condensed hydrocarbons that yield many aromatic products. Sequential pyrolysis also provides information on distribution and maturation. Almost 150 compounds have been identified from kerogen samples, including those from lignin, lipid, and condensed origin. Principal components analysis on 37 of these components allows prediction of the source rock hydrogen index (HI_0) from a single Py-GC analysis. The rank of coals may also be assessed by Py-GC, for example, by studying the oxygen functionalization of monocyclic derivatives, while the formation of a series of long-chain *n*-alkanes is indicative of a thermoplastic coal. Pyrograms from coal macerals (which are petrological unit of a geological sample) consist mainly of alkylbenzenes, alkylnaphthalenes, alkylphenols, alk-1-enes, and alkanes with quantitative differences depending upon precursor material and maturation. The development of life-detection systems for extraterrestrial exploration has also depended upon organic geochemical analysis. Even desert sands show abundant evidence of biomacromolecules and pyrograms are characterized by olefins, nitriles, benzenes, phenols, indoles, and furans. The lack of any such compounds from Lunar and Martian samples indicates their lifelessness.

Limitations

Although the applications described here have concerned diverse macromolecular samples, pyrolysis is also of utility in the analysis of smaller molecules, particularly quaternary ammonium compounds, which undergo quantitative thermal fragmentation to volatile products. For example, the specificity and sensitivity afforded by Py-GC/MS with mass fragmentography renders the technique suitable for the analysis of endogenous neurotransmitters such as acetylcholine at the 1–2 pmol level. However, in all cases, analytical throughput is limited by the retention times of the pyrolysis products, a condition that is particularly severe in taxonomic applications. Automation allows extended use, but direct Py-MS offers substantial reductions in analytical time, although a single pyrolysis product may give rise to several ions, a single ion may be derived from several pyrolysis products, and identical $M^{+\bullet}$ values result from isomers that may be resolved by Py-GC. Direct Py-MS also allows detection of larger or more polar pyrolysis products that are unlikely to be efficiently chromatographed. This may provide a substantial increase in structural information for complex samples of biological origin.

See also: **Coal and Coke**. **Forensic Sciences**: Paints, Varnishes, and Lacquers. **Gas Chromatography**: Multidimensional Techniques; Instrumentation; Detectors; Mass Spectrometry. **Geochemistry**: Inorganic; Soil, Major Inorganic Components; Soil, Minor Inorganic Components; Soil, Organic Components. **Laser-Based Techniques**. **Polymers**: Synthetic. **Quality Assurance**: Internal Standards.

Further Reading

The *Journal of Analytical and Applied Pyrolysis* (Elsevier) is dedicated to this field and, additionally, it publishes the proceedings of the biennial International Conference on Pyrolysis (from 1984). Formerly, proceedings were published as separate volumes as included below.

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Detectors

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Introduction

Many techniques have been described for the detection of compounds separated by gas chromatography. Space limitations, however, allow only those detectors that are widely used and have reached commercial maturity to be discussed in this article. The important spectroscopic detectors (e.g., mass and infrared spectrometry) used for structure elucidation as well as detection are discussed in separate articles.

The principal methods of detection can be categorized as ionization, bulk physical property, optical, and

electrochemical based on the principle of the detection mechanism. Further division into universal, element-selective, and structure-selective detectors is possible based on the characteristics of the detector response. The flame ionization and thermal conductivity detectors (TCDs) respond to nearly all organic compounds and are examples of general or (near) universal detectors. Other detectors respond only to a particular heteroatom (e.g., flame photometric, thermionic ionization, or atomic emission detectors) and are element-selective. Or they respond only to a structural feature related to the bond energy of two or several atoms in a compound (e.g., electron capture and photoionization detectors) and are structure-selective. Element-selective and structure-selective detectors are used for target compound analysis, for example, the analysis of a specific drug in biological fluids or pesticides in an environmental extract, where the matrix is often complex and masks the presence of the target compounds when a universal detector is used.

Detectors can also be compared by figures of merit that define their signal characteristics in quantitative terms. The fundamental properties of general interest are sensitivity, limit of detection, operational response range, response time, and noise characteristics. Sensitivity is defined as the detector response per unit mass or concentration of a substance and is determined as the slope of the calibration curve for detectors with a linear response. A detector with a high sensitivity, corresponding to a larger slope, is better able to discriminate between small differences in sample amounts. Sensitivity is often confused with the limit of detection, the latter defined as the concentration or mass flow of a substance that produces a detector response equal to some multiple (typically three times) of the average detector noise. The dynamic range is defined as the range of sample amount for which a change in sample size induces a discernible change in the detector signal. For many, although not all detectors, the relationship between response and sample amount is linear over a wide range. It is the extent of this range that is generally of most interest for comparing detector performance.

Ionization Detectors

Common carrier gases behave as near perfect insulators. In the absence of conduction by the gas molecules themselves, the increased conductivity due to the presence of very few charged species is easily measured, providing the low sample detection limits characteristic of ionization-based detectors. Common ionization detectors include the flame ionization detector (FID), thermionic ionization detector (TID), photoionization detector (PID), the electron-capture detector (ECD), and the helium ionization detector (HID). A different method of ion production is employed by each detector, but in all cases, the quantitative basis of the detector response is due to the change in ion current in the presence of sample vapors.

Flame Ionization Detector

The popularity of the FID is explained by its near universal response to organic compounds, low detection limits, simple construction, fast response, and exceptional linear range. Only the fixed gases (e.g., He, Xe, H_2, N_2), certain nitrogen oxides (e.g., N_2O, NO, etc.), compounds containing a single carbon atom bonded to oxygen or sulfur (e.g., CO_2, CS_2, etc.), inorganic gases (e.g., NH_3, SO_2, etc.), water, and formic acid fail to provide a significant response. Typical detection limits correspond to about $10^{-12}\,g\,s^{-1}$ with a linear response range of 10^6.

