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Selective Detectors in Gas Chromatography

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The present state of selective gas-chromatographic detection has been examined. The principles, developmental trends, and characteristic features of selective detectors of 14 types have been described briefly, and examples of their practical application have been given. Particular attention has been paid to the use of these detectors in the analysis of micro-quantities of harmful chemical compounds in environmental materials.
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I. INTRODUCTION

The recent increase in interest in highly sensitive selective detectors is related to the extension of the range of problems being solved by gas chromatography, and also to an increase in the complexity of the compositions of the mixtures being analysed. This applies particularly to the analysis of environmental materials and specimens of biological origin, where the resolving power of the most efficient gas-chromatographic columns combined with highly sensitive universal detectors is insufficient for the complete separation and determination of all the components present in a specimen.[1] At the same time, however, it is often necessary merely to know whether compounds of a given class are present. This information can be obtained using a detector which reacts selectively only to compounds of the given class. The use of selective detectors is particularly promising in the analysis of pollutants in air and water, where it is necessary to determine traces of harmful substances in the presence of large quantities of the main components.

The action of selective detectors is based on the most varied properties of the substances being analysed, such as their ability to undergo ionisation, emit (or absorb) light, undergo chemical reaction, etc. Many of these detectors are fairly simple to construct and convenient to use, and are firmly established in everyday gas-chromatographic analytical practice. Examples include the electron-capture detector, which is sensitive to halogen-containing organic substances, nitro-compounds, and other substances which act as electron acceptors; the thermo-ionic detector, which has an increased sensitivity to nitrogen-, phosphorus-, and halogen-containing compounds; the flame-photometric detector (S- and P-containing compounds); and the radiometric detector, used to detect substances labelled with radioactive isotopes.

The terms "universal" and "selective" are to some extent arbitrary when applied to detectors. Thus the universal flame-ionisation detector, which is highly sensitive to practically all organic compounds, is insensitive to most gases and vapours of inorganic substances, and the radiometric detector, selective with respect to different types of radiation, is non-selective in the sense that it cannot determine whether the labelled substance belongs to a particular class of chemical compound. A detector is usually regarded as selective if its sensitivities for substances of two different classes differ by at least an order of magnitude.[2]

The present review of the literature of the past ten years examines the present state and examples of the practical application of the most frequently employed selective gas-chromatographic detectors: flame-photometric, plasma-emission, photo-ionisation, etc.
tography has been combined with infrared and mass spectrometry and with chemical ionisation are also discussed.

II. SPECTROSCOPIC DETECTORS

1. The Flame-photometric Detector

The action of the flame-photometric detector (FPD) is based on the recording of the emission spectra produced by the thermal heating of the specimen in a burner flame.[1,3-24] A hydrogen–air flame with added oxygen is usually employed. The combustion of substances whose molecules contain atoms of sulphur, phosphorus, nitrogen, selenium, tin, and various other elements gives excited species (for example S_2^*, HPO^*, etc.), which emit a characteristic spectrum.[1,3]

The design of the FPD combines the cell of a flame-ionisation detector (FID) with an optical scheme for measuring the light flux.[3] The flame of the FPD is richer in hydrogen than that of the FID. The conditions of mixing of the streams of carrier gas and auxiliary gases in the burner, and their total consumption, influence the sensitivity and stability of operation of the FPD. The optimum conditions may therefore be different for different versions of this detector.[1,3-7] To prevent overheating of the optics and sensitive elements, the flame is enclosed in a quartz or Pyrex tube, or light pipes may be used. The background emission of the flame is absorbed by interference filters, which transmit only light of the required wavelength (λ = 394 nm for sulphur compounds, and λ = 526 nm for phosphorus compounds). The sensitivity and selectivity of the FPD with respect to a given substance are determined by the intensity of the analytical line in the

spectrum and the width of the transmission band of the light filter. The use of filters with narrower transmission bands increases the selectivity and the useful signal : noise ratio, but decreases sharply the sensitivity of the FPD, since the intensity of the light flux is proportional to the square of the transmitted band width.

The flame-photometric detector is a flow detector. For phosphorus compounds, the magnitude of the signal (the area of the peak) is directly proportional to the flux of the substance.[3] For sulphur compounds, this relationship is logarithmic; the exponent in the equation relating the area of the peak to the mass velocity of the substance being analysed in the detector should theoretically be equal to 2, but in practice it takes values from 1 to 2.5 for different substances; this is due to the fact that excited species S_n^* may be formed in the detector flame in addition to the species S_2^*.[6,9]

The sensitivity threshold of the FPD is $(2-100) \times 10^{-12}$ g s^{-1} for phosphorus compounds,[3,4,6,7] and $(6-300) \times 10^{-12}$ g s^{-1} for sulphur compounds.[4-6,10] This corresponds to approximately 10^{-9} g of the element being determined in the specimen.[7] The sensitivity of the determination of substances containing nitrogen, boron, tin, and other elements is slightly lower.

The linear range of the FPD is 10^4-10^5 for phosphorus compounds,[3,7] but is much lower ($\sim 10^2$) for sulphur compounds.[6,11] It has been proposed that the linear range of operation of the FPD in the analysis of sulphur compounds be increased by adding traces of carbon disulphide vapour (2–4 mg s^{-1}) to the carrier-gas stream[6] or by treating the detector connections with sulphur compounds.[10] This also leads to a decrease in the detectable minimum.[12] The sensitivity of the FPD with respect to sulphur-containing compounds is 10^4-10^7 times greater than that with respect to hydrocarbons and alcohols, and depends on the ratio of the gas flow velocities and on the design of the detector.[13] A slight decrease has been observed, however, in the magnitude of the signal for sulphur compounds, when eluted from the gas-chromatographic column together with hydrocarbons. The different extent of the decrease in the sensitivity of the FPD with respect to sulphur and selenium compounds, difficult to separate, when methane is added to the carrier gas has been used to identify these substances when present together.[12]

The high selectivity and sensitivity of the FPD have enabled it to be used to determine traces of thiols and organic sulphides in air,[14] isopropyl methylphosphonofluoridate (Sarin)[15] and butyltin[16] in water, sulphur-containing pesticides in wheat,[17] and various sulphur compounds in specimens of soil and air in regions of petroleum discharge or spillage.[18,19]

In the quantitative analysis of micro-quantities of sulphur compounds, difficulties arise as a result of the tendency of these substances to undergo irreversible sorption in the connections, and also the fact that the molar signal of the FPD depends on many factors, so that special calibration is required.[24] As shown for the analysis of dipropyl sulphide using the "Meloy Laboratories" 100 AT FPD,[9] the magnitude of the detector signal depends on the nature of the solvent, the number of successive analyses, and the duration of the intervals between analyses; for low concentrations, the difference in the magnitude of the signal may reach 200%. It is recommended[9] that the FPD should be used for the quantitative determination of organosulphur compounds at concentrations not lower than 10^{-4} g ml^{-1}. The accuracy of the determination of traces of hydrogen sulphide in the concentration range $10^{-4}-10^{-7}$ vol.% using the FPD produced by the Dzerzhinskii Special Design Office, with preliminary concentration, has been confirmed.[20] These detectors show "memory effects", which are stronger, the lower the concentration of the trace component. To obtain results with a mean-square deviation of ±10%, thorough purification of all the gases and prolonged flushing of the gas lines of the chromatograph and the connections through which the specimen is passed are required. If various precautions are taken, the FPD can be used for the quantitative determination of the concentrations of carbonyl sulphide, hydrogen sulphide, and sulphur dioxide at the level of $10^{-2}-10^{-7}$ mass % with a standard deviation of 7–5%.[21]

2. The Chemiluminescent Detector

Chemiluminescent detectors (CLD) record the luminescence spectra of the products of the chemical reaction of the substances being analysed and the reagents ozone[25-32] or atomic oxygen,[33] supplied continuously to the detector. The spectra are recorded using photomultipliers and photon counters; monochromators and electronic noise filters are also used.[27]

Luminescence is shown by the products of the reaction of ozone (or atomic oxygen) with alkenes,[28,33] sulphur dioxide[28,29] and nitric oxide. The analysis of nitrogen-containing compounds involves their thermal decomposition to give nitric oxide, which is then oxidised by ozone to excited nitrogen dioxide, which gives a luminescence spectrum. It is considered[33] that the method using atomic oxygen is more selective than that using the reactions of the substance being analysed with ozone.

