode. Despite the low degree of ionization of carbonic acid, a substantial amount of background signal can be observed which decreases the selectivity of the detector in the sulfur mode.

In addition to the selectivity difficulties in the sulfur mode, the detector is more difficult to operate and maintain than other GC detectors. Although the HECD can be used with capillary GC columns, the internal volume of the detector results in a loss of chromatographic resolution.

The selectivity of the HECD for nitrogen and chlorine with respect to carbon is greater than 10^6:1. The selectivity for sulfur to carbon is 5×10^4:1. The detection limit of the HECD for nitrogen and chlorine can be as low as 2×10^{-12} and 5×10^{-13} g/sec, respectively. The detection limit for sulfur is 2×10^{-12} g/sec.

The HECD can provide very selective detection with low detection limits for nitrogen and chlorine containing compounds in trace organic analysis. For instance, the HECD is recommended by the U.S. Environmental Protection Agency for the analysis of trihalomethanes in water. The detector has also been utilized in the analysis of pesticides, polychlorinated biphenyls, and herbicides.

The thermal energy analyser (TEA) detector

The TEA is an extremely selective GC detector with low detection limits for N-nitroso compounds (ref. 24), many of which are very toxic or carcinogenic. Nitrosamines can be formed from reaction of amines with nitrite which is present directly or as an impurity, and the TEA detector is very useful for survey analyses of samples for the possible presence of any nitrosamines.

The TEA detector depends on the relative instability of the N-nitroso chemical bond. The GC effluent is fed into a catalytic pyrolyzer where N-nitroso compounds are converted into a nitrosyl radical and an organic radical. The stream next enters a reaction chamber containing ozone, which reacts with the nitrosyl radical to yield electronically excited nitric oxide. The excited nitric oxide decays by emission of a photon in the near IR region which is detected by a photomultiplier tube.

With the TEA detector nitrosamines can usually be detected in the subnanogram range. The detection limit for N,N-dimethylnitrosamine is about 100 pg, and other nitrosamines should respond similarly on a molar basis. In addition, selectivity is very high against compounds not containing the N-nitroso functionality. The detector is not totally free of interferences, which can occur from some C-nitroso compounds, some dinitro compounds, organic nitrites and nitrates, and N-dimethylbenzylamine (ref. 25). Another problem which can occur is a high baseline if a sample containing a large amount of nitrate is injected into the GC. Generally speaking, some degree of sample cleanup will produce much better results for trace analysis of samples which contain high levels of potentially interfering components. One useful technique which can be employed to test for an interference is to irradiate the sample with 390 nm radiation and then reanalyze it; a true N-nitroso compound is decomposed by the irradiation and its peak will disappear from the chromatogram. However, if the sample contains strongly

ultraviolet absorbing compounds at a high level, then the N-nitrosamine may not be decomposed as it should be. In cases where confirmation of the presence of an N-nitrosamine is desired, analysis by GC/MS is probably the best confirmation technique.

The Fourier transform infrared spectrometer (FTIR) detector

Infrared spectroscopy has long been a valuable technique for organic analysis, but until recently it did not have low enough detection limits to be considered a trace analytical technique. With the advent of Fourier transform technology this limitation has been substantially removed, and now FTIR can be effectively interfaced to a gas chromatograph. GC/FTIR is especially useful since it is often complementary to GC/MS analysis.

There are currently two quite different major interfacing methods for GC/FTIR; each has advantages and disadvantages. In one type of instrument the effluent from the GC flows through a light pipe which is coated on the side walls (usually with gold) and has mirrors at both ends. The infrared beam passes through the pipe, and spectra of the GC peaks present in the pipe are collected as the peaks elute. With proper design of the dimensions of the light pipe and the addition of makeup gas, chromatographic fidelity can be maintained while still achieving low detection limits. The light pipe configuration works well for compounds of reasonable volatility, but is limited by the upper temperature limit for the interface, typically about 280°C. This temperature limit means that higher boiling compounds which can easily be handled by modern capillary GC technology cannot be analyzed by GC/FTIR using the light pipe interface. Recently Hewlett-Packard has introduced a light-pipe based FTIR instrument which has been especially designed as a GC detector. The detector is very compact and due to optimization for capillary GC has good detection limits, showing 20:1 signal-to-noise for 5 ng of a strong absorber.