The FID signal results from the combustion of organic compounds in a small hydrogen–air diffusion flame (**Figure 1**). The column carrier gas is mixed with hydrogen and burned at a narrow orifice in a chamber through which excess air is flowing. The ions produced in the flame are collected by application of a small voltage between the jet tip and a cylindrical electrode located a few millimeters above the flame. The small ion currents (10^{-14}–10^{-5} A) are amplified by a precision electrometer. Detector performance is influenced primarily by the ratio of air-to-hydrogen-to-carrier (and make-up) gas flow rates, the choice of carrier gas, and detector geometry. The optimum response plateau for detector gas ratios is fairly broad, however, permitting operation over a rather wide range of gas flow rates without incurring a large penalty in diminished response.

On account of the low thermal energy of flames it is believed that ionization results from chemical

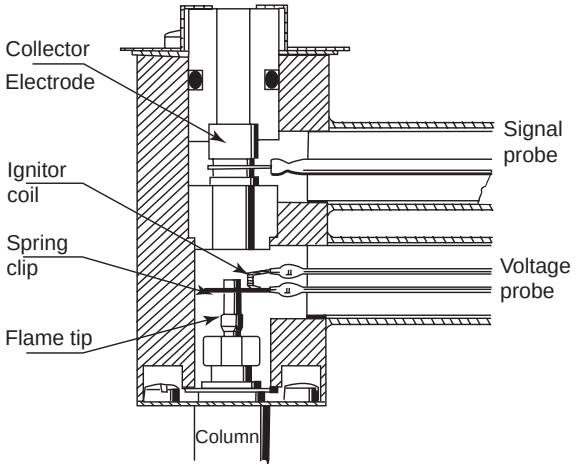

Figure 1 Cross-sectional view of a flame ionization detector.

Table 1 Contributions of structure to the response of the flame ionization detector

Atom	*Type*	*Effective carbon number*
C	Aliphatic	1.0
C	Aromatic	1.0
C	Olefinic	0.95
C	Acetylenic	1.30
C	Carbonyl	0
C	Carboxyl	0
C	Nitrile	0.3
O	Ether	−1.0
O	Primary alcohol	−0.5
O	Secondary alcohol	−0.75
O	Tertiary alcohol	−0.25
N	In amines	Similar to O in alcohols
Cl	On olefinic C	0.05
Cl	Two or more on aliphatic C	−0.12 per Cl

ionization process, such as the one shown below:

$$CH^{\bullet} + O^{\bullet} \rightarrow CHO^{*} \rightarrow CHO^{+} + e^{-}$$

Degradation of organic compounds in the flame likely results from attack by hydrogen atoms causing fission of carbon–carbon bonds. Fission of unsaturated bonds proceeds after hydrogenation. The hydrocarbon radicals produced by fission are unstable and undergo a cascade of fast fractionation and hydrogenation reactions such that all carbon atoms are eventually converted to methane. Consequently, each carbon atom capable of hydrogenation yields the same signal, and the overall FID response to each substance is proportional to the sum of these 'effective' carbon atoms. The FID response is highest for hydrocarbons, being proportional to the number of carbon atoms, while substances containing oxygen, nitrogen, sulfur, or halogens yield lower responses, depending on the characteristics of the carbon–heteroatom bond and the electron affinity of the combustion products. The lower response is due to competition between hydrogenation of the carbon–heteroatom bond and hydrogen abstraction with formation of neutral species (e.g., CO, HCN), which are poorly ionized in the flame. The effective carbon number for a particular compound can be estimated by summation of the various carbon and heteroatom contributions (**Table 1**), which in turn can be used to predict relative response factors with reasonable accuracy.

Thermionic Ionization Detector

All modern versions of the TID, also known as the nitrogen–phosphorus or NPD detector, employ a ceramic or glass bead or cylinder doped with an alkali metal salt, molded onto an electrical heater wire, heated to 400–800°C, as the thermionic source. Carrier gas is combined with hydrogen at the detector base and flows through a jet where it is mixed with air. The flow of detector gases is insufficient to establish a flame, but sufficient to maintain a plasma localized around the thermionic source. The thermionic source is located immediately above the jet tip and the cylindrical collector electrode either surrounds the source or is located immediately above it, depending on the detector design. A voltage set between the collector electrode and jet tip allows collection of (usually) negative ions and the ion current is measured by an electrometer.

Two different mechanisms have been proposed to explain the element-selective response of the TID to nitrogen- and phosphorus-containing compounds. These mechanisms differ principally in whether the interaction between the alkali metal atoms and organic fragments occurs as a homogeneous reaction in the gas phase or is purely a surface phenomenon. According to the gas-phase ionization theory, alkali metal atoms are vaporized from the hot source after acceptance of an electron from the heating wire or plasma. While in the boundary layer near the surface of the thermionic source, the alkali metal atoms are excited and ionized by collision with plasma particles. The negatively charged source rapidly recaptures the positively charged metal ions. This cyclic process results in a steady-state population of metal atoms in the boundary layer. If a process that results in ionization of metal atoms disturbs this equilibrium, then more metal atoms will leave the source to restore the equilibrium accompanied by an increase in the ion current. The selectivity of the detector results from the fact that only those radicals with electron affinities equal to or greater than the ionization potential of the metal atoms will contribute to the ion current. Among the many fragments generated by the decomposition of organic compounds in the plasma, only the $CN^{\bullet}$, $PO^{\bullet}$, and $PO_2^{\bullet}$ radicals meet this criterion for the alkali metals.

The surface ionization model assumes that the principal role of the alkali metal in the source is to lower the work function of the surface. Electronegative decomposition products from phosphorus- or nitrogen-containing compounds are then selectively ionized by extracting an electron from the surface of the thermionic source. These negative ions are responsible for the increase in observed ion current measured at the collector electrode. To account for the influence of experimental variables on the detector response, it is assumed that a combination of the heat from the source and the reaction of sample molecules within the boundary layer are responsible for sample decomposition. The active decomposition products must be similar and largely independent of molecular structure for nitrogen- and phosphorus-containing compounds to account for the narrow range of response factors.