The sensitivity threshold of the CLD is $\sim 10^{-9}$ g s^{-1}, and the linear range is 10^4. The detection limit for alkenes can be lowered by a factor of 200 by adding to the carrier gas traces of carbon disulphide or hydrogen sulphide, which undergo intermediate radical reactions and facilitate the reaction of the alkenes with ozone.[28]

The chemiluminescent detector has been used to determine the concentration of trimethylamine in air,[26] nitrosamines in the environment,[27,30,31] unsaturated hydrocarbons in industrial atmospheres,[33] and sulphur dioxide[29] and other substances in the troposphere and stratosphere. Many of these substances cause breakdown of the ozone layer and smog formation.[32] The simultaneous recording of chromatograms using a chemiluminescent detector and a universal detector (for example the FID) makes possible the group analysis of the concentrations of paraffins and aromatic hydrocarbons.[33]

3. The Plasma-emission Detector

Plasma-emission detectors (PED) record the emission from excited atoms and recombined diatomic fragments, obtained by the decomposition of the molecules of the compounds being analysed with a high-temperature helium or argon plasma.[4,34-43] The plasma, with a temperature of 4000–10000 K, consisting chiefly of the ionised gas, is formed either directly in a direct-current arc or by induction heating of the gas in the electromagnetic field of a high-frequency generator.[36] The excitation of the atoms and molecules of the substances being analysed may take place under the influence of electron impact, and also in collisions with metastable argon or helium atoms. The use of helium is preferred, since it has a simpler photon background spectrum and its metastable atoms have a higher energy.

The PED is now used to determine up to 30 elements in organic compounds, including non-metals difficult to excite, such as C, N, O, F, etc. The selectivity of this multi-element detector is achieved by tuning the spectrograph to the zero line of the spectrum by means of a monochromator, and by correction for the background.[36,39] Thus the chromatogram of petrol, recorded at $\lambda = 279.83$ nm (manganese line),

gave only the peak of the tricarbonylcyclopentadienyl-manganese present. The use of multi-channel PED appears promising, particularly for elemental analysis, since the molar signal of this detector is proportional to the number of atoms of the given element in the molecule of the substance being analysed, and is practically independent of the type of functional group.[36]

The discharge is usually produced in a thick-walled quartz capillary tube (internal diameter 0.5–1 mm). The carrier gas from the column and an additional stream of the same gas (0.05–6 litre min^{-1}) are supplied to the tube. The optimum ratios of the velocities of these two streams, and their overall velocity, are different for different elements.[36,41] Models of this detector operating at atmospheric pressure and at a reduced pressure have been described. The detector operating at atmospheric pressure is preferable, since direct axial observation of the plasma emission is possible (and not observation through the wall of the discharge tube, which introduces additional distortion).[41] It is useful to place a valve or a four-way tap with an additional gas-chromatographic detector between the column and the PED, to remove solvent from the specimen and avoid overloading the plasma with it.[35]

These detectors are promising for the analysis of specimens taken from the environment. The small internal volume of the detectors has made it possible to use them with capillary gas-chromatographic columns.[37,41] They have been used to determine traces of organic compounds of lead, silicon,[42,43] mercury, selenium, arsenic,[36] boron,[40] and fluorine[39] in water, air, soil, and various food products using specimens containing 10–600 pg of the substance being analysed. The selectivity of the determination of these elements relative to carbon varies from 70 to 360000; the linear dynamic range of operation of the detector is 10^2–10^3, and the reproducibility of the results when the operating conditions are strictly observed is 1–5%.[41,43]

4. The Combination of Gas Chromatography and Infrared Spectroscopy

Absorption infrared spectroscopy, combined with gas chromatography, is used for the qualitative identification of substances from their absorption spectra in the infrared range.[44] Continuous analyses are carried out by combining the gas chromatograph with an infrared spectrometer in which rapid scanning of the spectrum is carried out. Extensive use has been made of Fourier transform infrared spectroscopy[1,45–50] where a computer is used to store data on the intensity of absorption at different wavelengths and then substract the background. The complete spectrum or chromatogram is then reproduced by summation of the intensities of absorption of the compound being analysed, either throughout the entire spectrum or in a selected part of it.

The resolving power of fast-acting infrared spectrometers is lower than that of the ordinary instruments,[49] but the possibility of rapidly obtaining comparative data on the magnitude of the light absorption by the substances being analysed in the selected range of the spectrum makes this method extremely selective. There are at least five specific "windows" in the infrared spectrum, characteristic of five classes of compound: for example, the ranges 2930–3000 cm^{-1} for alkyl derivatives of benzene,[49] and 700–900 cm^{-1} for polyaromatic hydrocarbons.[47] The sensitivity of the determination and the useful signal : noise ratio are increased considerably if the chromatogram is reproduced from the intensity of the absorption in the range of the spectrum specific for the given class of compound.[47,49] Thus Fourier transform infrared spectroscopy can be used for the group analysis of various compounds in complex mixtures. Quantitative analysis by this method has also been reported, but the linear range of operation is very short (less than an order of magnitude). The minimum detectable quantity of pyrene in a specimen of the aromatic fraction of crude petroleum was 710 ng.[47]

New attachments and connecting units are being developed, which make it possible to work even with small-capacity capillary columns without loss of efficiency.[1,46–48,50] The device proposed in Ref. 47 consists of a gold-plated twelve-face copper receiver, placed in an evacuated (~10^{-6} mmHg) and cooled (to 17 K) compartment, to which the substance from the column is supplied through a heated glass-lined steel capillary. As the receiver is rotated, the fractions of the substance are deposited in turn on its faces; the absorption spectra of the trapped fractions are recorded at the moment when the corresponding faces pass in front of the spectrometer objective. The carrier gas (99.999% pure nitrogen) is not frozen under these conditions.

5. The Fluorimetric Detector

The action of the fluorimetric detector is based on the ability of various substances to fluoresce when irradiated or heated.[24,44,51–54] The intensity of the fluorescence is measured using a spectrofluorimeter. Since very few substances fluoresce, this method is highly selective, and is used in combination with all forms of chromatography, including gas chromatography. Methods are available, for example, for determining traces of anthracene, chrysene, and benz-α-pyrene in the atmosphere.[52] The selectivity of this method can be controlled by choosing an appropriate radiation source. Detectors have been described for the analysis of traces of nitrogen dioxide[53] and other substances[54] in air, based on the use of their long-wave fluorescence, induced by laser irradiation. The detection limit for nitrogen dioxide was 6×10^{-5}% (without preliminary concentration). Preliminary freezing of the traces of nitrogen dioxide made it possible to lower the detection limit to 2×10^{-6}% (preliminary gas-chromatographic separation was not used). The minimum detectable quantity of sulphur-containing gases is 100 ng.[24]

6. The Atomic-absorption Detector

Atomic-absorption spectroscopy, developed initially for the analysis of metals in inorganic materials,[55] has recently been used increasingly, combined with gas chromatography, in the analysis of organometallic compounds.[56–61] Dissociation of the molecules of the substances being analysed to atoms and absorption by the latter of the light from a standard source take place in the flame (or in a heated graphite cell). The light source usually consists of a special lamp in which the cathode is made of the metal which is being determined. The use of light sources with a line emission spectrum, in which the width of the lines is smaller than the width of the lines of the spectrum excited (~10^{-2} nm), makes this method exceptionally selective; the use of a monochromator (spectrophotometer) is necessary, to increase the signal : noise ratio.[55] The absorption spectra of most elements, obtained in an atomic-absorption spectrometer, are exceptionally simple, since they contain only the resonance lines corresponding to absorption transitions from the ground levels.

