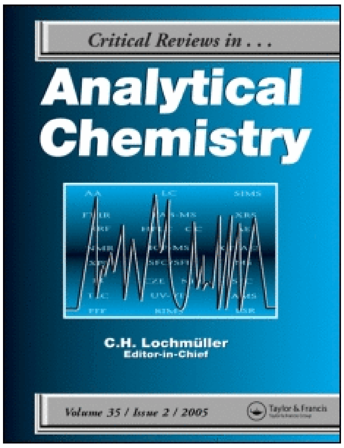

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Flame-Ionization Detection with Nontraditional Flame-Forming Agents

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FLAME-IONIZATION DETECTION WITH NONTRADITIONAL FLAME-FORMING AGENTS

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I. INTRODUCTION

Hydrogen flame ionization detection was invented more than 25 years ago in Australia by McWilliam and Dewar.[1-3] Independently, the same detection method was investigated by Harley and Nell and Pretorius[4,5] in South Africa. It is interesting that during 1958 two articles entitled *"A Flame Ionization Detector for Gas Chromatography"* were reported in *Nature* by these authors.

Dr. I. McWilliam, one of the authors, wrote in 1957:

> We have found that, surprisingly, the electrical conductivity of a hydrogen flame or the flame of a burning mixture of hydrogen and an inert gas such as nitrogen, burning in oxygen or diluted oxygen as air, is increased to a marked degree by adding the organic gas or vapour to the stream of hydrogen (or hydrogen mixed with inert gas) flowing to the burner, or by adding the organic gas or vapour to the oxygen in which the flame is burning. Accordingly, it is the principal object of the present invention to provide an apparatus whereby this increase in electrical conductivity may be used to detect the presence of organic gases or vapours.[1]

In the modern practice of gas chromatography, a highly sensitive flame ionization detector (FID) is currently used as the major method of detection. The FID can be used successfully in gas, liquid, and supercritical fluid chromatography.[6-10]

In Table 1 we present an estimation of the use of various detector types as they were reported in publications of the 1982 *Journal of Chromatography*. As can be inferred from this table, the FID has found application in more than 50% of all the 1982 articles. Such wide use of this detector type, when compared to other detectors, can be explained by the following advantages: (1) an almost universal response together with high sensitivity to organic compounds, (2) a wide linear dynamic range, (3) a relative independence of its characteristics on design and environmental conditions, (4) low effective volume, (5) fast response (small time constant), and (6) modest requirements for stability of the current supply.

The FID consists of an ionization chamber with a hydrogen flame serving as an ionizer. A metal burner usually serves as one electrode, with a second (collector) electrode being placed above the burner (see Figure 1A). Occasionally, a parallel system of electrodes can also be used (see Figure 1B). A voltage source and an electrometer that measures current between the detector electrodes are connected to the outer circuit of the detector electrodes. Hydrogen and air are constantly supplied into the chamber to maintain combustion. Hydrogen mixed with the carrier gas enters the detector through the burner, while air is supplied into the space surrounding the burner through a diffuser.

A simplified schematic diagram of the total gas chromatograph, including the FID, is shown in Figure 2. It should be noted that, in general, three reservoirs are used that contain

Table 1
APPLICATION OF VARIOUS TYPES OF DETECTORS IN GAS CHROMATOGRAPHY

Detector type	Application (%)
Flame ionization	54
Mass-spectrometric detector	20
Thermal conductivity cell	8
Electron capture detector	4
Flame-photometric detector	4
Other types of detectors	8

Note: Based on a survey of papers published by *J. Chromatogr.* in 1982.

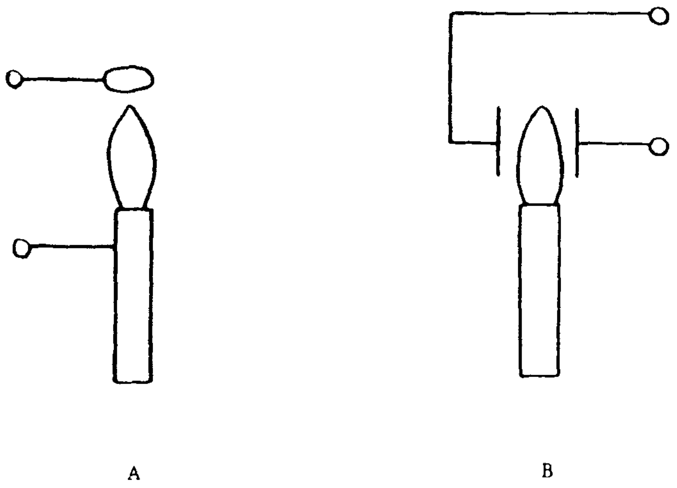

FIGURE 1. Schematic of the FID. (A) An upper collector electrode arrangement; (B) parallel electrode arrangement.

pressurized gases. These three reservoirs contain hydrogen, which is required as a flame-forming agent to feed the detector; air (or oxygen); and the carrier gas to supply the gas chromatographic column.

An air compressor can also be used to supply the FID instead of a high-pressure air cylinder. In addition, hydrogen can alternatively be obtained from an electrolytic unit. The task of replacing an inert carrier gas (nitrogen or helium) with hydrogen may be more involved. When dealing with certain reactive solutes, the use of hydrogen may not be advisable. However, to employ the same gas both as the carrier gas and as a flame-forming agent is advantageous in simplifying operation of the instrument.

II. FUNDAMENTALS OF HYDROGEN FLAME IONIZATION DETECTION

The principle of the hydrogen FID is based on a sudden increase in the electrical conductivity of a hydrogen flame when a trace organic compound enters the flame.[1-5,7-9]

Typically, the resistance of the interelectrode gas space is quite high (10^{13} to $10^{14}\Omega$), while the detector current is small (10^{-12} to 10^{-11} A). The detector noise current is primarily

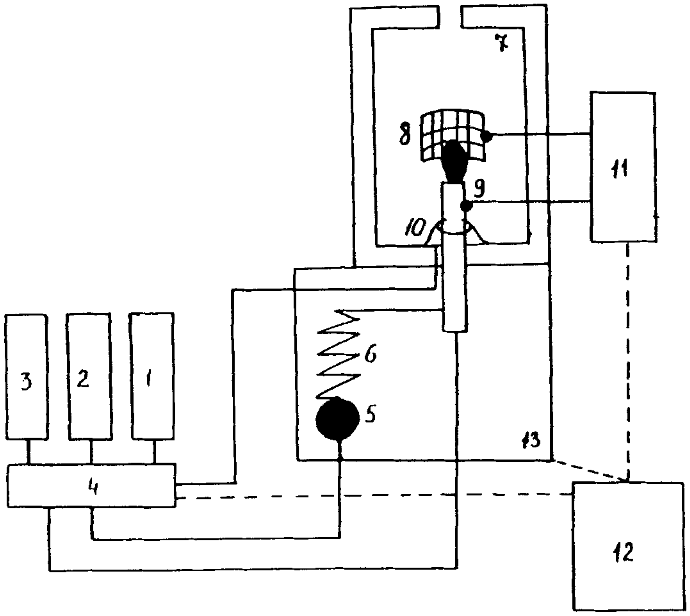

FIGURE 2. A simplified schematic diagram of the gas chromatograph with a FID. (1) High-pressure cylinder with a compressed gas oxidizer (air, oxygen), (2) high-pressure cylinder with compressed carrier gas, (3) high-pressure cylinder with hydrogen, (4) gas preparation module, (5) sample injection device, (6) chromatographic column, (7) detector housing, (8) collector electrode, (9) burner, (10) diffuser, (11) amplifier, (12) control device, (13) thermostat.

due to the ionization of organic impurities contained in the carrier gas, hydrogen, or air. The number of ions in the flame increases drastically when organic compounds eluted from a chromatographic column enter the flame together with the carrier gas and hydrogen. The resistance of the interelectrode space drops, and an increased ionic current is registered by the electrometer.