The response of the detector to compounds containing elements other than nitrogen and phosphorus depends on the thermionic source temperature, the work function of the source surface, and the chemical composition of the gas environment surrounding the source. With nitrogen as the plasma gas and a thermionic source with a low work function (high cesium content), the detector can be made selective to compounds containing functional groups of high electron affinity (e.g., nitro and thiol groups). With a relatively low source temperature (400–500°C) and air or oxygen as the plasma gas enhanced selectivity toward halogen-containing compounds is obtained.

Although details of the detector response mechanism are not certain, the TID is not a particularly difficult detector to use and affords reliable results. Typical detection limits for nitrogen-containing compounds are about 5×10^{-14} to 2×10^{-13} g N/s and for phosphorus-containing compounds about 1×10^{-14} to 2×10^{-13} g P/s. The selectivity against carbon is about 10^3 to 10^5 g C/g N and 10^4 to 5×10^5 g C/g P. Discrimination against phosphorus in the nitrogen mode is poor at 0.1–0.5 g P/g N. The linear range is about 10^4–10^5. The TID is widely used in environmental and biomedical research for determining pesticides residues and drugs as well as for obtaining element-selective profiles, where its high sensitivity and selectivity are useful in minimizing sample preparation requirements.

Photoionization Detector

Selective ionization of most organic compounds in the gas phase is possible by absorption of photons with energy either close to or greater than the ionization potential of the compounds. For typical organic compounds this requires photons in the far ultraviolet of about 5–20 eV. A cross-sectional view of a typical PID is shown in **Figure 2**. The photon source is a compact discharge lamp, containing an inert gas or gas mixture at low pressure, which emits monochromatic light of a specific energy, depending on the choice of fill gases and window material. Sources of different nominal energies (8.3, 9.5, 10.2, 10.9, and 11.7 eV) provide for the possibility of selective ionization of organic compounds with the 10.2 eV source used for general applications (**Table 2**). An optically transparent window made of a metal fluoride separates the discharge compartment from the ionization chamber. The carrier gas passes through the thermostatted ionization chamber and between two electrodes, positioned at opposite ends of the chamber. An electric field is applied between the electrodes to collect the ions formed (or electrons, if preferred) and the current amplified by an electrometer.

An alternative approach is based on an open-source design. Photons are generated by an atmospheric pressure helium discharge that can be doped with other inert gases to provide a range of photon energies. The detector is constructed from a quartz

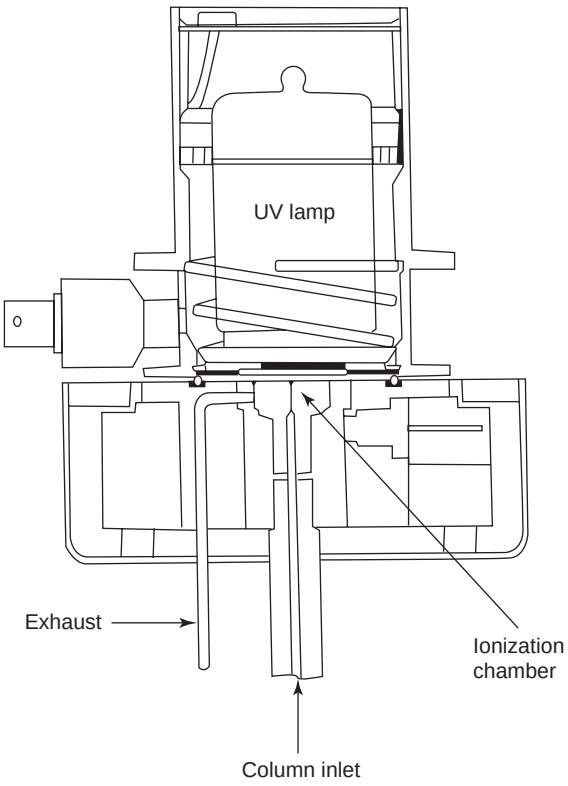

Figure 2 Cross-sectional view of a photoionization detector.

Table 2 Selectivity of the photoionization detector to different compound classes

Photon energy (eV)		*Fill gas*	*Compounds ionized*
Nominal	*Actual*		
8.3	8.44	Xe	Compounds with low ionization potential such as polycyclic aromatic compounds
9.5	8.44 (97.6%) 9.57 (2.1%) 10.4 (0.18%)	Xe	Simple aromatic compounds in the presence of alkanes, mercaptans in H_2S, amines in ammonia
10.2	10.03 (82.9%) 10.64 (17.1%)	Kr	Most organic compounds except permanent gases, C_1–C_4 alkanes, methanol, acetonitrile, and chloromethanes
11.7	11.62 (71.8%) 11.82 (26.2%)	Ar	Low molecular weight compounds with high ionization potentials (e.g., formaldehyde, ethane, chloromethanes, acetylene, etc.)

tube divided into two zones with electrodes located at the end flanges and middle section. A high-voltage pulse is used to initiate the discharge in the top section and a bias potential on the middle electrode to direct electrons to the collector electrode housed in the bottom section. The carrier gas is introduced at a point close to the middle electrode with photon ionization occurring in the region between the middle electrode and the collector electrode. Since there is no barrier between the source and ionization chamber the pulse discharge PID can be operated at lower wavelengths (13.5–17.8 eV) than the conventional PID design functioning as a near universal detector.

The response of the PID can be described by the relationship

$$i = IF\eta\sigma NL[\mathrm{AB}]$$

where i is the detector ion current, I the initial photon flux, F the Faraday constant, η the photoionization efficiency, σ the absorption cross-section, N Avogadro's number, L the path length, and [AB] the concentration of an ionizable substance. Thus, for a particular detector and source, the PID signal is proportional to the ionization yield, absorption cross-section, and molar concentration of the analyte. The product ($\eta\sigma$) is the photoionization cross-section, which expresses both the probability that a molecule will absorb a photon and the probability that the excited state will ionize. A number of secondary processes involving collisions with carrier gas molecules and electron-capturing impurities compete with the ionization mechanism reducing the detector signal. Detector design and control of the operating conditions minimize these effects.