The atomic-absorption detector has been used for the gas-chromatographic analysis of organic manganese carbonyl in air,[56] tetra-alkyllead,[58] metal chelates (chromium, iron, copper, and cobalt[59]), and organometallic compounds of gallium, indium,[57] tin,[60] and lead.[61]

The minimum detectable quantity of substance, calculated as the metal, corresponds to several nanograms in the specimen, and can be improved by preliminary concentration.[61] The necessary precautions are for the most part those characteristic of work with organometallic compounds.

III. IONISATION DETECTORS

1. The Photo-ionisation Detector

A large number of recently published papers describe the study and application of photo-ionisation detectors (PID) in gas chromatography.[1,2,4,62-76] This detector has been known for a long time,[4,62] but its construction was insufficiently convenient. The new version can be readily connected to a gas-chromatographic system, including a portable gas chromatograph, and it promises to become a standard detector for gas chromatography.[65]

The action of the PID is based on the ionisation of the molecules of the substances being analysed under the influence of ultraviolet radiation, and the recording of the resulting ion current. The sources of ultraviolet radiation which have been tested include helium (20.2 eV) and argon (11.7 eV) discharge lamps without windows,[63] hydrogen lamps with different windows transmitting quanta with energies of 9.5, 10.2, and 11.7 eV,[64,65,75] and dye lasers.[71] The use of discharge lamps without windows had the disadvantage that it was necessary to maintain a vacuum at the outlet from the chromatographic column. The most widely used source is a hydrogen lamp (10.2 eV) with an MgF_2 window, placed inside the ionisation compartment of the detector.

Unlike the flame-ionisation detector, which is destructive and requires the use of three gases (hydrogen, air, and an inert carrier gas), the PID is not destructive, since the ions recombine on the cathode and are blown from the detector; the PID requires only one carrier gas,[65,72] preferably argon or helium.[69]

The PID is a concentration detector; the areas of the peaks decrease sharply (almost exponentially[62]) with increase in the velocity of the carrier-gas stream; the optimum velocities lie below 10 ml min^{-1}, so that it appears promising to use PID combined with capillary columns, particularly when the radiation sources used are lasers, which make it possible to decrease considerably the volume of the detector.[71] The internal volume of a PID with a hydrogen lamp can be reduced to ~50 μl.[72-74] The efficiency of a system consisting of a capillary column with this PID is only 10% lower than that of a similar system with an FID. Its main characteristics (magnitude of the linear range, noise level, background current, and sensitivity) are comparable with those of the FID, and it is superior to the latter in its sensitivity to aromatic hydrocarbons.[63,72]

Under the influence of ultraviolet radiation, photochemical reactions take place in the photo-ionisation detector, and the following reactions can be regarded as the most important in the production of the signal in this detector.[77-82]

1. The primary photo-transformation — the absorption of a quantum of energy and the conversion of the molecules to the excited state.

2. The secondary reactions of the excited molecules: a) interconversion and triplet formation; b) photo-ionisation (removal of an electron and the formation of an ion pair); c) photo-decomposition (photolysis to give radicals or ions); d) photo-sensitisation (the breakdown of non-excited molecules to radicals or ions as a result of collision with excited sensitiser molecules); e) two-photon decomposition or ionisation; and f) photo-addition (photo-oxidation, photo-hydrolysis).

The probability and rate of a given reaction are determined by the energy of the photons of the excitation source, the structure and properties of the substances being analysed, and the conditions in the reactor (pressure, concentration of the substance, temperature, the presence of other substances, the flow velocity, etc.). If the energy of the exciting photons is greater than the ionisation potential of the substance being analysed, the most probable reaction is photo-ionisation, and it can be stated that this substance can be detected. In those cases where the ionisation potential of the substance is lower than the energy of the quanta, it may still be detected, although with a lower sensitivity, as a result of other reactions, for example reactions (d) and (e), whose probabilities depend on such characteristics of the molecules of the substance as the difference between the energies of the singlet (or triplet) excited levels and the energy of the ground singlet level, and the lifetime of possible triplet excited states. The Table gives as an example the values of the first adiabatic ionisation potentials and the characteristics of the excited states of various molecules. More extensive data can be found in the literature,[83-85] and also in Ref. 86, which gives the ionisation potentials for 500 organic substances.

Table. Values of the first adiabatic ionisation potential (IP), the excitation energies of the singlet (E^S) and triplet (E^t) states above the energy of the ground state, and the lifetimes of the triplets (τ) of various substances.[77,83-85 87-89]

Substance	IP, eV	E^t, eV	τ, s	E^S, eV
Methane	12.99	—	—	—
Ethane	11.65	—	—	9.15*
n-Butane	10.63	—	—	—
n-Pentane	10.35	—	—	—
n-Hexane	10.17	—	—	—
Ethylene	10.516	—	—	7.6*
But-1-ene	9.57	—	—	—
Methanol	10.85	—	—	6.9*
Ethanol	10.48	—	—	6.7
Acetone	9.69	3.38	10^{-3}	3.64
Acetonitrile	12.21	—	—	7.3*
Benzene	9.25	3.64	7	—
Phenol	8.50	3.53	—	—
Biphenyl	8.27	2.82	3.1	4.1
Naphthalene	—	2.64	2.3	3.9
Carbon tetrachloride	11.47	—	—	—
Water	12.59	4.76; 9.43	—	7.4
Oxygen	12.06	0.98**	0.05**	3—4*
Nitrogen	12.56	—	—	—
Nitrogen dioxide	12.3	—	—	—
Carbon dioxide	13.79	—	—	—
Sulphur dioxide	12.34	—	—	—

*For these substances, the values of E^S were estimated in the present work from the values of λ_{max} for the most intense absorption band in the ultraviolet range.[83-85]
**The energy and lifetime of the lowest excited singlet state are given (since the ground state is a triplet state).

A detector in which the lamp gives radiation with an energy of the quantum $h\nu$ = 20.2 eV is practically universal, and is used for the analysis of inert gases and all organic substances. A detector with a lamp for which $h\nu$ = 11.7 eV already shows some selectivity; it is not sensitive to simple gases, and gives a signal from aromatic hydrocarbons which is ~30% more intense than that from alkanes with the same

number of carbon atoms.[63] A higher selectivity is shown by detectors with lamps for which $h\nu = 10.2$ eV and $h\nu = 9.5$ eV. A detector with a lamp for which $h\nu = 10.2$ eV is not sensitive to simple gases and C_1–C_4 alkanes. C_5 and higher saturated hydrocarbons give a signal, but the sensitivity of the detector with respect to these compounds is lower than that for unsaturated and aromatic hydrocarbons. This behaviour of the detector is due to the high efficiency of the ionisation (that is the quantum yield of the photo-reaction) of compounds with a π-bond, whose electrons are localised to a much greater extent than the electrons of a mobile σ-bond.[63]

The relative molar sensitivity of the most widely encountered PID ($h\nu = 10.2$ eV) for n-alkanes (standard benzene) increases with increase in the number of carbon atoms, and that for polyaromatic compounds increases with increase in the number of benzene rings. It is greater for cyclic compounds and iso-alkanes than for the non-branched compounds. In general, for a given number of carbon atoms, the relative molar sensitivity increases in the order: n-alkanes < primary alcohols ≤ ethers < aldehydes < ketones. For substituted benzenes, electron-acceptor substituents decrease the sensitivity of the determination, and electron-donor substituents increase it.[68,69]

The fact that the relative molar sensitivity of the PID increases to a greater extent with increase in the number of π-bonds, particularly when conjugated, in the hydrocarbon molecule, compared with the increase in the number of carbon atoms has been used in a number of studies for the group identification of alkanes, alkenes, and aromatic hydrocarbons in mixtures,[63,70] and of phenols in car exhaust gases.[76] The substance at the outlet from the chromatograph is recorded simultaneously by two detectors, a PID and a universal FID, and their signals are compared. An equation has been proposed,[70] relating the ratio of the values of the normalised signals of these two detectors to the number of carbon atoms in the molecule of the substance, its ionisation potential, the number of electrons ionised in the molecule, and the energy of the photons. The experimental data almost always show sufficiently good agreement with the calculated results.