The mechanism of ion formation in a hydrogen FID has been explained from mass-spectroscopic investigations after combustion[8,10-14] by

1. Thermal dissociation of organic molecules in the preliminary heating zone, and the formation of reactive intermediates (for instance, formation of CH· radicals as a result of cracking)
2. Oxidation of reactive compounds to CHO^+ ions

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

3. Formation of hydroxonium ions, which, according to mass spectrometric data, are the main carriers of positive charge in the flame

$$CHO^+ + H_2 \rightarrow H_3O^+ + CO$$

The above mechanism of ion formation (thermal destruction with a subsequent chemionizaton) is in agreement with the fact that the molar sensitivity of the hydrogen FID is proportional to the number of carbon atoms in hydrocarbon molecules. The detector signal per unit mass is almost the same for various compounds within the homologous series.

It is interesting to note that the signal proportional to the number of carbon atoms in a molecule can be obtained[12] only for the electrodes arranged as in Figure 1A and not for the electrodes as shown in Figure 1B.

Many important results explaining the electrical behavior of the FID in terms of reactions occurring in the flame have been reported by Australian scientists. According to computer-simulation data by Nicholson,[13] alkanes, alcohols, and ethers decompose in an atmosphere of hydrogen to yield methane. For each additive substance, the calculated yield of methane equals the experimentally determined relative ionization yield. The response characteristics of the FID follow from this, provided that the additive decomposition and ionization reactions occur in separate regions of the flame. Using carbon monoxide as the flame-forming agent (instead of hydrogen) gives FID a very different response, but the methane yield and the ionic yield are still equal. In the cooler outer region of the FID, the current is carried by cluster ions $H_3O^+ \cdot n(H_2O)$ when the collector electrode is negative. These results were obtained through mass spectrometric and mobility analyses of the flames. Mobility measurements yielded an apparent n of 2.2, corresponding to an equilibrated mixture of hydrates that behave as single ions.[14]

For a positively charged collector, there are always at least two ions carrying the current: the predominant CO_3^- ions and HCO_4^-, which are not hydrated.[16] Removal of the trace of additive substance from the gas stream is very different in premixed and diffusion flames. In the former, the additive substance is largely oxidized; in the latter, it is pyrolyzed in an excess of hydrogen. In the FID there is enough time for the additive to be completely reduced to methane before it reaches the region where ionization takes place. Linearity of ion current with concentration and equal-per-carbon response are consequently observed. In the upper part of a flame, several ions are observed.[17]

An earlier static treatment of the electric current from the diffusion flame in a FID has been extended to include time-dependent currents. The nonlinear differential equation describing the electric field in space outside the flame has been solved analytically for a class of problems in which a time-dependent potential difference is switched on after a static current has been established.[18]

Schaefer has reported that response in the FID is dependent upon the temperature of the hydrogen diffusion flame. The maximum response is at about 2100°K.[18]

The most commonly used nitrogen-diluted flame giving the optimum ion current has a compostion index of about $I_d = 0.21$

$$I_d = F\,(H_2)/F\,(N_2) + 3.5\,F\,(H_2)$$

where the compositions are usually expressed in flow-rate units. For the initial gas temperature of 393°K, this flame has an experimentally determined temperature of about 2153°K. The temperatures of flames having diluents other than nitrogen (e.g., helium, neon, argon, and carbon dioxide) were all shown to be approximately the same as the temperature of the nitrogen-diluted flame. The composition giving the maximum ion current isotherms for the nitrogen-diluted micro-premixed flame and the diffusion flame is documented in Reference 19.

In concluding this part of the review, we would like to summarize some advances in the investigation of the nature of the hydrogen flame detector in accordance with a report by Nicholson.[17] He offered an explanation of the electrical behavior of the FID in terms of the reactions occurring in the flame. The relationships requiring explanation are the linearity of ion current with additive concentration, the equal-per-carbon response, and the universal relationship discovered by Bolton and McWilliam[20] between ion current and applied voltage. In the cooler outer region of the FID, the current is carried by cluster ions, $H_3O^+ \cdot n(H_2O)$, when the current is negative; mobility measurements give an apparent n of 2.2 corresponding to an equilibrated mixture of hydrates that behave as a single ion. For a positive collector,

Table 5
EXPLOSION HAZARD OF SOME FLAME-FORMING AGENTS

Compound	**Spontaneous combustion temperature (°C)**	**Gap between plane surface (25-mm long) at which the rate of explosion transmission is 50% (mm)**
Hydrogen	Above 450	Less than 0.35
Water blue gas	Above 450	Less than 0.35
Carbon disulfide	Above 100—135	Less than 0.35
Ammonia	Above 450	Less than 1.0
Carbon monoxide	Above 450	0.65—1.0

From instructions for manufacturing dangerously explosive and mining equipment, Energiya, Moscow, 1969. With permission.

Table 6
GAS AND VAPOR VISCOSITY AT A PRESSURE OF 1 ATM AND TEMPERATURE OF 100°C (HYDROGEN VISCOSITY IS 1.00)

Compound	**Viscosity (rel. units)**	**Molecular mass**
Hydrogen	1.00	2
Nitrogen	2.02	28
Ammonia	1.24	17
Argon	2.63	40
Helium	2.22	4
Oxygen	2.36	32
Superheated steam	1.24	18
Carbon monoxide	2.04	28
Carbon dioxide	1.08	44
Carbon disulfide	1.22	76
Butane	0.92	58
Methane	1.29	16
Propane	0.98	44
Ethyl alcohol	1.06	46
Methyl ether	1.14	32
Ethyl ether	0.93	74

From instructions for manufacturing dangerously explosive and mining equipment, *Energiya*, Moscow, 1969. With permission.

Detection sensitivity toward different organic compounds by the FID using carbon monoxide as a flame-forming agent was investigated in this laboratory.[29] Table 8 summarizes the data on the relative detection sensitivity for paraffins, aromatic hydrocarbons, and their chlorine derivatives.[29] As shown by the acquired data, the sensitivity of the FID for hydrocarbons is approximately the same with both carbon monoxide and hydrogen. It is approximately twice as large for chlorobenzene, chloroform, and other chlorinated hydrocarbons. A 6.5-fold increase is experienced with carbon tetrachloride when using carbon monoxide. It is of interest to note that the sensitivity of the carbon monoxide detector is enhanced with an increase in the total carbon monoxide flow, i.e., when using carbon monoxide as both a flame-forming agent and a carrier gas.

Table 2
DUAL USES OF SUBSTANCES AS FLAME-FORMING AGENTS AND CARRIER GASES

Demands Flame-forming agent in FID	 Carrier gas
The flame electrical conductivity of flame-forming agent must be sufficiently low	The carrier gas viscosity must be small
The electrical conductivity of the flame must increase considerably when traces of an analyzed substance enter the flame	The sorption-displaceable properties must be high
The detector signal must be directly proportional to the mass flow of a substance entering the detector	The chemical activity must be small
Detector must have a wide linear dynamic range	
Operation of the detector must be simple	

Note: Explosive hazards must be as low as possible. Storage capacity should be high.

for three fuel vapors. Consequently, the analytical properties of the hydrogen flame were found to be paralleled by the flames of carbon monoxide, ammonia, formic acid, carbon disulfide, and formamide.

While comparing any of the above nonhydrogen flame-forming agents, it is necessary (in accordance with a complex approach to evaluation of these compounds) to consider various general characteristics (explosion hazard, viscosity, solute diffusion coefficients, etc.). Tables 5 and 6 provide such data. As evidenced by the tables, certain nonhydrogen media are attractive for use. We now analyze certain nonhydrogen flame-forming media agents in more detail.