The PID is inexpensive, of rugged construction, and easy to operate. Due to the low efficiency of photoionization ($<0.1\%$) the detector is classified as nondestructive. Since no combustion gases are required the PID can be used in environments where combustion gases are considered hazardous or in portable instruments, where the additional weight of several gas bottles is undesirable. For compounds with favorable ionization properties the PID is 5–50 times more sensitive than the FID with a comparable linear range ($\approx 10^7$). For individual compounds detector response factors vary over a wide range allowing the PID to be used as a selective detector for some applications. Major uses include the analysis of volatile organic compounds from environmental samples and in field-portable gas chromatographs.

Electron-Capture Detector

The ECD owes its popularity to its unsurpassed sensitivity to a wide range of environmentally important and biologically active compounds. Examples of general applications include the determination of pesticides and industrial chemicals in the environment, assessment of the fate of ozone-depleting chemicals in the upper atmosphere, and the determination of drugs and hormones in biological fluids. To maintain optimum detector performance some experience with the operation of the detector is required as well as familiarity with the causes and effect of detector contamination.

The ECD is available in several different designs dominated by two alternative methods for generating thermal electrons responsible for the detector's operating characteristics. From inception, high-energy β electrons generated by the decay of a radioisotope have been used as the primary source of ionizing radiation. Either ^{63}Ni or ^{3}H radioisotope sources supported by a metal foil are used in commercial detectors. These β-particle emitters produce a large number of secondary electrons through multiple collisions with carrier gas molecules forming a plasma of thermal electrons (mean energies 0.02–0.05 eV), radicals, and positive ions. Radioisotope-based detectors require periodic wipe tests to ensure safety as well as compliance with regulations concerning storage, use, and transport of radioactive materials. Regulatory constraints provided the impetus for the development of a non-radioactive detector. The non-radioactive ECD uses high-energy photons from a pulsed discharge in pure helium to ionize a support gas added downstream of the discharge. A plasma of thermal electrons and positive ions is formed in the ionization chamber with properties similar to the plasma generated by the radioisotope-source ECD.

Application of a fixed or pulsed potential to the ionization chamber allows collection of the thermal electrons establishing the standing (or baseline) current. When an electron-capturing compound enters the ionization chamber, thermal electrons are removed by formation of negative ions. The increased rate of neutralization of these ions by positive ions, or their reduced drift velocity during collection of the thermal electrons, is responsible for the detector signal. In contrast to the other ionization detectors a decrease in the detector standing current proportional to solute concentration is measured rather than an increase in the number of ions or electrons produced.

The majority of detectors with radioisotope sources in current use are based on either the coaxial cylinder or asymmetric configurations, as shown in **Figure 3**. The low specific activity of the ^{63}Ni source requires a relatively larger source area to provide a suitable background current that is easier to accommodate in these designs. Virtually all contemporary detectors employ pulse-sampling techniques to collect the thermal electrons based on the variable frequency constant

current mode. In this case, the pulse frequency is varied throughout the separation to maintain the cell current at a fixed reference value. The detector signal is a voltage proportional to the pulse frequency. The two principal advantages of this method are an increased linear response range of 10^4–10^5 and reduced detector disturbance from column contamination except for a few compounds with ultrafast electron attachment rate constants, which exhibit a nonlinear response, and are better measured with a constant pulse frequency.

Oxygen-free nitrogen is the most common carrier gas for packed columns and hydrogen or helium for open tubular columns. Argon–methane or nitrogen is then added as make-up gas at the column exit to minimize extra column peak broadening due to the relatively large effective detector volume. Pure argon and helium are unsuitable make-up gases as they readily form metastable species, which can transfer their excitation energy by collision with sample vapors, resulting in undesirable ionization effects (Penning reaction). The addition of 5–10% of methane to argon removes these ions by deactivating collisions as quickly as they are formed. Oxygen and water vapor traps should be used to purify all gases.

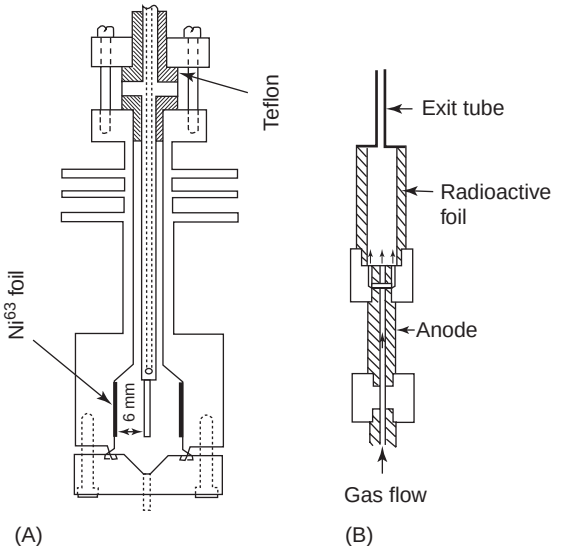

Figure 3 Cross-sectional view of a coaxial cylinder (A) and asymmetric (B) electron-capture detector.

The ECD is a structure-selective detector with a response range that covers about seven orders of magnitude (**Table 3**). The greatest response is observed for compounds containing halogen atoms ($I > Br > Cl \gg F$ increasing synergistically for multiple substitution on the same carbon atom) or nitro groups, to organometallic compounds, and to compounds containing conjugated electrophores. This latter group is the least well defined, and is comprised of compounds containing two or more weakly electron-capturing groups, connected by some specific bridge that promotes a synergistic interaction between the two electron-capturing groups. Examples of compounds containing conjugated electrophores include conjugated carbonyl compounds (benzophenones, quinones, phthalate esters, coumarins), some polycyclic aromatic hydrocarbons, some sulfonamides, and certain steroids.