A photo-ionisation detector with interchangeable lamps has also been proposed, giving radiation with an energy of the quantum of 9.5 eV, 10.2 eV, and 11.7 eV; the lamp with $h\nu = 11.7$ eV can fulfil the role of FID.[75] Replacement of the lamps does not involve breakdown of the connections between the outlet from the column and the detector, and this is particularly important when working with brittle glass capillary columns. The ratio of the values of the normalised signals obtained with lamps with $h\nu = 9.5$ eV and 10.2 eV to the signals with the lamp with $h\nu = 11.7$ eV has been used to identify alkanes and aromatic and polyaromatic hydrocarbons in complex mixtures derived from petroleum, at the level of nanogram quantities. The higher selectivity of the PID with the lamp with $h\nu = 9.5$ eV with respect to polyaromatic hydrocarbons has been emphasised.[75]

The change in the sensitivity of the analysis of aromatic and aliphatic pesticides on going from the lamp with $h\nu = 9.5$ eV to the lamp with $h\nu = 10.2$ eV has also been used for their group identification in complex mixtures.[64]

The use as radiation source of a pulse laser emitting in the wavelength range 270–335 nm, which ensures the two-photon ionisation of substances which tend to form triplets (in particular naphthalene derivatives), has made possible the selective detection of these compounds.[71] The total energy of the two photons in the wavelength range indicated is 7.4–9.2 eV. By tuning the laser to a definite wavelength, it was possible to obtain the peak of only one substance on the chromatograms; the minimum detectable quantity was 10 pg. These chromatograms are shown in Fig. 1.

The choice of the solvent for the specimens being analysed is of considerable importance when working with PID, particularly in the determination of micro-quantities using preliminary concentration and extraction. The chief requirement which must be satisfied by the solvent is transparency in the wavelength range corresponding to the lamp used — a condition which is satisfied for substances with high values of the ionisation potentials and high energy levels of the excited states. Thus acetone, hexane, and aromatic hydrocarbons cannot be used as solvent when working with a PID with $h\nu = 10.2$ eV, since the background current which they give is too high. Only carbon tetrachloride has been found to be suitable for the analysis of chlorobenzenes in air and in human blood and urine using this PID.[67] Other workers,[63] who also used a PID with $h\nu = 10.2$ eV, used acteonitrile and spectroscopically pure methanol to extract pesticides concentrated on active carbon. Acetone has been used as solvent for the specimens in work with a laser source (3.7–4.6 eV), although it gave a peak due to possible multi-photon ionisation.[71]

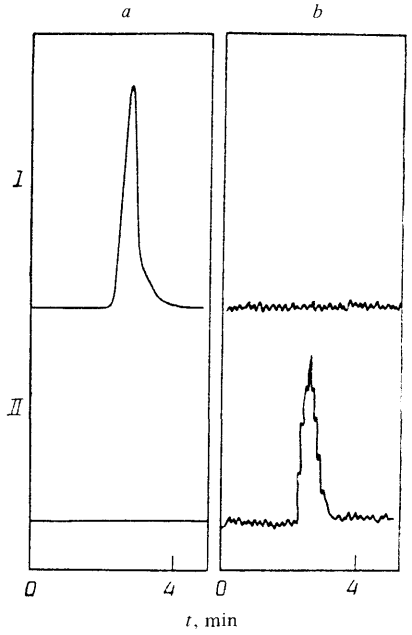


Figure 1. Chromatograms of anthracene (I) and phenanthrene (II), obtained using a PID with tunable selectivity at laser source wavelengths of 310.0 nm (*a*) and 285.0 nm (*b*). 1.3 m × 3 mm column containing 3% OV-17 on 80–100 mesh Chromosorb W; carrier-gas velocity (argon + methane in the ratio 90 : 10) 20 ml min^{-1}.[71]

The authors cited do not discuss the question of the behaviour of water in a PID. This question requires special study, since the sensitivity of gas-chromatographic detectors to water is a very important characteristic in the analysis of aqueous solutions and specimens of polluted air, water, and other environmental materials. The ionisation potential of water is greater than the energy of the quanta of the hydrogen lamps used in the PID (see Table), so that direct ionisation of its molecules is unlikely. Data have been published,

however, indicating considerable absorption by water in the ultraviolet range at 186–143 nm (6.67–8.67 eV) and 143–124 nm (8.67–10.00 eV) and the existence of a whole series of excited singlet and triplet states of its molecule.[87–89] The excited water molecules can sensitise the ionisation of other substances, eluted with it from a gas-chromatographic column. Many of these excited states of the water molecule are dissociative, and are accompanied by its breakdown to give chemically active radicals OH, H, and O, which can react with the molecules of other substances to form ions. The formation of charged and uncharged fragments of the water molecule is also possible as a result of its capture of electrons present inside the PID. All this can lead to a change in the sensitivity of the PID and an increase in its background signal at the moment when the water peak appears. Another important feature may be the deleterious influence of water vapour on the lamp window, particularly at high temperatures.

2. The Surface-ionisation Detector

The operation of the highly selective surface-ionisation detector (SID), first developed in the Soviet Union,[4,91] is based on the phenomenon of the ionisation of the molecules during their thermal desorption from a surface.

When organic substances are adsorbed on the surface of many metals, both reversible (multi-layer) adsorption and irreversible adsorption (chemisorption) take place. At high temperatures, the reversible adsorption is slight, whereas chemisorption increases with increase in temperature and with increase in the specific surface of the metal.[92] The desorption of chemisorbed molecules is often completed by their degradation, and the charge state of the species removed is determined by the nature of the charge distribution between the adsorbed molecule and the surface of the solid. For most substances, positive ions are formed.[91]

The most effective thermo-emitters for the ions of organic compounds are oxidised tungsten, molybdenum, nickel, and Nichrome, and non-oxidised tungsten, molybdenum, nickel, rhenium, and iridium. Mass spectrometry has been used to study the ability of substances of different classes to undergo surface ionisation, and the regular features of ion formation; at temperatures of 340–375 °C, amines, hydrazines, and some of their derivatives ionise readily; phosphines, arsines, and various oxygen-containing compounds (phenols, organic acids, and substances containing the benzoyl group) ionise less readily.[91,93]

Unlike many other selective detectors, the SID is selective not with respect to a heteroatom but with respect to a functional group on a heteroatom.[94] This provides the basis for the functional gas-chromatographic analysis of nitrogen-containing compounds, which involves the determination of the ratio of the heights of the peaks of each substance when chromatograms are recorded simultaneously using two parallel detectors: SID and FID. The study of 23 amines[95,96] showed that this ratio varies from 4 to 12 for primary amines, from 30 to ~300 for secondary amines, and from 700 to 6000 for tertiary amines. The existence of this clearly defined relationship between the ratio of the signals of these detectors and the type of amino-group made it possible to recommend this method for identifying amines. It is of course possible to have cases where the values of this ratio are similar for amines from different groups, but these substances generally have markedly different gas-chromatographic retention characteristics, and this is also taken into account in the identification. The selectivity of the SID with respect to amines is illustrated in Fig. 2. The SID also records the amides of carboxylic acids,[95,96] but with a lower sensitivity than in the case of the corresponding amines. The minimum detectable level is ~5×10^{-15} g s^{-1} (with respect to triethylamine), and the linear range is ~10^4–10^8. The selectivity with respect to hydrocarbons is ~10^5–10^8.[91]

