



Review

Ionization-based detectors for gas chromatography



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ABSTRACT

The gas phase ionization detectors are the most widely used detectors for gas chromatography. The column and makeup gases commonly used in gas chromatography are near perfect insulators. This facilitates the detection of a minute number of charge carriers facilitating the use of ionization mechanisms of low efficiency while providing high sensitivity. The main ionization mechanism discussed in this report are combustion in a hydrogen diffusion flame (flame ionization detector), surface ionization in a plasma (thermionic ionization detector), photon ionization (photoionization detector and pulsed discharge helium ionization detector), attachment of thermal electrons (electron-capture detector), and ionization by collision with metastable helium species (helium ionization detector). The design, response characteristics, response mechanism, and suitability for fast gas chromatography are the main features summarized in this report. Mass spectrometric detection and atomic emission detection, which could be considered as ionization detectors of a more sophisticated and complex design, are not discussed in this report.

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1. Introduction

Those analysts working in the field of gas chromatography were fortunate that shortly after its introduction a group of mainly ionization-based detectors became available that enabled most common applications to be tackled [1–7]. This allowed the focus of research to move quickly to other areas such as sample introduction and column technology. In more recent times there has been no revolution in the detection principles employed in gas chromatography, although detector designs have continued to evolve with improvements in materials, and in particular, microelectronics for control, data acquisition and storage, and data display and analysis. The common detectors in use today are rugged, require minimal maintenance and are simply expected to work on demand. Even if they generally fit this description, there is much to be gained by acquiring a little wisdom concerning the relationship between the detector response and experimental variables, response mechanisms, and matrix interferences.

For classification purposes gas chromatographic detectors can be grouped in different ways according to their characteristic properties [8]. Appropriate descriptions for classification terms for ionization detectors are summarized in Table 1. By application they can be grouped into universal, selective or specific and by response type, as mass or concentration dependent. The most important gas-phase ionization detectors are the flame ionization detector (FID), thermionic ionization detector (TID or NPD), photo-ionization detector (PID), electron-capture detector (ECD), helium ionization detector (HID), and pulsed discharge detector (PDD). Other common detectors used in gas chromatography are described

Table 1
Classification terms for ionization-based gas chromatography detectors.

Term	Description
Response type	Universal, selective, specific, reaction based
Response	Mass- or concentration-dependent
Sensitivity	The signal output per unit concentration or mass of test substance in the carrier gas
Minimum detectability (minimum detection level)	Amount of test substance that produces a detector signal equal to twice the noise Mass detector = $(2 \times \text{noise} \times \text{mass on column/area})$ units = mass/time (e.g., pg/s) Concentration detector = $(2 \times \text{noise} \times \text{mass on column/area} \times \text{total gas flow through detector})$ units = mass/volume (e.g., pg/ml)
Dynamic range	The range for the amount of test substance over which a change in amount produces a change in the detector signal
Linear range	Range over which the detector response per sample amount injected is constant to within $\pm 5\%$ as determined from a linearity plot
Noise	The amplitude of the baseline envelope which includes all random variations of the detector signal of a frequency ≥ 1 cycle/min
Selectivity	Relative response of the detector for one compound type (or element) versus another compound (or element) Element-selective (defined atom identity) Structure-selective (defined arrangement of atoms in a portion of a molecule)
Specific	A selective detector with a very high degree of selectivity

elsewhere in this special issue. It would be reasonable to consider the mass spectrometer as a gas phase ionization detector but the added complexity from an instrumental perspective of ion formation, mass separation and ion detection are worthy of a separate and singular discussion, as is the case for the ion mobility detector. These detectors also provide facilities for structural identification of unknown compounds as well as quantification, which places them in a league of their own and worthy of a separate discussion in this special issue.

Gas chromatography is strongly associated with the separation of volatile organic compounds. Salts are not analyzed directly and inorganic compounds with the exception of some organometallics are usually handled by other techniques. Detection requirements are therefore largely limited to compounds containing the elements carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorous and the halogens. These elements provide a large number of target compounds presenting difficulties for separation but simplify general requirement for detection. In particular, this is true for element-selective detectors, and also justifies their development for gas chromatography, as the number of detectors required is manageable compared to the larger number of elements comprising the periodic table. The ionization detectors provide access to universal, structure-selective and element-selective detection options as described in this article.

The defining characteristic feature of the ionization detectors is that at the typical temperatures and pressures associated with their use the common carrier gases employed for separations in gas chromatography behave as perfect insulators. This allows any mechanism that result in the production of charged species to be an effective detection mechanism. In the absence of conduction by the carrier gas, the increase in conductivity due to the presence of a few charged species is easily measured and amplified, providing low detection limits. In addition, any gas phase element-selective or structure-selective ionization process can afford a mechanism for the design of selective detectors with low detection limits and high discrimination against compounds poorly ionized under the same detector conditions. The fact that ions can be generated from neutral compounds by several mechanisms provides a range of options for detector design. In all cases, the quantitative basis of detector operation corresponds to the fluctuation of the observed ion current as an organic vapor is transported through the detector in an inert carrier gas.

2. Flame ionization detector

The flame ionization detector (FID) is the most popular detector for gas chromatography. It provides a near universal response to organic compounds, low detection limits, long-term stability, simplicity of operation, low dead volume, a fast response and an exceptional linear response range. Typical performance characteristics are summarized in Table 2. Only the fixed gases (e.g., He, Ar, Ne, Xe, H₂, N₂, O₂), certain nitrogen oxides (N₂O, NO, etc.), compounds containing a single carbon atom bonded to oxygen or sulfur (e.g., CO₂, CS₂, COS, etc.), inorganic gases (e.g., NH₃, SO₂, etc.), water, formamide and formic acid provide a weak or insignificant detector response. The detector is sometimes described as a carbon-selective detector with a near equal molar response for hydrocarbons based on their carbon atom number and a relative response for

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