IV. GASEOUS FLAME-FORMING AGENTS

A. Carbon Monoxide

Long ago, carbon monoxide was among the first flame-forming agents suggested by Baddiel and Cullis.[26] They considered it superior to hydrogen in reducing the detector corrosion problems due to some combustion products of halogenated solutes.

However, the most important reason for applying carbon monoxide as a flame-forming agent appears to be an increased detection sensitivity toward halogen-containing organic compounds, as compared to the hydrogen FID. Table 7 contains data reported by Onkiehong[59] on the quantitative analyses obtained with the hydrogen flame detector. The coefficient "C" is the correction factor for the peak area in determining a mixture composition. Multiplying the experimentally determined peak area by the coefficient "C", one obtains the corrected peak area, which is used to determine the weight content of the components analyzed by the standardization method.[60] As seen from Table 7 chlorine-containing compounds, e.g., chloroform and carbon tetrachloride, have lower detection sensitivity than corresponding hydrocarbons by a factor of 10 to 12.8.

Figure 3A shows a chromatogram obtained from a mixture of fluoromethane and fluorochloromethane, using carbon monoxide as a flame-forming agent. A 260-cm × 4-mm column packed with 20% dinonylphthalate on C-22 firebrick was used for the separation. To detect such a mixture, the FID with a 2-mm burner diameter and with a carbon monoxide flow rate of 35 ml/min was used together with an air flow rate of 400 ml/min. Figure 3B shows the dependence of peak area (in arbitrary units) on the partial pressure of the analyzed substance. These results illustrate the fact that carbon monoxide can be successfully utilized as a flame-forming agent for detecting halogen-containing compounds.

Table 3
GASEOUS FLAME-FORMING AGENTS FOR FIDs IN GC

Flame-forming substances	Phase state of starting substances in storage	Method of production in chromatographic system	Application features	Refs.
Hydrogen	Compressed gas	Water electrolysis Application of compressed gas	Hydrogen as a flame-forming agent provides high sensitivity, has a wide linear dynamic range, is stable and simple to handle, but is dangerously explosive, chemically active, has low capacity and low sorption-displacement characteristics	1—5,7—10
Hydrogen-nitrogen mixture (3:1)	Ammonia, liquefied gas	$NH_3 \xrightarrow[450—600°C]{\text{catalyst}}$	As a flame-forming agent, this mixture is equivalent to hydrogen; ammonia (starting gas) may be used as the carrier gas in separating amines and other polar compounds	21,22,25
Carbon monoxide			Carbon monoxide allows for increasing the sensitivity of detection for halogenated compounds and reduces corrosion of apparatus	26,27
Carbon monoxide	Starting substances: carbon dioxide (liquefied gas) and solid carbon	$CO_2 + C \rightarrow 2CO$ (1200—1500°)	Carbon monoxide is obtained from accessible, safe, and "capacious" compounds; carbon monoxide or carbon dioxide can be used as carrier gas	26,27 28,29 28—31
Water blue gas (a mixture of carbon monoxide and hydrogen (1:1)	Starting substances: carbon (solid), water (liquid)	$H_2O + C \rightarrow CO + H_2$ (1000—1100°)	Water gas is obtained from cheap, accessible, and "capacitous" reagents; water gas used as a carrier gas (instead of hydrogen) permits increasing the efficiency of a chromatographic column; water used as a carrier gas considerably improves chromatographic characteristics of separation for many analyzed mixtures	32 33 34—37

Table 3 (continued)
GASEOUS FLAME-FORMING AGENTS FOR FIDs IN GC

Flame-forming substances	Phase state of starting substances in storage	Method of production in chromatographic system	Application features	Refs.
Ammonia	Ammonia, liquefied gas; oxygen, compressed gas		Ammonia as a *flame-forming agent* increases detection sensitivity for organochlorine compounds (as compared with a hydrogen detector); ammonia as a carrier gas improves the separation of amines and other polar compounds, decreasing pressure drop	25,28 22—24,38,39

Table 4
VAPOR FLAME-FORMING AGENTS FOR FLAME IONIZATION DETECTION

Flame-forming agent	Boiling point (°C)	Combustion principle	Application features	Ref.
Formic acid	100.7	$2H_2CO_2 + O_2 \rightarrow$ $\rightarrow 2CO_2 + 2H_2O$	Formic acid as a carrier gas improves chromatographic characteristics for the separation of organic acids and other polar compounds	40—50
Carbon disulfide	46.2	$CS_2 + 3O_2 \rightarrow$ $\rightarrow CO_2 + 2SO_2$	Carbon disulfide as a carrier gas improves to some extent chromatographic characteristics, such as a decrease in HETP	51—53
Formamide	211	$4H_3CON + 50_2 \rightarrow$ $\rightarrow 4CO_2 + 2N_2 + 6H_2O$	Formamide as carrier gas improves chromatographic characteristics of polar compounds	51,54,55

Table 7
QUANTITATIVE ANALYSIS OF HYDROCARBONS AND HALOGEN-CONTAINING COMPOUNDS WITH A HYDROGEN FID[56,58]

Mixture	Actual content of components in mixture (% wt)	Experimental determination of peak area (%)	Correction factor	Found content of components in mixture (% wt)
Chloroform	43.9	16.8	10.0	42.0
Carbon tetrachloride	40.6	11.7	12.8	37.6
n-Heptane	7.5	33.2	1.19	9.9
Toluene	8.0	38.3	1.09	10.5
Methylchloride	37.9	22.1	4.2	37.2
n-Butane	30.6	74.2	1.21	37.7
Carbon tetrachloride	31.5	4.7	12.8	25.2

Sensitivities of both the carbon monoxide detector and the hydrogen FID[25] increase by approximately a factor of 2 when negative potential is applied to the collector electrode.[29]

Water vapor appears important for stability of the carbon monoxide flame. A bubbler with water, for instance, may be used as a source of gas moisture.

As shown in a previous communication,[28] the carbon monoxide FID has a number of special design features. A study of different collector electrode shapes (cylindrical [Figure 4A], antenna-shaped [Figure 4B], pin, and ring-shaped) show that the highest sensitivity can be realized with a cylindrical or an antenna-shaped electrode. The optimum interelectrode distance for a cylindrical collector electrode appears to be 3.5 mm. With this distance, the highest detector sensitivity can be realized. An optimum diameter of the burner jet is 1.8 mm. The height of a carbon monoxide flame under these conditions is 2.5 times greater than the height of a hydrogen flame.

Sternberg and co-workers[61] reported that carbon tetrachloride gives a slightly greater response than methane in the carbon monoxide flame. However, it is necessary to mention that contrary results were obtained by McWilliam.[62] With relatively large concentrations of carbon tetrachloride, no significant signals for carbon tetrachloride, hydrogen, and water were obtained.

The linear dynamic range of the carbon monoxide FID was determined with propane by the method of exponential dilution (8) to be 10^7.[29] The detector signal appears linearly dependent on the number of carbon atoms in an organic molecule.

Analogous analytical characteristics of hydrogen and carbon monoxide FIDs can be explained by the similarity of chemical processes occurring in both flames and by a relatively large concentration of atomic oxygen within a carbon monoxide flame, as proven experimentally.[63] The manner in which a carbon monoxide flame is sustained is of great importance to the detector's proper functioning. In our experiments,[28,29] carbon monoxide was obtained through the reaction of carbon dioxide with carbon. This procedure permits using safe and cheap starting substances. The reaction between carbon and carbon dioxide, resulting in a formation of carbon monoxide, occurs at temperatures between 1150 and 1200°C, and typical yields are 95 to 98%. According to our experience, the use of carbon monoxide as a flame-forming agent generally does not complicate the ordinary benefits and operation of the FID, but adds the following advantages: (1) the explosion hazard associated with the experiment is decreased, (2) the sensitivity of detecting halogenated compounds is enhanced, and (3) the operation of the gas chromatograph becomes simplified.