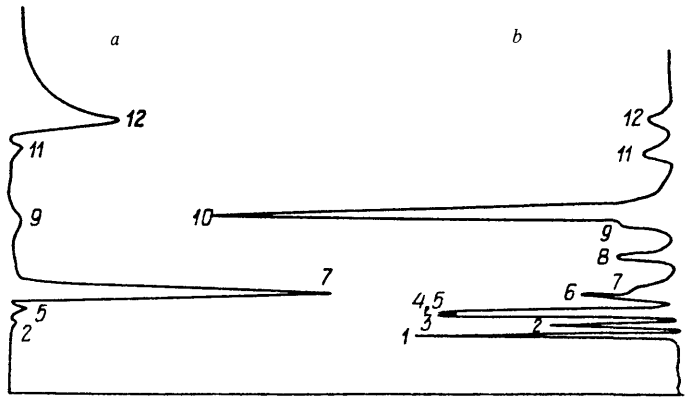


Figure 2. Chromatograms of a mixture of organic substances, obtained using an SID (*a*) and an FID (*b*) on a column containing PEG-1000 at 100 °C; emitter temperature 370 °C, velocity of air through the SID 75 ml min^{-1}. The stream of carrier gas (helium) from the column, 30 ml min^{-1}, was divided in the ratio 3:7 for the SID and the FID respectively; peaks on the chromatograms: *1*) diethyl ether, *2*) n-propylamine, *3*) methyl ethyl ketone, *4*) benzene, *5*) n-propylisobutylamine, *6*) isobutyl acetate, *7*) dipropyl-n-butylamine, *8*) di-isobutyl sulphide, *9*) pyridine, *10*) chlorobenzene, *11*) morpholine, *12*) methyl-n-octylamine, amplifier scale 1.9 × 10^{-8} A (*a*) and 10^{-10} A (*b*).[95]

The high sensitivity and selectivity of the SID make it possible to recommend it for the analysis of traces of various compounds with heteroatoms of the Va sub-group in air and other environmental materials. In general, it can be used for the analysis of substances which can be converted into amines.[91]

3. The Thermo-ionic Detector

The thermo-ionic detector (TID) was based on the flame-ionisation detector, and is familiar as a selective detector for phosphorus-, nitrogen-, and halogen-containing compounds.[1–4,23,44] Its action is based on the sharp increase in the rate of the ionisation of these substances in the presence of alkali metal vapour, so that it is sometimes called the "alkali" FID. The alkali metal salt is used in the form of a deposited layer or in the form of beads or a coating of a melt of the salt with quartz or a ceramic on a suitable holder, which are heated by a burner flame or electrically; the salt can also be introduced into the flame in the form of an aerosol.[97]

Single-flame and double-flame TID are used. In the latter, the lower part, which operates as an ordinary FID, is separated from the upper part by a grid covered with the alkali

metal salt. The products of combustion and ionisation from the lower compartment, after recombination, pass together with the alkali metal vapour into the zone of the flame of the upper burner, where specific ionisation of the molecules and fragments containing nitrogen, phosphorus, and halogen atoms takes place. Comparison of the chromatograms obtained simultaneously from the upper and lower compartments makes it possible to detect these substances in the mixtures being analysed.[3,4]

The mechanism of the ionisation in thermo-ionic detection is complex, and has not yet been fully studied. Depending on the design characteristics and operating conditions of the detector, the ionisation may take place preferentially either in the vapour phase as a result of collisions of the molecules of the substances being analysed or their fragments with the alkali metal atoms, or on the surface of an activator containing this metal. In the last case, the most important characteristics are the electronic work function and the temperature of the activator surface, and also the composition of the gaseous medium.[98]

The mechanism of surface ionisation has been realised in new TID models.[98–102] In the double-flame TID described in Refs.99 and 100, ion formation takes place on a thermo-cathode made of platinum, nickel, or stainless steel (the cathode does not contain added alkali metal, and it is heated by the flame of the upper burner). The optimum cathode temperature is established by studying the dependence of the sensitivity of the detector on the rate of supply of hydrogen and air to the upper and lower burners. The double-flame TID is 10^2–10^3 times more sensitive than the ordinary TID. The sensitivity with respect to acetonitrile and methylene chloride is 8×10^{-10} g s^{-1} with a linear range of 10^3 and a selectivity with respect to hydrocarbons of 10^4. This detector has a simple design, its operation is stable, and it can be used in a standard chromatograph (in particular, the Tsvet-104 chromatograph).

Patterson and coworkers[1,98,102] proposed a flameless TID, which operates at low hydrogen concentrations, insufficient to support a flame, or in an inert gas (nitrogen) atmosphere. The electrically heated thermo-cathode consists of a rod with a ceramic covering containing a caesium compound; it is surrounded by a cylindrical ion collector. This TID shows a selective sensitivity with respect to nitrogen- and phosphorus-containing compounds (Fig.3), depending on the concentration of the alkali metal on the surface of the thermo-electrode, its temperature, and the composition of the surrounding gas. At a temperature of 600–800 °C, selectivity is not observed; under these conditions, the source apparently becomes sufficiently hot for the formation of chemically active hydroxyl, hydrogen, and oxygen radicals, which may undergo ionic reactions on the surface and facilitate the ionisation of a large number of substances. The flameless TID has been used to identify environmental pollutants such as parathion (thiophos), methylparathion, malathion, nitrophenols, nitroglycerine, and other nitro-compounds. The minimum detectable quantity of nitrogen- and phosphorus-containing compounds is 10^{-14}–10^{-13} g s^{-1}, calculated for the heteroatom, with a selectivity with respect to hydrocarbons of 10^5; the linear range is 10^4–10^5.[98]

An apparatus and procedure for regulating the sensitivity of the TID with respect to substances of different classes by means of a displacement potential applied to the activator containing the alkali metal have been proposed.[102] The magnitude of the applied voltage determines the sign of the ions formed, which are collected by the collector (the burner jet acts as the second electrode; the activator is placed between the burner and the ion collector). The dependence of the magnitude of the TID signal on the displacement potential has been given for compounds of nitrogen, sulphur, phosphorus, and iodine. At definite values of the displacement potential, characteristic for each heteroatom, it is possible to take the signals of the corresponding substances from the chromatogram and hence to identify these substances. It is possible to record simultaneously chromatograms with and without the displacement potential.