A second type of configuration used for GC/FTIR analysis, available from Mattson Instruments, is a matrix isolation technique. Helium spiked with about 1.5% argon is used as the carrier gas, and the GC effluent exits just above the surface of a drum held at 12 K under vacuum. Under these conditions the sample components are condensed on the drum in a matrix of frozen argon, while the helium is pumped away. The drum slowly rotates in a spiral fashion and collects the entire chromatographic run as a continuous band. After the run is completed, the drum is positioned so that the FTIR beam hits the drum at a spot where a peak of interest is located. The drum is gold coated to reflect the beam back toward the detector. This instrument configuration has three major advantages. First, the matrix isolation spectra are high quality and give very sharp lines compared to gas phase spectra. Second, signal averaging techniques can be used to significantly improve detection limits since the component may be sampled as long as desired. Third, it is possible to obtain GC/FTIR data for less volatile compounds with the matrix isolation interface. Normally at the end of data collection the drum is allowed to warm to room temperature, and the sample and argon matrix sublime from the drum and are pumped away. However, if very high boiling compounds have been analyzed, it may be necessary to open the system and clean the drum.

FTIR is useful in the detection and identification of most organic compounds. However, the response of the detector is significantly compound dependent. This factor complicates quantitative analysis of components in complex mixtures. Generally speaking, very useful IR data are obtained from compounds containing functional groups such as alcohols, ketones, nitriles, acids, esters, and amines. GC/FTIR is very useful as a survey technique to see what classes of compounds are present in a complex mixture; indeed, there is no other technique which can so rapidly provide this kind of general class information.

Detection limits for GC/FTIR vary with the compound being analyzed and the instrument configuration. With the light pipe design usually a detection limit in the range of about 10-40 ng is possible. The matrix isolation instrument has lower detection limits and can identify GC peaks containing about 200-400 pg of a compound with an average absorptivity; a high quality IR spectrum can normally be produced from 1-10 ng (ref. 26).

The mass spectrometer (MS) detector

The MS is one of the most complex and expensive detectors used for GC. However, due to major advantages in selectivity and detection limits, it is widely used despite the expense and expertise required. There are a number

of modes of operation possible for GC/MS, each of which has its advantages depending on the analysis. MS data are usually collected by scanning the MS over a range of masses to collect an entire mass spectrum. However, when analyzing a sample for a particular component of interest, the MS can be set to collect data for a small number of masses in a procedure called selected ion monitoring (SIM). SIM provides the best possible detection limits.

The most important types of instruments for GC/MS analysis are the quadrupole MS, the ion trap detector (ITD), the magnetic sector MS, and the relatively new Fourier transform MS (FTMS). The most common GC/MS systems presently use the quadrupole and sector instruments, but the ITD and FTMS instruments appear to have a bright future in GC/MS. The principles of operation of these mass spectrometers have been discussed by Biemann in another IUPAC paper of this series (ref. 27) and will not be repeated here.

An MS can be interfaced to a GC which uses either capillary or packed columns. The capillary column GC/MS is usually the optimum configuration for trace analysis because of higher selectivity and lower detection limits produced by greater resolving power and better sample transfer. There are several interfaces available for capillary GC/MS. In our opinion the best interface for handling a wide variety of analyses is a direct coupling, although other types of interfaces have advantages for ease of operation or other factors. The most suitable column diameter for capillary GC/MS analyses is usually the 0.32 mm internal diameter column, which combines reasonable sample capacity (about 500 ng per component) with good resolution and detection limits.