Alternatively, one can use both carbon monoxide and carbon dioxide as the carrier gas. It is widely known[64] that the choice of a carrier gas can have a profound effect on plate-height values and band-broadening processes. The longitudinal diffusion can be decreased

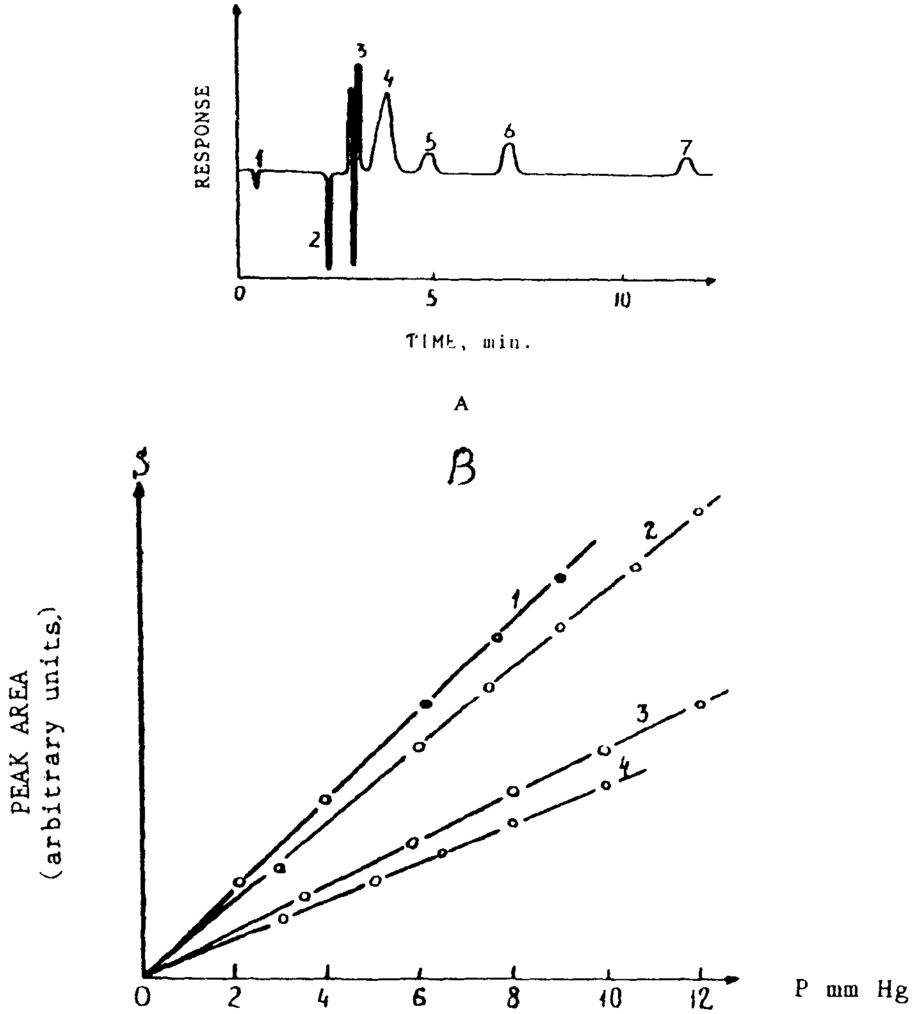

FIGURE 3. Application of carbon monoxide as a flame-forming agent. (A) Chromatogram of a mixture of halogenated methanes, (1) sample injection, (2) air spike, (3) CF_3Cl, (4) CHF_3, (5) CH_2F_2, (6) CF_2DL_2, (7) CHF_2Cl. Experimental conditions: 300 cm × 4 mm, i.d., column, packed with 20% of dinonylphthalate on C-22 acid-washed firebrick; temperature, 25°C, carbon monoxide flow rate, 35 ml/min, air flow rate, 400 ml/min. (B) Peak area vs. sample partial pressure (mmHg); (1) CHF_2Cl, (2) CHF_3, (3) CF_2Cl_2, (4) CHF_2F_2. From Baddiel, C. B. and Cullis, C. F., *Chem. Ind.*, 1155, 1960. With permission.

by increasing the molecular mass of the carrier gas. This could have beneficial effects in some circumstances. The use of carbon monoxide or carbon dioxide as the carier gas will allow a decrease in the minimum plate-height as compared to hydrogen.[28,29]

It should also be noted that the chemical reactivities of carbon dioxide and carbon monoxide toward certain solutes are lower than that of hydrogen. While considering the possibility of using carbon dioxide or carbon monoxide as the carrier gas, one should appreciate that these heavy carrier gases may have a profound effect on the adsorptivity and separation of gases and volatile compounds in gas-solid chromatography,[64] especially while using molecular sieves.

Overall, the use of carbon monoxide and carbon dioxide as the carrier gas and carbon monoxide as a flame-forming agent may widen the scope of some gas-chromatographic

Table 8
RELATIVE SENSITIVITY OF THE FID FOR HYDROCARBONS AND THEIR CHLORINATED DERIVATIVES, USING CARBON MONOXIDE AS A FLAME-FORMING AGENT

	Relative sensitivity (with respect to a hydrogen detector)	
Analyzed compound	**Flame-forming agent carbon monoxide**	**Flame-forming agent and carrier gas carbon monoxide**
n-Decane	0.42	1.03
Benzene	1.2	3.2
Cumene	0.86	2.3
Chlorobenzene	2.8	—
Carbon tetrachloride	2.5	—

Note: Sensitivity of hydrogen flame ionization detection equal to unity.

From Tsitsishvilli, G. U., Berezkin, V. G., Andronikashvili, T. G., and Gvelesiani, Z. A., *Izu. Akad. Nauk. Gruz. SSR.*, 8, 275, 1982. With permission.

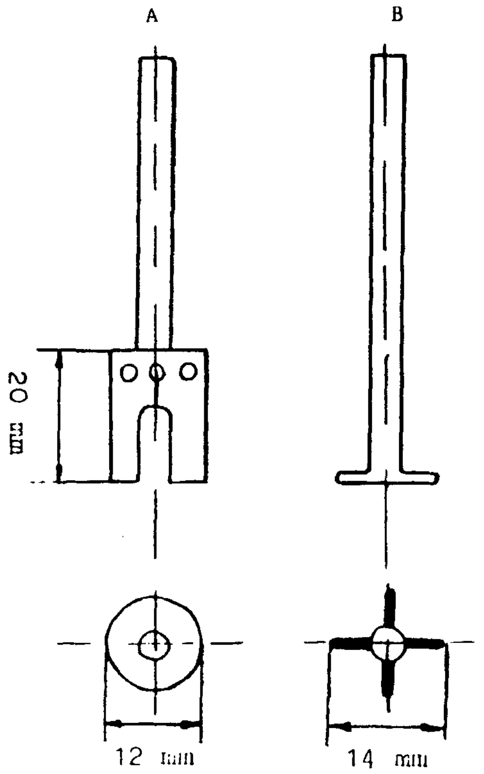

FIGURE 4. Optimal shape of collector electrodes for carbon monoxide FID. (A) Cylindrical collector electrode, (B) antenna-shaped collector electrode. (From Berezkin, V. G., Tsitsishvili, G. U., Andronikashvili, T. G., and Gvelesiani, Z. A., *Izu. Akad. Nauk. Gruz. SSR.*, 8, 121, 1982. With permission.)

methods. In conclusion, we would like to note that it is possible to use carbon monoxide as a flame-forming agent not only in the FID. The expediency of using carbon monoxide as the flame-forming agent in a thermionic detector of modified design has been shown.[66] Optimal conditions for detection are achieved with gas consumptions of 30, 40 to 45, and 400 to 500 ml/min for carbon monoxide, nitrogen (mobile phase), and air, respectively, with an interelectrode gas of 5 to 7 mm and a burner nozzle diameter of 1.8 to 2 mm. The sensitivity of the thermionic detector toward nitrogen-containing substances is 2 to 4 times greater with the use of carbon monoxide. For another organic compound under investigation, the sensitivity of the thermionic detector with carbon monoxide differs slightly from the thermionic detector with hydrogen as the flame-forming agent.