The effect of temperature on the detector response is frequently overlooked. The detector response can vary by as much as 100–1000-fold for a 100°C change in detector temperature. In most cases electron capture occurs by either of two mechanisms. By nondissociative electron capture resulting in the formation of a stable molecular ion, or by dissociative electron capture with formation of a molecular ion in an excited state that instantaneously decomposes with elimination of a negative ion fragment. Nondissociative electron capture is generally associated with compounds containing a conjugated electrophore and dissociative electron capture with halogen-containing compounds. An increase in detector temperature favors the populating of vibrationally excited states

Table 3 Relative response of the electron-capture detector to various organic compounds

General organic compounds	*Relative response*	*Fluorocarbon compounds*	*Relative response*
Benzene	0.06	$CF_3CF_2CF_3$	1.0
Acetone	0.50	CF_3Cl	3.3
Di-*n*-butyl ether	0.60	$CF_2{=}CFCl$	1.0×10^2
Methylbutyrate	0.90	CF_3CF_2Cl	1.7×10^2
1-Butanol	1.00	$CF_2{=}CCl_2$	6.7×10^2
1-Chlorobutane	1.00	CF_2Cl_2	3.0×10^4
1,4-Dichlorobutane	15.00	$CHCl_3$	3.3×10^4
Chlorobenzene	75.00	$CHCl{=}CCl_2$	6.7×10^4
1,1-Dichlorobutane	1.1×10^2	CF_3Br	8.7×10^4
1-Bromobutane	2.8×10^2	$CF_2ClCFCl_2$	1.6×10^5
Bromobenzene	4.5×10^2	$CF_3CHClBr$	4.0×10^5
Chloroform	6.0×10^4	$CF_3CF_2CF_2I$	6.0×10^5
1-Iodobutane	9.0×10^4	CF_2BrCF_2Br	7.7×10^5
Carbon tetrachloride	4.0×10^5	$CFCl_3$	1.2×10^6

and thus the dissociative mechanism. Conversely, nondissociative electron capture may be destroyed if the rate constant for thermal detachment is too fast, and a higher detector response is usually observed at low detector temperatures. The optimum detector response for practical work is usually obtained at either the maximum temperature recommended for the radioisotope source for compounds with a dissociative mechanism for electron capture, or at the lowest practical operating temperature for compounds with a nondissociative mechanism of electron capture.

Helium Ionization Detector

The HID is a universal and ultrasensitive detector used primarily for the analysis of permanent gases and some volatile organic compounds that have a poor response to the FID and are present in too low a concentration for detection with a TCD. Typical detection limits are around $10^{-13}\,g\,s^{-1}$ with a linear range of about 10^4. Many features of the design of the HID are similar to those of the pulsed discharge ECD. Metastable helium ions thought to be primarily responsible for ionization of organic compounds are produced by bombardment of helium atoms with high-energy β-particles from a radioisotope source (e.g., ^{63}Ni) or produced directly in a pulsed discharge. The HID has a reputation as a difficult detector to use and must be operated under stringent conditions with respect to contamination from carrier gas impurities and the ingress of air or column bleed. Because applications have remained focused on inorganic gases and simple volatile organic compounds, gas–solid columns are often used for separations to minimize contamination problems and drifting baselines with contaminated liquid stationary phases.

Bulk Physical Property Detectors

Bulk physical property detectors respond to some difference in a carrier gas property due to the presence of the sample. Usually, a large signal for the carrier gas property is desirable to provide a reasonable working range, but for low sample concentrations the detector signal corresponds to a very small change in a large signal, and is noise limited. The sensitivity of the bulk physical property detectors tends to be poor compared with ionization detectors. The most important of the bulk physical property detectors is the TCD. Other examples include the gas density balance and ultrasonic detector.

Thermal Conductivity Detector

The TCD is a universal, nondestructive, concentration-sensitive detector that responds to the difference in thermal conductivity of the carrier gas and the carrier gas containing sample. It is generally used to detect permanent gases, light hydrocarbons, and compounds that respond poorly to the FID. Typical detection limits are 10^{-6} to 10^{-8} g per peak with a linear range of about 10^4. If lower detection limits are required for compounds with a poor response to the FID, then the HID is a suitable alternative.

In a typical TCD, the carrier gas flows through a heated thermostatted cavity that contains the sensing element, either a heated metal wire or thermistor. With carrier gas flowing through the cavity the heat loss from the sensor is a function of the temperature difference between the sensor and cavity and the thermal conductivity of the carrier gas. When carrier gas containing sample vapors enters the cavity, there is a change in the thermal conductivity of the carrier gas mixture resulting in a change in the sensor temperature. The sensor may be operated in a constant current, constant voltage, or constant mean temperature mode as part of a Wheatstone bridge circuit. A temperature change in the sensor results in an out-of-balance signal proportional to the concentration of sample vapor in the sensor cavity.

The TCD has appeared in several different designs, some of which have advantages for particular applications. They usually represent some variation of the three basic geometries: the flow-through, semidiffusion, and diffusion cells. In the flow-through cell, carrier gas passes over the sensor and in the diffusion cell the sensor is located in a recess into which a portion of the carrier gas stream enters by diffusion. The diffusion and semidiffusion cells have a slow response and are relatively insensitive. They are used mainly for packed column analytical and preparative gas chromatography. Flow-through cells with volumes of 1–100 µl are easily fabricated for use with open tubular columns. To improve thermal stability two or four cells are mounted in the detector oven block, half of which are used as reference cells through which only carrier gas flows, generating a difference signal proportional to sample concentration. In an alternative design, flow modulation is used to switch the carrier gas between two channels, one of which contains a single filament (**Figure 4**). Every 100 ms a switching valve fills the filament channel alternately with carrier gas and column effluent. With an effective detector volume of 3.5 µl, it can be used with even narrow bore open tubular columns.