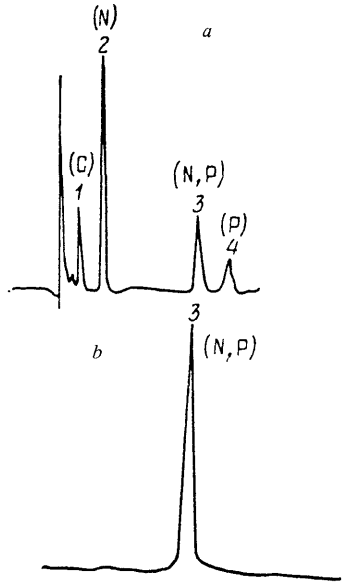


Figure 3. Comparison of the chromatograms of a mixture containing 4000 ng μl^{-1} heptadecane (*1*), 2 ng μl^{-1} azobenzene (*2*), 2 ng μl^{-1} methylparathion (*3*), and 4 ng μl^{-1} malathion (*4*) in iso-octane, obtained using a TID with a low (*a*) and with a high (*b*) concentration of caesium on the surface of the thermo-electrode in a hydrogen atmosphere containing air (*a*) and nitrogen (*b*); amplifier scale 128×10^{-12} A (*a*) and 16×10^{-11} A (*b*).[98]

The high selectivity and sensitivity of the TID, and the relative simplicity of its use, are leading to the extensive application of this detector in the analysis of micro-quantities of many harmful substances in natural materials. Methods have been described for the analysis of nitrogen-containing compounds and ammonia,[103] symmetrical triazines,[104] nitrosamines,[105] and derivatives of thiocarbamic acid.[106]

The sensitivity of the TID with respect to water has been studied;[99] although water itself does not give a signal, it decreases the sensitivity of the determination of other substances. In particular, the magnitude of the signal from a double-flame TID due to acetonitrile in the analysis of aqueous solutions was only half that in the analysis of alcoholic solutions. This was attributed[99] to a decrease in the temperature of the surface ionisation electrode.

4. The Electrical-conductivity Detector

The operation of the electrical-conductivity detector (ECD) is based on the decomposition of the substances being analysed to give ionogenic products; absorption and dissociation of these products then take place in a stream of water or other solvent, and the electrical conductivity of the resulting solution is measured continuously.[1,4,107] The decomposition of the substances can be carried out in an oxidising medium (by heating in oxygen or in air, by passing over heated copper oxide, etc.) or by heating in a stream of hydrogen in the presence of a catalyst. Organic substances containing sulphur, halogen, and nitrogen atoms in the oxidising version give mixtures CO + CO_2, SO_2 + SO_3, NO_x, HX, and H_2O, and in the reducing version NH_3, H_2S, HCl, CH_4, and H_2O.[108,110]

If conditions are created for dissolving carbon dioxide (oxidising version), the ECD operates as a universal detector. In this case the signal is proportional to the number of carbon atoms in the molecule of the substance being analysed. This detector is particularly convenient for chromatography in a stream of water vapour.[109] It is also possible to create conditions under which the measuring part of the detector contains only one of the above products, and the ECD then becomes exceptionally selective. Work in recent years has been devoted mainly to improving the selective version of this detector.[1,111–115]

The Hall detectors (Tracor 700) produced commercially have a high sensitivity and a small internal volume, so that they can be used with capillary gas-chromatographic columns and coupled with another detector, for example an FID.[1,114,115] The advantage of the latest model (700 A) over the earlier model is that it can be tuned for the selective detection of any of the following classes of substance: halogen-, sulphur, and nitrogen-containing compounds, hydrocarbons, and nitrosamines.[115]

The main parts of the ECD are the reactor with the furnace for converting the substances being analysed into the compounds detected; the absorber, in which the reaction gases are brought into contact with the solvent (de-ionised water, alcohol, or a suitable mixture); the separator for separating the solution from the insoluble gases; the cell for measuring the electrical conductivity; the system for circulating and regenerating the solvent; and electronic circuits for controlling the temperature of the reactor furnace and for measuring the electrical conductivity of the solution in the cell. In the 700 A model,[112] the reactor consists of a nickel capillary, which acts simultaneously as the catalyst; a quartz capillary can also be used. A scrubber is placed between the reactor and the measuring cell to extract interfering components from the mixture of decomposition products. The use of a bipolar pulse voltage, applied to the electrodes in the 700 A model (the duration of the pulses is one tenth that of the intervals between them) makes it possible to avoid such undesirable phenomena in the electrical conductivity measurement as polarisation of the electrodes, the capacity effect, and heating of the cell.

The magnitude of the ECD signal is determined primarily by the concentration of the product being recorded in the cell, its dissociation constant in the solvent, and the equivalent ionic conductivity due to the cations and anions. Selectivity of action is achieved by the correct choice of chemical decomposition reaction and absorption conditions, under which the required product is readily soluble and readily dissociated to give ions, while other substances either are insoluble in the solvent used or do not ionise in it.[1]

In the analysis of sulphur-containing compounds, the optimum conditions correspond to the combustion of the substance in oxygen or air at 800 °C in a nickel reaction tube with the use of pure methanol as electrolyte.[112,114,115] The hydrogen chloride which may be obtained from chlorine-containing impurities is removed in the scrubber by the action of silver; oxides of carbon are sparingly soluble in the alcohol, and their quantity is also restricted by removing the excess of solvent before introduction into the reactor. The yields of soluble oxides of nitrogen (from possible traces of nitrogen-containing compounds) are slight under these thermal decomposition conditions.

For the detection of nitrogen-containing compounds, the optimum conditions correspond to the reducing version; with decomposition in a nickel reactor, all nitrogen-containing compounds are detected, but when a quartz or gold reaction tube is used, nitrosyl compounds can be determined selectively.[1] The electrolyte in the absorber consists of a mixture of water and n-propanol (1:1). Hydrogen chloride and hydrogen sulphide obtained from chlorine- and sulphur-containing impurities are removed in the scrubber by the action of a suitable base; the ionisation constant of methane is too low, and it does not give a signal.

In the analysis of halogen-containing compounds using the ECD under both oxidising and reducing conditions, the hydrogen halide is formed, but reduction in a quartz tube at 800–900 °C gives a more favourable composition for the side products, which does not require the use of a scrubber.[1]

The molar signal of the ECD is directly proportional to the number of corresponding heteroatoms in the molecule of the substance being analysed, so that the ECD is particularly sensitive to compounds containing a large number of sulphur, halogen, or similar atoms. The detection limit is $(2-4) \times 10^{-12}$ g s^{-1} for N-containing compounds, 2×10^{-12} g s^{-1} for S-containing compounds, and 5×10^{-13} g s^{-1} for Cl-containing compounds, calculated for the heteroatom; the linear range is 10^4 for N- and S-containing compounds, and 10^5–10^6 for Cl-containing compounds. The selectivity with respect to hydrocarbons is 10^5–10^6.[1]

The ECD has been used successfully for the gas-chromatographic analysis of hydrogen sulphide and sulphur dioxide in air[108,112] and natural gas,[1] nitrogen- and sulphur-containing compounds in petroleum products,[114] nitrosamines, pesticides with a high sulphur content (malathion, parathion, trithion, etc.), polychlorinated biphenyls and other chlorinated insecticides in natural materials at the level of several nanograms or below in the specimen.[1,112,115]

5. Detectors Based on Electron Capture

The action of a group of selective gas-chromatographic detectors — electron-capture, aerosol-ionisation, plasma chromatographic, and mas-spectrometric with chemical ionisation — is based on similar ionisation processes, chief of which is the capture of thermal electrons by the molecules of the substances being analysed. In the first two detectors, the useful signal is the change in the concentration of electrons in the measuring cell at the moment when the substance being analysed passes through, and in the other two detectors the composition and properties of the ions formed are studied. The plasma chromatograph records the spectra of the mobility of the ions, and the mass spectrometer with chemical ionisation analyses the composition of the positive or negative ions.

The source of the electrons in these detectors is most frequently the β-radiation of radioactive elements (for example tritium or ^{63}Ni). The energy of the electrons of the β-rays, equal to 17.6 keV for tritium and 67 keV for ^{63}Ni, is too high to ensure the electron capture mechanism; the energy is lowered by flushing the ionisation compartment with a suitable carrier gas, which has a high electron affinity and a high

ionisation potential; this gas may be nitrogen, noble gas (argon, helium) containing 5–10% methane, and other gases and mixtures. As a result of elastic and inelastic collisions with the atoms and molecules of the carrier gas at atmospheric pressure, the electrons of the β-radiation lose their excess energy until their energy becomes suitable for reactions giving ion pairs: positive ions from the molecules (or atoms) of the carrier gas, and low-energy electrons (0–10 eV).