B. Water Blue Gas

Some authors[32,34] have suggested using a water blue gas (an equimolar mixture of hydrogen and carbon monoxide) as a flame-forming agent for the FID[32] and as a carrier gas.[33] The water blue gas is obtained during the passage of water vapor through a quartz reactor (100 × 30 mm) filled with granules of pure carbon. At temperatures between 1000 and 1100°C, the major chemical event is the reaction of water vapor with carbon, yielding carbon monoxide and hydrogen. Sensitivity obtained with the water blue gas in the FID is about the same as that measured with hydrogen alone. However, the absence of large amounts of explosive hydrogen adds safety to the analytical experiment, while the utilization of a water blue gas[33] and water steam[34,35] as carrier gases may extend the separation scope. When a water blue gas is used as the carrier gas, the height equivalent to a theoretical plate (HETP) at velocities between 1 and 3 cm/s for a packed column is approximately 1.0 mm, while for hydrogen it is about 2 mm. For fast separations (more than 5 cm/s), the ratio changes, and the efficiency of a chromatographic column with hydrogen as the carrier gas becomes higher.

Figure 5 shows the dependence of HETP of a packed column for the decane solute on the linear velocity for hydrogen (curve 1) and water blue gas (curve 2). It can be easily demonstrated that a similar dependence for carbon monoxide is very much like that for a water blue gas, as shown in Figure 5.

When in gas-solid chromatography a water blue gas is used as the carrier gas (e.g., on molecular sieves), symmetry of the chromatographic zones is often improved, and the time of analysis is reduced. Water vapor itself can also be used as a mobile phase. This type of chromatogrphy, originally suggested by Dumazert and Chiglione[34] and further developed by Nonaka,[35] Vigdergauz and co-workers,[65] and other researchers[67] has certain merits when compared with traditional carrier gases.

In our opinion, the main advantage of water vapor and other similar media lies in the fact that a mobile vapor phase can become an active factor in solute migration. It could significantly influence not only the column efficiency, but also the selectivity of chromatographic separations. The role of the "vapor" mobile phase now becomes similar to the active role of the mobile phase in modern liquid chromatography. Therefore, it becomes feasible and expeditious to make use of gradient solution techniques with this form of chromatography.[37,68] We have already shown[69] that water steam can be used successfully as the carrier gas in capillary gas chromatography.

The methods for obtaining a water vapor mobile phase are not complicated. Usually, the production of a water vapor, or a carrier gas containing some water vapor, consists of the following steps: (1) production of vapor in a heated flash evaporator containing the liquid,[70] (2) production of vapor in a heated flash evaporator into which water is supplied at a given rate,[71] and (3) production of a mixed carrier gas by saturating the gas flow with water vapor while bubbling the gas through a water layer.[65]

As already indicated, such devices are not intricate in design and provide a means to

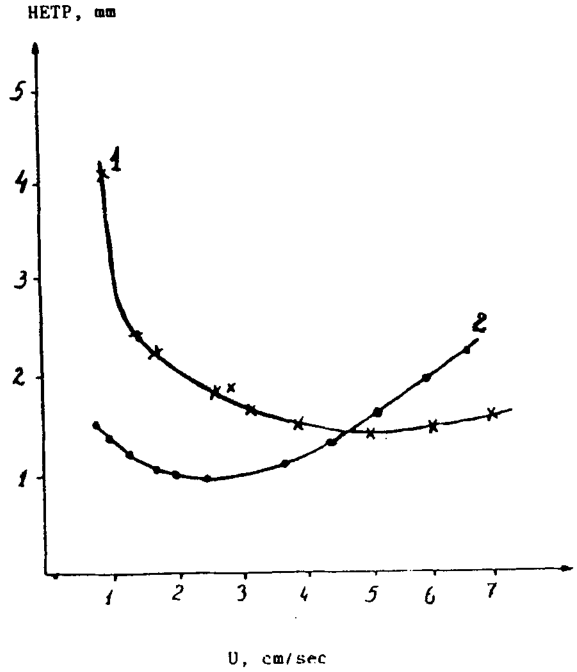

FIGURE 5. Plate-height vs. linear velocity curves for decane. (1) Hydrogen carrier gas, (2) water-carbon monoxide mixture (water blue gas). (From Berezkin, V. G., Tsitsishvili, G. V., Andronikashvili, T. G., and Gvelesiani, Z. A., *Bull. Izobr.*, 17, 1981. With permission.)

supply water vapor at a required rate for either obtaining a water blue gas (a flame-forming agent) or providing the necessary mobile-phase flow. Similar devices can also be used to obtain a vapor flow with other substances.

C. Ammonia

Ammonia can also be used[25,38] as a flame-forming agent in the FID if the combustion medium is either oxygen or an air enriched with oxygen. Ammonia is usually stored as a liquefied gas in cylinders; at a temperature of 20°C, the saturation vapor pressure is approximately 8.6 kg/cm^2. Ammonia is not as dangerously explosive as hydrogen (see Table 5). It should be noted that the ammonia FID has a higher detector sensitivity with respect to chlorine-containing organic compounds (see Table 8) than other flame detectors. It is of some interest that by varying the ammonia/oxygen ratio, the relative detection sensitivity of the ammonia-oxygen ratio was clearly shown (Figure 6). This feature of the ammonia detector may become useful during the identification of separate groups of compounds. The detector signal is linear for various sample components (hydrocarbons, amines, chlorocarbons, etc.).

Berezkin et al.[26] also suggested using ammonia to obtain mixed flame-forming agents consisting of 3 volumes of hydrogen and 1 volume of nitrogen. This mixture is formed during decomposition of ammonia over an iron catalyst originally used for the synthesis of ammonia at several atmospheres of pressure and at temperatures between 500 and 600°C. When using ammonia as the carrier gas and a hydrogen-nitrogen mixture (3:1) as a flame-forming agent, the detection sensitivity for chloroform increases five times (compared to the hydrogen detector) and for lindane, seven times.

The use of ammonia as the carrier gas appears promising, first because the viscosity of ammonia is much lower than that of widely used carrier gases such as nitrogen and helium,

Table 9
RELATIVE SENSITIVITY OF THE AMMONIA FID TO SOME ORGANIC COMPOUNDS (NORMALIZED TO SENSITIVITY OF A HYDROGEN FLAME DETECTOR)

Compound	Relative units
Octane	1.9
Benzene	1.9
Ethanol	2.3
Buylamine	2.1
Hexamethyleneimine	2.0
Chloroform	5.2
Carbon tetrachloride	10.3

Note: Experimental conditions: ammonia flow rate, 30 ml/min; oxygen flow rate, 200 ml/min; column, 1 m × 2 mm; temperature, 80°C; sorbent, 3% KOH and 10% Apiezon L on Chromasorb W.

From Berezkin, V. G. and Shkolina, L. A., *J. Chromatogr.*, 119, 33, 1976. With permission.