The ionization techniques most commonly used for organic trace analysis are electron ionization (EI), positive ion chemical ionization (CI), negative ion chemical ionization (NICI), and atmospheric pressure ionization (API). EI, bombardment of the sample with a beam of electrons (usually at 70 eV), is the most common ionization method. EI gives spectra which are very structurally informative, often containing both a molecular ion and fragment ions which are analytically useful. Essentially all organic compounds yield EI mass spectra with good response. However, for highly functionalized or labile compounds, EI often yields no molecular ion or a very weak one which is not analytically useful. In these cases CI can often provide the molecular weight of unknown compounds since, if the reagent gas is properly chosen, the ionization process is gentle and little or no fragmentation of molecular ions occurs. In CI the electron beam ionizes a reagent gas present in great excess relative to the sample; the reagent gas ions then transfer a proton to the sample, provided the proton affinities of the sample molecules are greater than that of the reagent gas ions. Since CI is based on ion-molecule reactions, the technique offers a great deal of flexibility and selectivity. Many compounds have been used as CI reagent gases; methane, isobutane, and ammonia are most common. In the analysis of known compounds, it is often possible to achieve a more selective analysis with lower detection limit by concentrating most or all of the MS signal into a protonated molecular ion. CI may also improve the detection limit by decreasing the background level from fragment ions of other compounds.

NICI is one of the most responsive and selective methods available for GC/MS analysis. Negative ions are formed by capture of near-thermal energy electrons present in the CI reagent gas plasma. Only compounds with a high cross section for electron capture will form negative ions efficiently; for such compounds NICI yields the lowest possible GC/MS detection limits. Compounds not suitable for NICI analysis can often be converted to highly responsive derivatives, such as trifluoroacetates and pentafluorobenzoates. The NICI response is highly variable, but in the best cases detection limits in the low picogram and femtogram range have been obtained. The combination of GC with NICI-MS is often valuable for separating the analyte from large interferences which could saturate the ion source; saturation may occur due to the relatively limited population of near-thermal energy electrons available.

API is another powerful technique for organic trace analysis. In the API source the sample enters at atmospheric pressure and is ionized by a corona discharge. The ions exit the source through a small hole and are focussed into the mass analyzer. Operation at atmospheric pressure makes API well suited for gas or air analysis. API is a soft ionization technique which primarily produces ions characteristic of molecular weight. Similarly to other types of CI, the response of API is variable, but generally it is possible to detect on the order of 1-10 ng in full scan mode and 10-20 pg in SIM mode.

The quadrupole MS is currently the instrument most widely used for GC/MS. It is easy to operate and maintain and is less susceptible to contamination than, e.g., magnetic sector instruments. The quadrupole MS can operate with unit mass resolution up to about 2000 atomic mass units. The detection limits which can be obtained with a quadrupole MS are generally in the low nanogram range for full mass scans and in the picogram range for SIM. Factors such as ionization mode will influence the detection limit for a particular analysis. The quadrupole MS is relatively inexpensive for an MS. At the low end of the price range are instruments which are especially designed to interface to capillary GC and to be relatively easy to operate and maintain.

The magnetic sector MS is often used for GC/MS; this combination has the advantages of low detection limits and high mass resolution. Its disadvantages are instrument complexity and increased susceptibility to contamination. The double focussing instrument can achieve very high resolution and thus separate ions which differ in mass by only a small fraction of an atomic mass unit. This feature can be very valuable in organic trace analysis, since it separates a number of interferences which are close but not identical in mass to the analyte. However, detection limits decrease as resolution increases, since narrow slits must be used to achieve high resolution. The detection limit of magnetic sector instruments is thus variable depending on the resolution required. For example, detection limits at unit resolution are normally in the range of 1 ng for full scans and 10 pg for SIM. At a resolution of 10 000 the corresponding detection limits would be about 10 ng and 100 pg, respectively.

The ITD is an interesting mass spectrometer for use as a GC detector. While the concept of this type of MS dates back to the introduction of the quadrupole MS, for various reasons the design was never commercially developed for the analytical market. However, recent improvements in technology have made this instrument potentially a very attractive option for GC/MS. The Finnigan MAT Corporation has introduced the ITD as a low-cost, easy-to-maintain detector for capillary GC. Similarly to the GC-detector type quadrupole MS, the ITD is designed to interface only to capillary GC. The current commercial instrument is a three-electrode ion trap (ref. 28). The advantages of the ITD are its relatively low cost, ease of operation, and ease of maintenance due to fewer parts to be cleaned and aligned. A disadvantage was that ITD mass spectra were not always identical to those produced by quadrupole and magnetic sector MS, due in some cases to ion-molecule reactions occurring in the instrument. Very recently changes have been made in the ITD which may essentially remove this problem.