Carrier gases of low molecular weight and high thermal conductivity (e.g., H_2 and He) are required to maximize the detector response and to maintain a large linear response range. Heavier carrier gases such as nitrogen, as well as influencing sensitivity and linearity, may give rise to negative or split top sample peaks. A number of response factor compilations for

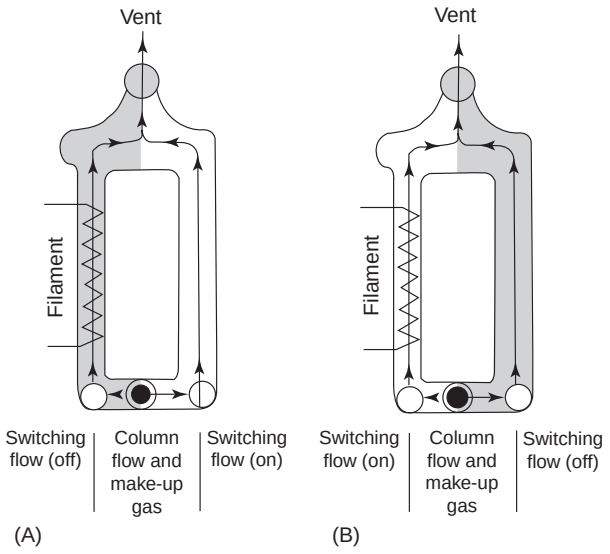

Figure 4 Schematic diagram of a single-filament thermal conductivity detector with flow modulation. In (A) the carrier gas is directed to flow over the filament and in (B) bypasses the filament.

different carrier gases are available, usually expressed on a weight or molar response basis relative to benzene. These values are generally sufficiently accurate for estimating sample concentrations. For more accurate results it is necessary to calibrate the detector for each substance individually.

Optical Detectors

The use of flames as atom reservoirs is a well-established technique in atomic spectroscopy. The principal emission lines for most nonmetallic elements of interest for gas chromatography occur in the ultraviolet region, where flame background contributions are troublesome. About 28 elements, including phosphorus and sulfur, can be determined by their chemiluminescence emission in hydrogen-diffusion flames with a flame photometric detector (FPD). For direct atomic emission detection, microwave induced and inductively coupled plasmas provide more appropriate atom sources for organic compounds. A number of chemiluminescence reaction detectors are also used in gas chromatography for the specific detection of sulfur- and nitrogen-containing compounds and nitrosamines.

Flame Photometric Detector

The FPD is an element-selective detector commonly used for the determination of sulfur- and phosphorus-containing compounds. The FPD uses a hydrogen-diffusion flame to first decompose and then excite to a higher electronic state the fragments generated by the combustion of sulfur- and phosphorus-containing

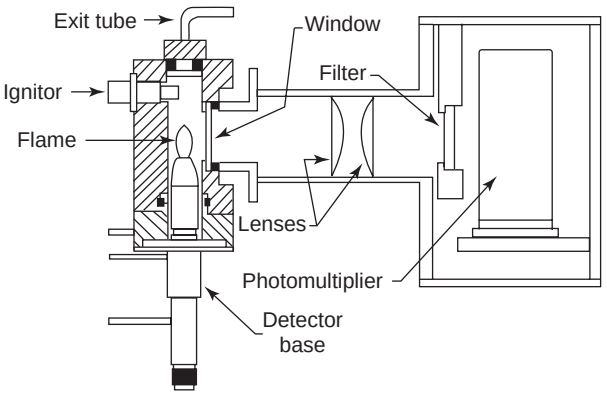

Figure 5 Cross-sectional view of a flame photometric detector. (Reproduced with permission from Patterson PL, Howe RL, and Abushumays A (1978) Dual-flame photometric detector for sulfur and phosphorus compounds in gas chromatographic effluents. *Analytical Chemistry* 50: 339–344.)

compounds in the effluent from a gas chromatograph. These excited state species subsequently return to the ground state, emitting characteristic band spectra. This emission is isolated by a filter and monitored by a photomultiplier detector.

In the single-flame detector the carrier gas and air are mixed, conveyed to the flame tip, and combusted in an atmosphere of hydrogen. With this burner and flow configuration interfering emissions from hydrocarbons occur mainly in the oxygen-rich flame regions close to the burner orifice, whereas sulfur and phosphorus emissions occur in the diffuse hydrogen-rich upper portions of the flame. Problems with solvent flameout, hydrocarbon quenching, and structure–response variations for different sulfur- and phosphorus-containing compounds with the single-flame detector can be partially overcome using a dual-flame design (**Figure 5**). The lower flame is hydrogen rich and functions as a matrix-normalization reactor in which all compounds are decomposed to a highly reduced state (e.g., H_2S, S_2, H_2O, CH_4, etc.). The combustion products from the first flame are swept into a second longitudinally separated flame where the desired optical emission is generated under optimized flame conditions. The pulsed-flame detector is based on a flame source and flame gas flow rates that cannot sustain a continuous flame. The combustion gases (H_2 and air) are mixed together in a small chamber and flow to a continuously heated wire igniter. The ignited flame then propagates back to the gas source and is self-terminated once all of the combustible gas mixture present in the combustion path is consumed. The continuous gas flow removes the combustion products and creates additional ignition in a periodic fashion. The pulsed flame emission provides enhanced detection sensitivity and selectivity by time resolution of the various

flame luminescent species. The luminescence from hydrocarbon and flame combustion products (e.g., OH^*, CH^*, C_2^*, etc.) is limited to the time duration for the flame front to pass across the photomultiplier viewing area. Because of lower bond energies the sulfur- and phosphorus-containing species continue to emit in the cooler, yet reactive, postpulse flame conditions. By gating the detector the heteroatom emission can be time resolved from the hydrocarbon and flame background emission.