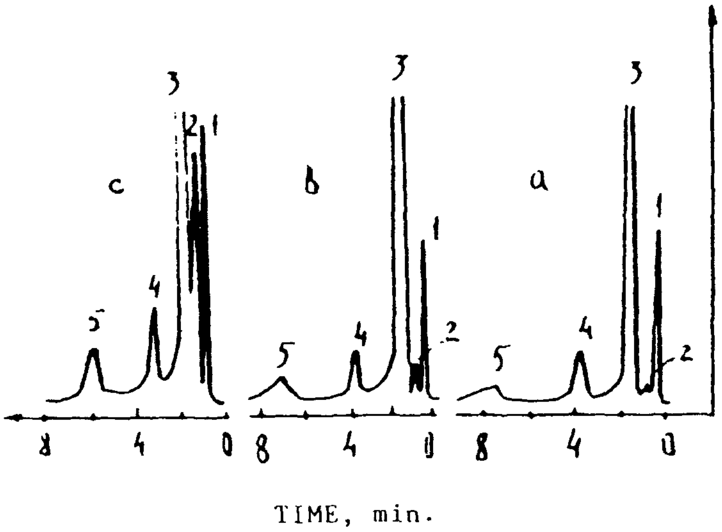

FIGURE 6. Chromatogram obtained of a model organic mixture with different flame-forming agents. Solutes: (1) ethanol, (2) chloroform, (3) benzene, (4) octane, (5) hexamethyleneimine. Separation conditions: 1 m × 2 mm, i.d., column, packed with 10% Apiezon L and 3% potassium hydroxide on Chromasorb W; column temperature 80°C. Detection conditions: (a) hydrogen (20 ml/min), air 200 ml/min; (b) ammonia (30 ml/min), oxygen (oxidizer) 180 ml/min; (c) ammonia (40 ml/min), oxygen (oxidizer), 220 ml/min. (From Berezkin, V. G. and Shkolina, L. A., *J. Chromatogr.*, 119, 33, 1976. With permission.)

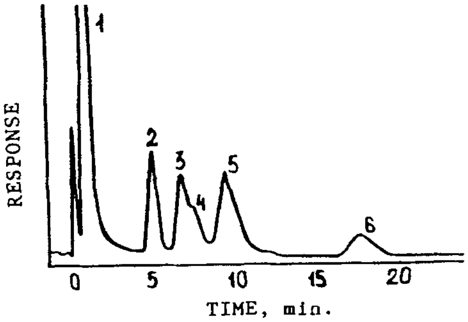

FIGURE 7. A chromatogram of amino acid butyl esters. (1) Solvent, (2) alanine, (3) valine, (4) glycine, (5) isoleucine and leucine, (6) proline. Experimental conditions: 90 mm × 6mm, i.d.; column packed with 20% polyethylene glycol adipate on solid support; carrier gas: nitrogen (50 cm^3/min) and ammonia (8 cm^3/min), column temperature, 130°C. (From Sarrof, H. A., Karmen, A., and Healy, J. W., *J. Chromatogr.*, 9, 122, 1962. With permission.)

and, second, ammonia readily forms hydrogen bonds with silanol groups at the surface of solid support and is likely to form stable complexes with a number of metals that could be present as surface contaminants. Consequently, through the use of ammonia as a carrier gas, or as an additive to a carrier gas, losses of polar compounds (especially amines) on the columns are minimized. Symmetry of chromatographic zones is improved, together with shortened retention times. The interested reader may find a more detailed description of the role of a solid support in a quantitative and qualitative analysis, and the methods of suppressing undesirable (reversible and irreversible) adsorption of the analyzed compounds in a book by this author and others.[72]

Saroff and co-workers[22] were the first authors to suggest the use of ammonia as a carrier gas. They had already shown various analytical possibilities of ammonia in GC. Their paper describes a direct chromatographic analysis of amino acids as their butyl esters, with hydrochlorides of amino acid esters being converted to free bases immediately in the chromatograph sampling port. A representative chromatogram of the amino acid butyl esters, reproduced from their paper, is shown in Figure 7. Ilkova and Mistryukov[23] have also demonstrated that the use of ammonia as the carrier gas improves chromatographic separation characteristics for amines as well as other polar compounds.

Additional references deal with the use of ammonia as a carrier gas.[24,25] Further application of ammonia in GC appears promising.

V. VOLATILE FLAME-FORMING AGENTS

To date, numerous reports have dealt with the applications of volatile flame-forming agents, such as formic acid, carbon disulfide, and formamide, for flame ionization detection (see Table 4). Because under ordinary temperatures these compounds are liquids, their application is, in our opinion, simpler than the application of gaseous flame-forming media. In the ordinary procedure, liquid combustible compounds can be introduced into the FID by the methods used to saturate GC columns with certain volatiles.[35,65] Alternatively, some special methods of introducing liquid reagents into the flame were suggested by Rudenko and Zabokritskii.[73] Two FIDs are shown in Figure 8 which emphasizes differences from the conventional way of supplying liquid combustible reagents.[73] Figure 8A shows a schematic diagram of a detector in which combustible liquid is supplied by the "wick" method.

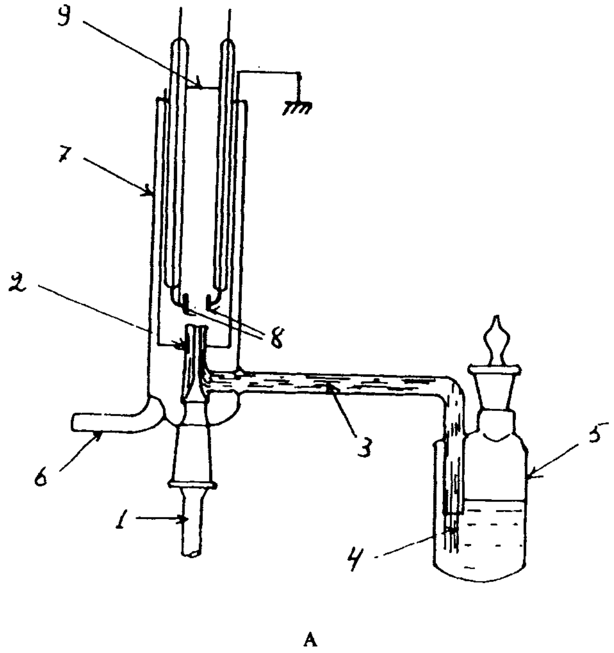

FIGURE 8. The FIDs designed for liquid flame-forming agents. (A) Detector with injection of a combustible substance over a layer of porous material. (1) Chromatographic column outlet, (2) burner, (3) tube for injecting combustible substance, (4) porous material (wick), (5) reservoir with a combustible substance, (6) air-supply tube, (7) detector housing, (8) electrodes, (9) metal screen. (B) Detector with a pressurized injection of combustible substance into the detector/burner through a capillary. (1) Chromatographic column outlet, (2) detector burner, (3) capillary for introducing a combustible substance, (4) a syringe pump, (5) screw drive, (6) electric motor housing with a reducer, (7) air-supply tube, (8) detector housing, (9) electrodes, (10) metal screen. (From Rudenko, B. A. and Zabokritskii, M. P., *Zh. Anal. Khim.*, 37, 174, 1982. With permission.)

Noncombustible porous materials, such as asbestos, glass fiber, etc., are used as the raw material for wicks. Figure 8B shows the detector with a pressurized introduction of a liquid reagent along a capillary into the burner jet. In both detector designs, a grounded metal screen is provided to shield the detector. The first design is simplest, as it can be set up in any laboratory.

We now discuss the individual flame-forming agents in more detail.