The ITD, like the quadrupole and magnetic sector instruments, is essentially a universal detector for organic trace analysis using capillary GC. The mass range of the ITD is currently restricted to 20-650 atomic mass units. Although this instrument has been introduced relatively recently, a number of useful applications have already been demonstrated, particularly in the field of environmental analysis. Detection limits for the ITD are comparable to the quadrupole MS. Full-scan EI mass spectra can be obtained from samples of about 1 ng, while in the SIM mode detection limits of less than 100 pg have been reported.

The FTMS is a unique and powerful MS with several advantages. Use of the FTMS as a detector for GC is still in the developmental stage, but GC/FTMS seems to have great potential, especially for trace organic analysis, due to its high resolution and potentially low detection limits. The FTMS was developed from the ion cyclotron resonance (ICR) instrument, which has been in use for many years and found its primary application in the study of ion-molecule reactions. Comisarow and Marshall (ref. 29) introduced the application of Fourier transform techniques to ICR. An FTMS instrument is available from Nicolet Analytical Instruments.

FTMS resolution is directly proportional to magnetic field strength and inversely proportional to mass at constant pressure. FTMS can achieve very high resolution; for example, at a pressure of about 10 Pa, a resolution of 1 500 000 has been reported for mass 166 at a magnetic field of 4.7 T (ref. 30). An important limitation of FTMS is the requirement for very low pressure in the cell to avoid scattering of the ions by collisions. The resolution which can be achieved decreases as the pressure in the cell increases; the operating pressure produced by the carrier gas is a major problem for GC/FTMS. Nicolet has recently introduced a divided cell with differential pumping between the two parts of the cell (ref. 31), which

allows introduction of the entire effluent from a capillary GC into one half of the cell while maintaining low enough pressure in the other half of the cell to achieve good mass resolution. Recent data have demonstrated a resolution of 7000 at mass 150 while scanning a broad mass range during a GC run (ref. 32). The highest resolution reported as of this writing for GC/FTMS over a narrow mass range is about 150 000 at mass 120 (ref. 33). Detection limits for GC/FTMS analysis are currently on the order of a few nanograms of material (ref. 33). A disadvantage of GC/FTMS for trace analysis is the limited dynamic range currently available, which is due to space charge effects occurring if too many ions are present in the cell. As of this writing Nicolet has not reported the dynamic range of their GC/FTMS system, but it seems to be lower than that of other GC/MS instruments.

The FTMS is a relatively expensive instrument but combines a number of features which normally are not present all in one instrument configuration, such as high resolution, low detection limits, and MS/MS capability. However, with current FTMS systems only one of these capabilities can be achieved at a time.

Perhaps the ultimate detector for organic trace analysis is the tandem mass spectrometer. The MS/MS instrument basically combines two or more mass analyzing elements in series; a large number of instrument configurations are available based on combinations of quadrupoles, electrostatic analyzers, and magnetic analyzers. Currently the most popular MS/MS instrument for organic trace analysis is the triple quadrupole (QQQ) configuration. The QQQ instrument has the advantages of the speed and simplicity of quadrupole operation, relative lack of susceptibility to contamination from "dirty" samples, and highly advanced computer control for ease of operation. The MS/MS instrument can be thought of as analogous to GC/MS except that it uses a mass analyzer rather than a GC to perform the initial separation. However, the combination GC/MS/MS represents an even more selective analyzer since it combines two different stages of separation with the low detection limit and selectivity of the final mass spectrometer.