In the relatively low-temperature and hydrogen-rich flame, sulfur-containing compounds are decomposed to species such as H_2S, HS, S, S_2, SO, and SO_2 in relative proportions that depend on the flame chemistry. Excited state S_2^* species are formed from these primary species in low yield by several two- or three-body collision reactions. The relaxation of S_2^* results in broadband emission over the wavelength range from 320 to 460 nm with a maximum emission at 394 nm. The response for sulfur is inherently nonlinear and proportional to the concentration of sulfur atoms entering the flame ($[S]^n$). The theoretical value for n is 2, but in practice, values between 1.6 and 2.2 are frequently observed for the single-flame detector. Nonoptimized flame conditions, compound-dependent decomposition, hydrocarbon quenching, and competing flame reactions that lead to de-excitation all contribute to the deviation of n from its theoretical value. Decoupling the compound decomposition process from the excitation process in the dual-flame and pulsed-flame detectors results in a more truly quadratic response.

In the case of phosphorus, phosphorus-containing compounds are first decomposed to PO molecules and finally to electronically excited HPO^* species in three-body collisions. A linear relationship between detector response and the concentration of phosphorus atoms entering the flame is expected for phosphorus-containing compounds, at least for low sample concentrations.

Typical detection limits are 5×10^{-13} to 1×10^{-14} g P/s (all detector types) and $5\text{–}50 \times 10^{-12}$ g S/s (single flame), 1×10^{-11} g S/s (dual flame), and 2×10^{-13} g S/s (pulsed flame). The linear range for phosphorus usually exceeds 10^3 while the selectivity is more than 5×10^5 g C/g P. Sulfur selectivity varies in the range 10^4–10^6 g C/g S (single flame), 10^3–10^4 g C/g S (dual flame), and $> 10^7$ g C/g S (pulsed flame).

Chemiluminescence Detectors

Nitrosamines can be detected after thermal cleavage and nitrogen-containing compounds after oxidation to nitric oxide, which reacts with ozone to form nitrogen dioxide in an excited state with photon emission in the near-infrared around 1200 nm. Sulfur-containing compounds can be decomposed by thermal oxidation to sulfur monoxide and subsequently reacted with ozone to form sulfur dioxide in an excited state with photon emission centered $\sim$360 nm.

A typical chemiluminescence detector consists of a series-coupled thermal decomposition and ozone reaction chambers. The selective detection of nitrosamines is based on their facile low-temperature (275–300°C) catalytic pyrolysis to release nitric oxide. Thermal decomposition in the presence of oxygen at about 1000°C affords a mechanism for conversion of nitrogen-containing compounds to nitric oxide (catalytic oxidation at lower temperatures is also possible). Decomposition in a hydrogen-diffusion flame or thermal oxidation in a ceramic furnace is used to produce sulfur monoxide from sulfur-containing compounds.

The products of the conversion reaction flow into the ozone reaction chamber, which is maintained at a pressure of 10–30 mmHg. Reduced pressure operation has three advantages: it improves sensitivity by diminishing collisional deactivation of the excited state reaction products; it prevents condensation of water in the reaction chamber; and it reduces the effective detector volume maintaining compatibility with open tubular columns. Ozone is generated by a high-voltage discharge in air or oxygen and enters the reaction chamber by a separate connection. The chemiluminescence emission produced is isolated by an optical filter and detected by a photomultiplier. If one of the reactants in the chamber is maintained in large excess (e.g., ozone), the reaction becomes pseudofirst order for the other reactant, resulting in a linear response.

The most important applications of the chemiluminescence detector are the determination of volatile nitrosamines in food, environmental, and industrial products (detection limits $\sim$0.5 ng per peak with a linear range of 10^5) and sulfur-containing compounds in complex matrices, for example, in the petroleum and gas industries for process control and regulatory compliance, and in the beverage industry to characterize flavor compounds. The response of the chemiluminescence detector to sulfur-containing compounds is almost equal on a per gram of sulfur basis. This allows the use of a single calibration curve for the determination of all sulfur-containing compounds in many cases. The detection limit for the flame-based detector is about 10^{-12} g S/s, with a linear range of 10^4–10^5, and selectivity $> 10^6$ g C/g S. For the flameless detector the detection limit is about 10^{-13} g S/s, with a linear range of 10^4–10^5, and selectivity $> 10^7$ g C/g S. In the nitrogen-selective mode detection limits are about 10^{-12} g N/s, with a linear range of 10^4–10^5, and selectivity 10^7 g C/g N.

Atomic Emission Detector

The atomic emission detector (AED) is a relatively complex instrument and is described below in outline only. Coupling of the separation column to the thermostatted microwave cavity is made through a heated transfer line. The plasma is produced in a thin-walled silica discharge tube within a microwave 'reentrant' cavity (**Figure 6**). Power is supplied by a magnetron, and coupled to the plasma through a waveguide. The exit of the cavity is closed with a fused silica window and purged with helium to prevent back-diffusion of air into the cavity, and to allow flow reversal so that the solvent peak can be vented in front of the cavity to minimize carbon build-up in the cavity. The plasma is generated in an atmospheric pressure flow of helium made up of the column flow and additional make-up flow, as required. Depending on the elements being determined, low concentrations of various scavenger gases (e.g., O_2, H_2, and CH_4) are also added. An elliptical mirror collects emissions from 2 mm inside the end of the discharge tube. The emission sensor consists of a flat focal-plane spectrometer with a movable photodiode array detector with a range of about 25 nm. This determines which element combinations can be measured simultaneously. In general, up to four elements can be detected and displayed as element-specific chromatograms at the same time. Typical figures of merit are summarized in **Table 4**. Obviously, the AED is capable or replacing most of the element-selective detectors described in this article. It is more complex and expensive to operate, however, and has made only modest in roads into the detector market place. On the other hand, it is almost uniquely suited to the detection of organometallic compounds.