A. Formic Acid

Formic acid has long been used successfully in chromatography as a volatile reagent to suppress the adsorption of solutes at the surfaces of apparatus and solid supports.[46-50,74]

As shown during the last 2 decades, gas-liquid chromatography could frequently be called "gas-liquid-solid chromatography".[75] Consequently, suppression of adsorption on the surface of solid supports results in (1) improvements in the symmetry of chromatographic zones, (2) significant gains in the reliability of analytical qualitative data, (3) more reproducible quantitation, and (4) overall improvements in interlaboratory reproducibility.[72,75]

Formic acid is a relatively strong organic acid. It effectively suppresses the adsorption of acidic and polar compounds at the solid surface. As shown in Figure 9, formic acid can

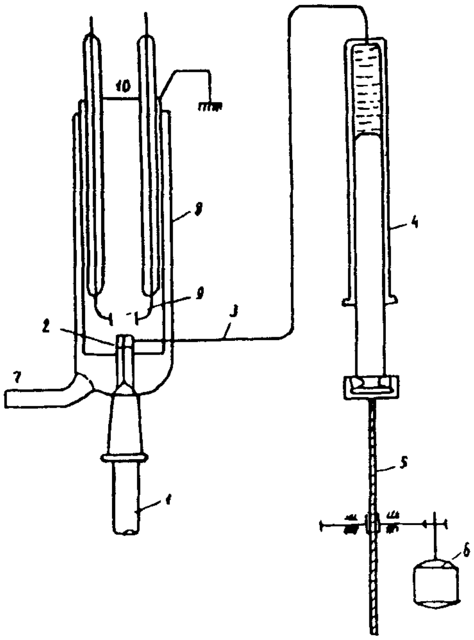

FIGURE 8B

have beneficial effects on the analysis of C_2 to C_6 organic acids if added to the carrier gas. Comparison of the two chromatograms clearly demonstrates that the presence of formic acid vapor in the carrier gas improved symmetry of the chromatographic zones, increased the efficiency of chromatographic separation (through narrower zones), and even improved the selectivity of this separation.

The above findings are further substantiated in another application.[74] In practical terms, free fatty acids could not be recovered from a column packed with alkaline glass packing, even when the packing was treated with a polar phase such as polyethyleneglycol. However, symmetrical peaks were obtained after saturating the carrier gas with the formic acid vapor at room temperature. Once again, the symmetry of chromatographic zones was considerably improved, while the detection sensitivity remained unchanged. A sufficiently high column efficiency (around 2000 t.p. per meter) was maintained. Rudenko et al.,[40] who extended this method for higher acids (palmitic acid included), also noted a considerable decrease in the analysis time following the use of formic acid with the carrier gas.

It should be noted that the use of a carrier gas containing formic acid vapor is advisable not only in gas-liquid chromatography, but also in gas-solid chromatographic situations. Along these lines, Ackman[47] noted the beneficial effects of formic acid addition during the analysis of organic acids on porous polymers (Porapak and Chromasorb 101). Information about the improvement of analytical results with C_2 to C_5 organic acids on Porapak N was conveyed in another paper.[76] Their procedure was based on a sequential injection of 5 μl formic acid on the column between the analyses.

Determination of organic acids continues to be an important analytical problem. Obviously, the addition of formic acid improves the results.

Formic acid can also be used as a flame-forming agent directly. Kucherov and coworkers[42-45] were the first to establish this fact.

B. Carbon Disulfide and Formamide

Carbon disulfide and formamide were also suggested[51-55] as carrier gases and flame-forming agents in the FID. The use of carbon disulfide as a mobile phase in GC makes it

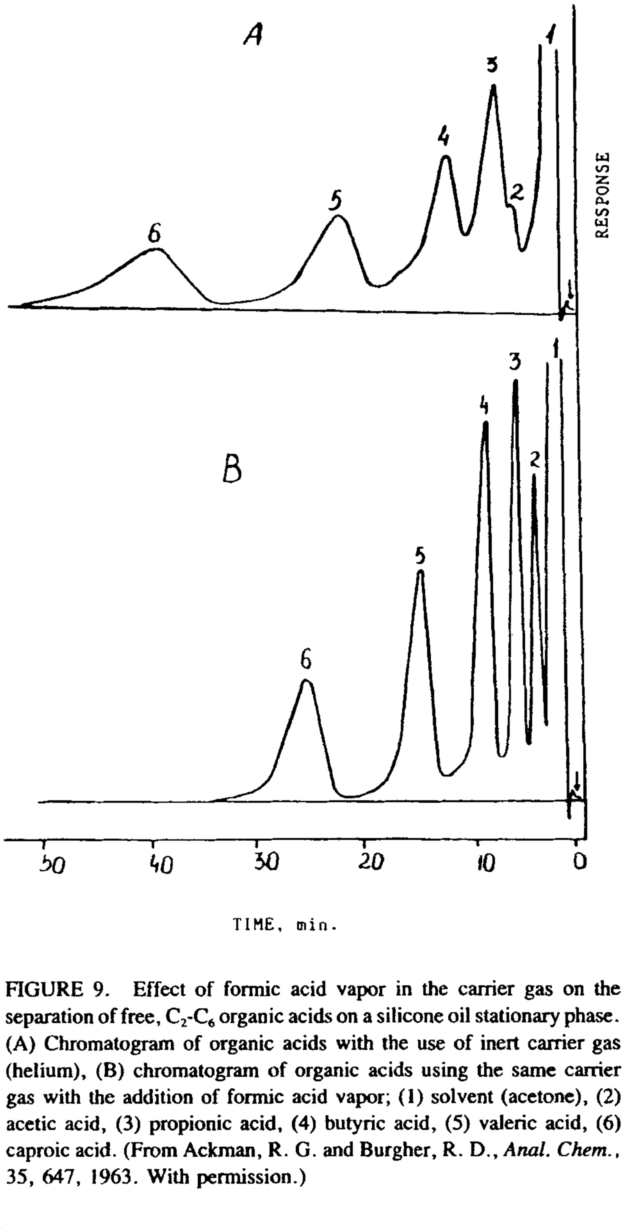

FIGURE 9. Effect of formic acid vapor in the carrier gas on the separation of free, C_2-C_6 organic acids on a silicone oil stationary phase. (A) Chromatogram of organic acids with the use of inert carrier gas (helium), (B) chromatogram of organic acids using the same carrier gas with the addition of formic acid vapor; (1) solvent (acetone), (2) acetic acid, (3) propionic acid, (4) butyric acid, (5) valeric acid, (6) caproic acid. (From Ackman, R. G. and Burgher, R. D., *Anal. Chem.*, 35, 647, 1963. With permission.)

feasible to modify a wide range of sorbents, because carbon disulfide is one of the most universal and effective solvents used in chemistry.

The employment of formamide as the carrier gas becomes beneficial in separating polar amines, because formamide is a compound with a pronounced basicity. Formamide has been proven to improve the symmetry of chromatographic zones for basic solutes and other polar compounds.

Figure 10 demonstrates the separation of the esters of phthalic acid in carbon disulfide vapor. Thirty ml of carbon disulfide were placed in a 100-ml steam generator and heated to 47°C. Under these conditions, a flow of carbon disulfide, used as a mobile phase (43 ml/min), was supplied into the column heated to 196°C from the steam generator. Separation was achieved on a 200 cm × 4 mm-column, packed partially with a silicone SE-30 on a silanized Chezasorb support. In 10 min, the phthalic esters (ranging from dimethyl to dinonyl) were successfully separated under these conditions.