Other reactions may take place in parallel between electrons, ions, and neutral species (additives in the carrier gas, impurities, etc.). By selecting the carrier gas, its pressure, the magnitude and character of the voltage at the electrodes, the temperature, the velocity and direction of the flushing gas, and the design of the ionisation compartment, it is possible to achieve the required distribution of electrons with respect to energies in these detectors and to create conditions for particular ionisation reactions in them.

6. The Electron-capture Detector

The principles of the operation and practical application of the electron-capture detector (ECpD), which is the most widely encountered selective gas-chromatographic detector, have been examined in detail in many papers, monographs, and reviews.[1–3,44,110,116–128] Recent work has involved a detailed study of the mechanism of the reactions taking place in the ECpD and the production of the signal, and the search for ways of increasing the selectivity and sensitivity, extending the linear range, decreasing the volume, and optimising the design and operating conditions.

The theory of the ECpD[1,118,119] is based on the idea of an ideal-mixing reactor; it is assumed that the current of the detector is due entirely to electrons; the latter may disappear as a result of capture by the molecules of the substances being analysed and by recombination with positive ions, and also as a result of the wall effect and flushing.

According to Ref.117, the magnitude of the measured current is determined not only by the electron density but also to a large extent by the field of the negative ions, which are localised close to the cathode under the influence of the counter current of the flushing gas.

New data on the composition of the ions and their behaviour inside the ECpD, obtained using a mass-spectrometric detector with chemical ionisation (MSCI),[122,129] plasma chromatography (PC),[130,131] and a system of two ECpD connected in series and operating under different supply conditions,[126] show better agreement with the field theory of electron-capture detection. In particular, it has been suggested that in the detector there is a centrally located zone of electrons; under pulse supply conditions, this zone becomes broader with increase in the time interval between the pulses, and during the pulse all the electrons leave the cell. In some cases it has been possible to estimate the contributions of the space charge of the negative ions[126] and the current created by the selective migration of positive ions[128] to the recorded ECpD signal.

The molar ECpD signal increases with increase in the number of atoms or functional groups with an electron affinity in the molecule of the substance being analysed, and a synergistic effect is observed when a certain number has been reached. This feature, and also the tendency for the relative sensitivity to be influenced by various factors such as the presence of impurities in the carrier gas, the electric field potential, the temperature of the detector, etc., make it difficult to carry out the theoretical calculation of the relative molar sensitivity coefficients, so that it is necessary to calibrate the detector in each specific case, although a whole series of correlations exists.[121,132,133]

A study of the influence of traces of oxygen in the carrier gas on the sensitivity of the ECpD with respect to various chlorinated hydrocarbons showed that the addition of 0–3.5% oxygen to the carrier gas leads to a sharp increase in the intensity of the signal of monochloroalkanes,[134] whereas the signal from polychlorinated hydrocarbons changes little. An increase in the sensitivity in the presence of oxygen has also been detected for dichloromethane,[136] carbon dioxide,[135] and polycyclic aromatic and related hydrocarbons,[137,138] and the difference in the magnitude of the signals obtained in the presence and in the absence of oxygen can be used, for example, for the qualitative identification of the structural isomers of polycyclic aromatic hydrocarbons in air.[138] Sensitisation of the ECpD is also observed when N_2O is added to the carrier gas.[139–142] This was attributed to reversible reactions of O_2 and N_2O with slow electrons, leading to the formation of the negative ions O_2^-, O^-, NO^-, etc., and if the substance can react with these species to give stable secondary negative ions, its appearance in the detector in fact leads to a decrease in the electron concentration, that is to the appearance of a signal.

An ECpD signal can be obtained from normal saturated hydrocarbons by increasing considerably the electric field by raising the voltage at the electrodes and using highly pure argon as carrier gas. With increase in the kinetic energy of the electrons, there is a change in the ionisation mechanism (use of the Penning effect).[143] These techniques lower the selectivity of the ECpD in the general sense, but they may be useful for solving particular problems, for example for determining Kovacs indices.[139,143] Usually, however, in the determination of retention indices in work with the ECpD, the standards used are some homologous series of electron-acceptor substances, such as esters of trichloroacetic acid[144] and n-bromoalkanes;[145] the latter have also been recommended for standardising the ECpD signal in quantitative analysis.

The introduction of electron-acceptor substituents into the molecule of the substance being determined is widely used to increase the sensitivity of the ECpD.[1,146] For example, the replacement of the chlorine atom in the methyl chloride molecule by an iodine atom leads to an increase in the signal by a factor of 10^4 with a methyl iodide detection limit of 3.1×10^{-14} g; the detection limit for N,N'-dipentafluorobenzoylpentafluoroaniline is 1.6×10^{-19} mole ($\sim 10^{-16}$ g).[147] The introduction of electrophors, however, should not lead to a significant decrease in the volatility of the substance, hindering its analysis.

Examples of the use of gas chromatography with an ECpD include the determination of micro-quantities of peroxyacetyl nitrate,[148] the chlorides of phosphorus, silicon, tin, and germanium, sulphur hexafluoride, phosphine, etc.[149] in air; 2,4-dichlorophenol and various forms of hexachlorocyclohexane in soil and plants;[150] and water in solvents.[151] The improvement of the design and the optimisation of the operating conditions of the ECpD have made it possible to extend the linear range to $(1–5) \times 10^3$,[152] improve the stability,[153, 154] decrease the volume, and use the ECpD in combination with capillary columns.[155,156] A method has been proposed for purifying a solvent (n-pentane) from contaminants which give a signal with this detector.[157]

7. The Aerosol-ionisation Detector

The action of the comparatively new aerosol-ionisation detector (AID) is based on the formation of large aggregates of molecules of the substance being analysed and some reagent, in order to increase their ionisation cross-section

when the ECpD is used.[158–160] AID models in which the processes of aerosol formation and ionisation either take place in different compartments[159] or are combined in a single compartment[160] have been described. The concentration of the reagent for generating the aerosol in the carrier gas (air) is 10^{-2}–10^{-3} vol.%. This gives sol particles containing tens of molecules. The temperature of the detector is determined by the stability of the aerosol used.

The development of the theory of this method has made it possible to calculate the minimum detectable quantity of substance from data on the values of the saturation current, the coefficient of adhesion of the ions to the aerosol particles, and the number of aerosol particles per unit volume.[159,160] The AID is selective and sensitive with respect to halogen-containing hydrocarbons, amines, organometallic compounds, SO_2, SO_3, NO_2, etc.[159,160] The reagents for the formation of the aerosol particles are selected with allowance for the chemical properties of the substances being analysed; trifluoroacetic acid is used for compounds with basic properties, and amines for acidic compounds; halogen-containing hydrocarbons are passed over heated copper oxide, and organometallic compounds are subjected to thermal decomposition. Additional reactions are also used to convert the substances being analysed into strong acids or bases, for example SO_2 into SO_3 with subsequent reaction with an amine. The linear range for all substances is 10^2; the limit of detection for different groups of substances varies in the range 10^{-11}–10^{-10} g s^{-1}.[158–160]

8. Plasma Chromatography

The name itself of this detector reflects the principle of its operation: in it, the plasma formed by the ionisation of the molecules of the substance being analysed is separated, and the ratio of the ions present in it is determined; this is essentially analogous to chromatography.[130,131,161–166]