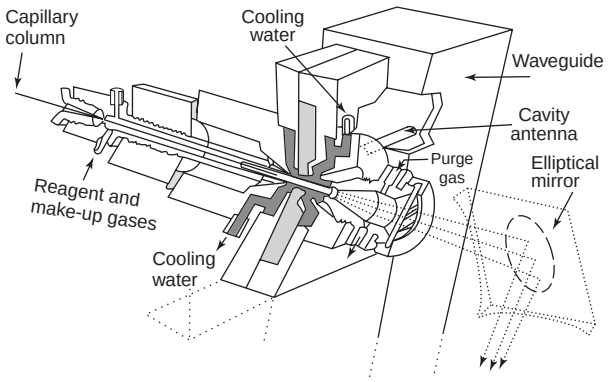

Figure 6 Cross-sectional view of the cavity block of an atomic emission detector. (Reproduced with permission from Sullivan JJ and Quimby BD (1989) Detection of C, H, N and O in capillary gas chromatography by atomic emission. *Journal of High Resolution Chromatography* 12: 282–286.)

In theory, it should be possible to determine the empirical formula for each compound in the chromatogram from the ratio of the AED response to the individual elements. A lack of plasma stability, incomplete compound destruction, and deviations from linearity of the individual element responses, however, limits the accuracy of such measurements. Accurate formula values for oxygen and nitrogen can be particularly difficult to determine due to entrainment of atmospheric gases into the plasma. In addition, it is not always possible to use a single compound internal standard for quantification with the desired accuracy for the same reasons that affect the accuracy of empirical formula determinations.

Electrochemical Detectors

There are two general problems associated with electrochemical detection in the gas phase. First, few electrochemical detectors are gas-phase sensing devices, and therefore the separated sample components must be transferred into solution for detection.

Table 4 Response characteristics of the atomic emission detector to different elements

Element (X)	*Wavelength (nm)*	*Minimum detectable amount (pg s^{-1})*	*Selectivity (g C/g X)*	*Linear range*
C	193.1	2.6		2×10^4
H	486.1	2.2		6×10^3
Cl	479.5	39	2.5×10^4	2×10^4
Br	470.5	10	1.1×10^4	1×10^3
F	685.6	40	3.0×10^4	2×10^3
S	180.7	1	3.5×10^4	1×10^4
P	177.5	1	5.0×10^3	1×10^3
N	174.2	15	2.0×10^3	4×10^3
N	388	15	8.0×10^5	1×10^4
O	777.2	50	3.0×10^4	3×10^3
Sn	303.1	0.5	3.0×10^4	1×10^3
Se	196.1	4	5.0×10^4	1×10^3
Hg	253.7	0.1	3.0×10^6	1×10^3

Second, the majority of organic compounds separated by gas chromatography are neither electrochemically active nor highly conducting. The electrolytic conductivity detector (ELCD) solves both of these problems by decomposing the gas-phase sample into small inorganic molecules, which are detected by their conductivity in a support solvent. The ELCD is used primarily as an element-selective detector for halogen-, sulfur-, and nitrogen-containing compounds.

The carrier gas is mixed with a reaction gas and then passed through a small diameter nickel tube at 850–1000°C. The nickel tube acts as catalyst for the decomposition reaction. With hydrogen as the reaction gas, halogen-containing compounds are converted to hydrogen halide (HCl, HBr), and nitrogen-containing compounds are converted to ammonia. Sulfur-containing compounds are reacted with air to produce sulfur dioxide with a small amount of sulfur trioxide. A chemical scrubber mounted at the exit of the reaction tube is used as needed to enhance the specificity of the detection process. For example, silver wires are used to remove hydrogen halides or hydrogen sulfide, potassium hydroxide supported on quartz fibers to remove acidic species, and aluminum silicate to remove sulfur oxides.

The reaction products from the furnace are swept into a gas–liquid contactor where they are mixed with an appropriate solvent (**Figure 7**). The support solvent is selected to promote ionization of the reaction species over ionization of interfering compounds. This solvent is usually circulated through a closed system containing beds of ion exchange resins to purify and condition the solvent for reuse. From the gas–liquid contactor the support solvent flows to the conductivity cell, where detection takes place, either after separation of the liquid from insoluble gases, or as a mixed phase, depending on the detector design.

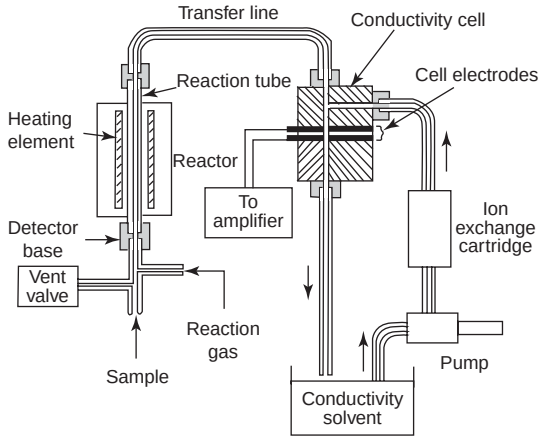

Figure 7 Cross-sectional view of an electrolytic conductivity detector. (From McMinn DG and Hill HH (eds.) (1992) *Detectors for Capillary Chromatography*. New York: Wiley.)

The ELCD has the reputation of being a demanding detector to operate and its popularity has declined as other element-selective detectors with simpler operating features became available. Common practical problems include the loss of response, excessive noise, poor linearity, and poor peak shape. The ELCD is capable of high sensitivity and selectivity with detection limits of about 10^{-12} g N/s, 10^{-12} g S/s, and 5×10^{-13} g Cl/s with a linear range of 10^3–10^5. Selectivity varies with the heteroatom detected as well as detector operating conditions. Values of 10^4–10^9 g C/g N, S, or Cl are possible. The ELCD is used primarily for the determination of chlorine- and nitrogen-containing compounds in environmental samples and for the determination of sulfur-containing compounds in petroleum products.

See also: **Atomic Emission Spectrometry**: Microwave-Induced Plasma. **Chemiluminescence**: Gas-Phase. **Derivatization of Analytes**. **Gas Chromatography**: Mass Spectrometry; Fourier Transform Infrared Spectroscopy.

Further Reading

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