The QQQ instrument consists of a linear arrangement of three quadrupole mass filters. The first quadrupole selects the precursor ion (the component of the mixture to be analyzed). The second quadrupole is pressurized with a collision gas, normally an inert gas such as argon. The ions selected by the first quadrupole collide with the gas molecules and fragment to form daughter ions, which are then analyzed by the third quadrupole. A number of different types of scans are possible in MS/MS analysis, but we shall consider here the daughter ion scan, which is generally the most useful for organic trace analysis. The molecular ion or fragment ion of the compound to be analyzed is separated from all other ions by the first quadrupole. This ion M is then broken down in the collision cell to yield characteristic fragments F_i which are analyzed in the third quadrupole. Other ions which have the same mass as M should not generally fragment to yield the same ions; thus interferences are mostly or completely removed by looking at the sequence $M \rightarrow F_i$. This analysis is sometimes referred to as "selected reaction monitoring."

The improved detection limits often obtained using GC/MS/MS as opposed to GC/MS result from the elimination of "chemical noise." Indeed, the MS/MS generally has a lower response than MS on an absolute scale because of higher transmission losses. However, often in organic trace analysis the detection limit of the analysis is not determined by the absolute limit of the detector but rather by a significant background level which obscures small signals. Thus the extra degree of selectivity of MS/MS often provides a lower detection limit by minimizing or eliminating the background or "chemical noise."

The MS/MS instrument is the most complex GC detector, yet its tremendous analytical power can make it the detector of choice for difficult GC/MS analyses. A very interesting development announced recently (ref. 34) is the modification of an ITD for MS/MS analysis. Depending on how developments proceed, a relatively low-cost MS/MS instrument could result from this technology.

Instruments designed to operate as "routine" GC detectors are generally intended to operate with a high degree of reliability and to be relatively easy to maintain. On the other hand, the very sophisticated GC/MS systems, such as those using high resolution and MS/MS instruments, are so complex that periodic breakdowns must be expected.

Miscellaneous detectors

The atmospheric microwave-induced plasma provides selective and highly responsive detection for GC. The detector measures the optical emission from elements which are excited in a microwave plasma. The use of the microwave plasma as a GC detector was first described by McCormack (ref. 35). A commercial apparatus has recently become available (ref. 36). Elements which can be detected selectively are carbon, nitrogen, hydrogen, oxygen, phosphorus, sulfur, chlorine, bromine, and fluorine. Determination of empirical formulas for eluting components from relative emission intensities via simultaneous element detection is possible. Detection limits are in the picogram range for some elements, and the linear dynamic range is 1×10^4.

A far-ultraviolet absorbance detector with three line sources at 120, 129, and 147 nm has recently been described (ref. 37). Strong absorption in this region of the spectrum occurs with virtually all compounds. Since the ultraviolet lamps used are very stable, this detector should prove useful for certain GC applications.

Ion mobility spectrometers are also used as detectors for GC (ref. 38). In ion mobility spectrometry, ions generated from GC peaks migrate in a gas at atmospheric pressure in an applied electric field. Detection of ion current and ion mobility provides information on the amount of compound present and on ion size and charge. By monitoring ions of a particular mobility, selective detection of mixture components can be accomplished, although mass spectrometry provides considerably higher resolution.

Laser multiphoton ionization has been applied to the detection of capillary GC effluent both as a stand alone detector (ref. 39) and as the ionization source for a time-of-flight GC/MS (ref. 40). In this methodology, ionization of a molecule is typically accomplished via the absorption of two photons of appropriate energy. Laser multiphoton ionization can be accomplished in the resonant or nonresonant mode. The high intensity of the laser light provides high ionization efficiency, resulting in low limits of detection. Polyaromatic hydrocarbons have been detected in the low femtogram range.

A recent development in GC detectors (ref. 41) is the redox chemiluminescence detector (RCD). In the RCD the GC effluent is mixed with nitrogen dioxide in helium and reacted over a gold catalyst to produce nitric oxide. The nitric oxide is then further reacted with ozone in a second cell, and the chemiluminescence generated is measured by a photomultiplier tube and associated electronics. By adjusting operating conditions the selectivity of response can be varied. The RCD has low detection limits, is selective, is complementary to the FID, and can be used with capillary GC columns.

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