The mechanism of operation and the fields of application have been reviewed.[161] The original ions are generated as a result of the interaction of the molecules of the carrier gas (purified nitrogen or air containing water vapour) with electrons, the source of which is ^{63}Ni foil. In the carrier gas (nitrogen), the positive nitrogen ions formed initially react with water molecules to give the ions NH_4^+ and NO^+ and the cluster ions $(H_2O)_nH^+$, $(H_2O)_nNO^+$, etc. When the carrier gas is air, the negative ions O_2^-, O_4^-, $(H_2O)_nO_2^-$, CN^-, CO_3^-, and CNO^- are also formed.[130,131,161,162,166] The relative concentration of the ions and their degree of hydration depend on the concentration of water vapour and on temperature. In addition to ions, the PC ionisation compartment also contains electrons with an energy of ~0.5 eV.[131,161,162,164]

The molecules of the substances being analysed enter the ionisation compartment and interact with the above ions and electrons to give new quasi-molecular and simple dissociative ions. The mixture of ions and carrier gas is directed for separation into a drift tube (usually by pulses of duration 0.25 ms at time intervals of 0–20 ms). The drift tube is flushed continuously with an additional counter current of gas (nitrogen, air, sulphur hexafluoride) at atmospheric pressure. The rate of movement of the individual ions in it, and in some cases the composition of the ions[162,166] depend not only on their mass and charge and the field intensity (as in the analyser of the mass spectrometer) but also on the size of the ions and on the mass, size, and polarisability of the molecules of the drift gas. The successive recording of the ions at the outlet from the drift tube gives the spectrum of their mobility, characteristic for each substance. To observe the mobility of large ions, it is preferable to use a drift gas with a high molecular mass, such as sulphur hexafluoride.[162]

The mobility spectra of ions with a mass of up to 400 are usually obtained in 20 ms. They are recorded using digital signal averagers, which make it possible to carry out the summation of several thousand such spectra in several minutes and present them in convenient form. The spectra are interpreted by comparing them with the spectra of the individual compounds, obtained under the same conditions, and also by comparing them with analogous spectra obtained by the MSCI method.[161,162]

PC is specially designed for the analysis of tracer quantities of materials (10^{-8}–10^{-14} g) and is more sensitive than, for example, the FID. Large specimens overload the detector, and as a result of secondary reactions the interpretation of the spectra is difficult. An important feature is that PC makes it possible to obtain the spectra of the mobility of positive and negative ions, and this makes it more informative. The ratio of the intensities of the spectra of the positive and negative ions provides an additional specific characteristic of a substance.

As in the sensitised ECpD, in PC the negative ions are formed only by substances which are electron acceptors, and the spectrum of the mobility of the negative ions makes PC selective with respect to the same classes of compound. There are both associative and dissociative mechanisms for the addition of an electron.[131,161] Thus monohalogeno-derivatives of aromatic hydrocarbons undergo dissociative splitting, and nitrobenzene shows only associative interaction, giving a negative molecular ion, whereas the halogen derivatives of nitrobenzene and nitrotoluene react by both mechanisms. There is a correspondence between the PC and MSCI data with identical reaction gases for alkanes, halides, nitroaromatic compounds, etc.[161] At the same time, these methods show appreciable differences. One of these is the ease of formation of the groups of ions M_2H^+ and M_3H^+ by polar substances (alcohols, esters, etc.[161]) in PC.

PC has been used for the qualitative identification of alcohols, alkyl halides, substituted and polynuclear aromatic compounds, aliphatic N-nitrosamines, and pesticides, various isomers of fluorotoluenes and picolines, and the methyl esters of toluic and phthalic acids.[131,161,165] There are as yet comparatively few published data on quantitative analysis.[130,161]

9. Mass Spectrometry with Chemical Ionisation

The combination of a gas chromatograph with a mass spectrometer and a computer is widely used to identify substances in complex multi-component mixtures, and various countries now produce standard commercial instruments: chromatograph–mass–spectrometers, fitted with libraries of mass spectra and computers.[44,167,168] Like the Fourier transform infrared spectrometer, the chromatograph–mass–spectrometer can act as a universal detector if the chromatogram is recorded with respect to the total ion current, or as a selective detector, if only ions with definite masses are recorded. MSCI at a low pressure ($\leq$ 1 mmHg) and at atmospheric pressure makes it possible to combine the fast action and informative character of mass spectrometric technique with the selectivity of detectors based on ion–molecule and electron–molecule interactions.[169–176] The spectra obtained by MSCI for the most part contain the peaks of the molecular ions and fragments of the molecules being analysed, which are simpler than the ions formed in the ordinary mass spectrometer as a result of the bombardment of the specimens by electrons in a high vacuum. It is possible to record the spectra of the positive and negative ions separately.

The selectivity of MSCI, as in the case of PC and the sensitised ECpD, can be controlled by creating the necessary set of working ions and electrons in the ionisation compartment

by appropriate selection of the source of primary electrons, the carrier gas (most frequently nitrogen), and the reagent gas (methane,[167,172] oxygen,[173,174] oxygen and methane,[175] ammonia,[176] etc.). The source of electrons in MSCI is ^{63}Ni at atmospheric pressure,[169,173,174] and a heated rhenium cathode at low pressure.[170,171,175,176] The composition of the working ions in the ioniser also depends on the concentration of traces of water and other substances in the gases used and on temperature.[130,169] The normal operation of the mass analyser in MSCI requires powerful vacuum pumps (for example two pumps with a speed of 800 litre s^{-1} are used simultaneously.[173])

MSCI combined with capillary gas-chromatographic columns has been used to analyse micro-quantities of aliphatic alcohols[172] and also polychlorinated and polybrominated benzenes in foodstuffs.[173–175] It is possible to determine selectively the most toxic 2,3,7,8-tetrachlorobenzo-*p*-dioxin in the presence of a large number (21) of isomers of this compound and other related substances.[174] The successive use of NH_3 and ND_3 as reaction gas made it possible to identify primary, secondary, and tertiary amines in a complex mixture of hydrocarbons and nitrogen-containing compounds (from the increase in the mass of the deuteriated molecular ion in the spectrum of the positive ions, compared with the protonated ion).[176]

MSCI is used mainly for the qualitative identification of substances in complex mixtures. The minimum detectable quantities of the substances being analysed is 10^{-9}–10^{-12} g.[169,172,174] Together with mass spectrometry, MSCI is also used to study the composition of the ions in other detectors (ECpD, PC, AID, and SID) to obtain a deeper understanding of the mechanisms of ionisation in these detectors and to determine the optimum conditions for their operation.[94,130,161,162]

IV. SOME CHARACTERISTIC FEATURES OF WORK WITH SELECTIVE GAS-CHROMATOGRAPHIC DETECTORS

The use of selective detectors raises a number of specific problems. One concerns qualitative analysis from the Kovacs indices, since almost all selective detectors are insensitive to n-paraffins, which provide a series of standards in this identification system. The introduction of phosphorus, sulphur, halogen, and other indices, and the use of reaction gas chromatography, are helping to solve this problem.[145,177,178] To increase the reliability of identification, selective detectors are often used in combination with universal detectors.[23,179–182] Success in these cases is to a large extent determined by the quality of the connections.[183,184]

The fields of application of many selective detectors overlap; for comparison of their data, it is proposed that selectivity coefficients for selected substances be normalised under standard conditions.[183]

The principal requirements to be satisfied by the gas-chromatographic system in work with highly sensitive selective detectors reduce to the use of thermally stable materials and sorbents, which do not contain elements or groups to which the given detector is sensitive. Dexsil 300, SE-30, OV-225, and other silicones, PEG-20000, and Versamid-900, deposited in small quantities on silanised inert carriers, are used as stationary liquid phases. Concentration is carried out using porous polymers and graphitised carbon black. Increased demands are made on the purity of the gases used.

Selective gas-chromatographic detection is now at the stage of intensive development. The appearance of fundamentally new methods has been accompanied by the revival of older and simpler methods on the basis of new techniques using new materials. The possibilities opened up by the use of selective detectors for the gas-chromatographic control of pollution in the environment are acquiring particular importance in connection with the improvement of measures for its protection.

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