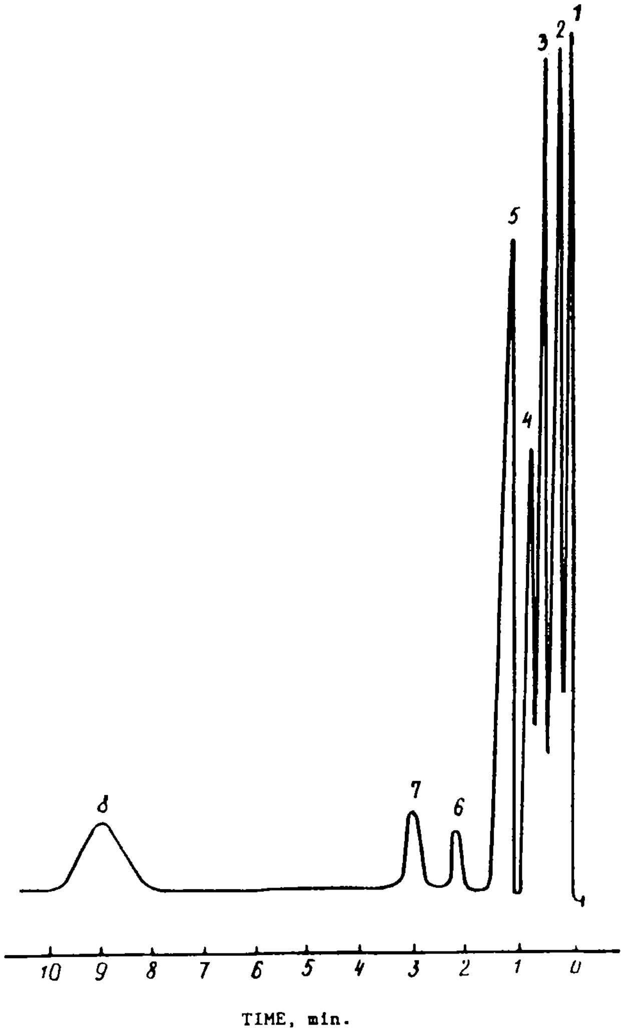

FIGURE 10. Chromatogram of a mixture of phthalic acid esters in carbon disulfide vapor (mobile phase). Phthalic acid esters: (1) dimethyl, (2) diethyl, (3) diisoamyl, (4) dihexyl, (5) dibenzyl, (6) dioctyl, (7) isomers, (8) dinonyl. Experimental conditions: 200 cm × 4 mm, i.d., column packed with 5% SE-30 silicone polymer coated on silanized Chezasorb: column temperature, 196°C. Mobile phase: carbon disulfide vapor. (From Berezkin, V. G., Rudenko, B. A., Popova, T. P., Zabokritskii, M. P., Agayeva, M. N., Lipavskii, V. N., and Sokolin, G. F., *Bull. Izobr.*, 1, 1977. With permission.)

Figure 11 demonstrates a chromatogram where high-boiling aromatic hydrocarbons (ranging from methylnaphthalene to acenaphthene) were separated by the formamide vapor. To obtain a flow of formamide vapor (45 ml/min), 40 ml of formamide were placed in a 100-ml steam generator and then heated to 218°C. Aromatic hydrocarbons were separated on a 96 cm × 4 mm-column packed with 5% silicone SE-30, coated on a Chezasorb support that was previously treated with hexamethyldisilazane.

The use of formamide and carbon disulfide as flame-forming agents is further described in additional papers.[51,52,54,73]

Figure 12 shows a chromatogram of miscellaneous organic compounds on a column (96 cm × 4 mm) packed with 5% SE-30 silicone phase, coated on a Chezasorb support, and

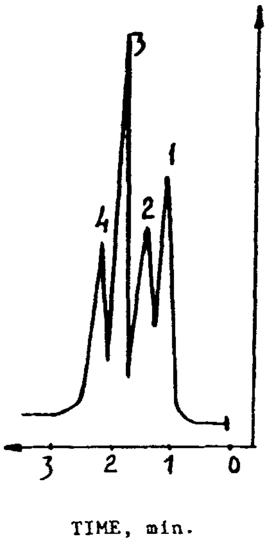

FIGURE 11. Chromatogram of aromatic hydrocarbons, using formamide vapor as the mobile phase. Solutes: (1) methylnaphthalene, (2) diphenyl, (3) diphenyl methane, (4) acenaphthene. Experimental conditions: 96 cm × 4 mm, i.d. column, packed with 5% SE-30 silicone phase, coated on silanized Chezasorb; column temperature, 220°C. Formamide vapor was used as both the mobile phase and a flame-forming agent. (From Berezkin, V. G., Rudenko, B. A., Popova, T. P., Lipavskii, V. N., Sokolin, G. F., and Agayeva, M. N., *Bull. Izobr.*, 39, 1976. With permission.)

previously modified with hexamethyldisilazane. In this application, nitrogen was used as the carrier gas. To record the results of this chromatographic separation, the FID was used with formamide as the flame-forming agent (43 ml/min of vapor). Formamide vapor was produced in a steam generator at 215°C. This method is characterized by its overall simplicity. It should be noted, however, that with the application of the above-mentioned compounds as flame-forming agents, the detector noise level increases in comparison to the hydrogen flame detector. Sensitivity may decrease by a factor of 2 to 10. The causes of this phenomenon are not sufficiently clear at present. Most likely, the organic contaminants present in formamide and carbon disulfide are responsible for this behavior.

Organic modifiers, such as carbon disulfide, formamide, or formic acid, can reasonably be used as solvents during direct sample injection onto capillary columns. The flame ionization response caused by these compounds will be minimal. Moreover, some of the compounds (e.g., formic acid) may further suppress column adsorption phenomena and thus improve chromatographic resolution.

VI. ESTIMATION OF NONHYDROGEN FLAME-FORMING AGENTS

The electrical conductivity of a flame with carbon monoxide, ammonia, formamide, formic acid, and carbon disulfide, as is certainly the case with hydrogen, will sharply increase when traces of organic compounds enter the flame. This permits their use in various mixtures (e.g., a mixture of carbon monoxide and hydrogen) as flame-forming agents in FIDs.

The bilateral use of these compounds as flame-forming agents on the one hand, and as mobile phases in GC on the other, provides considerable perspective. In a number of cases, the operation of a gas-chromatographic apparatus can be simplified, while the methods of

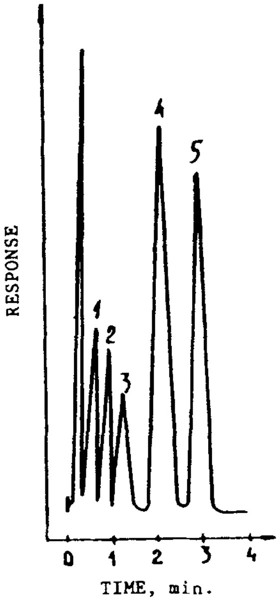

FIGURE 12. Chromatogram of a model organic mixture obtained with FID, using formamide vapor as the flame-forming agent. Solutes: (1) Diethyl ester of a succinic acid, (2) octanol, (3) butylamine, (4) dibutyl ester of sebatic acid, (5) dihexyl ester of phthalic acid. Experimental conditions: 96 cm × 4 mm i.d., column, packed with 5% SE-30 silicone phase coated on a solid support. Column temperature, 220°C, carrier gas, nitrogen (40 ml/min). (From Berezkin, V. G., Rudenko, B. A., Popova, T. P., Zabokritskii, M. P., Agayeva, M. N., Lipavskii, V. N., and Sokolin, G. F., *Bull. Izobr.*, 8, 1977. With permission.)

separating certain groups of chemical compounds are simultaneously improved. In addition, increases in sensitivity of detecting halogen-containing organic compounds may be realized.

The choice of an optimum reagent for detector use and a mobile phase is defined in GC by the nature of a particular analytical problem to be solved and the possibilities of a particular laboratory. Additional substances might be used as flame-forming agents for the determination of various organic compounds, i.e., carbon disulfide, formaldehyde, and carbon oxysulfide. These compounds all produce a very weak signal with the FID.[77]

In our opinion, it might be feasible to apply flame-forming agents (as either pure substances or in a mixture with water) as the mobile phase for liquid chromatography. When employing mixed eluents (such as water-ammonia, water-formamide, water-formic acid, and other mixtures), it will evidently be possible to perform gradient elution. While evaporating the mobile phase after the chromatographic column and directing the entire vapor flow (or part of it) into the FID, we could continuously record the results of chromatographic separations with a universal, highly sensitive FID. Here, the well-known methods[78-84] of eliminating the liquid eluent, or its continuous introduction into the gas detectors, may be applicable. Under these circumstances, advantage could be taken of the mobile phases to which the FID is largely unresponsive.

The selectivity of FIDs with nontraditional flame-forming agents, we hope, may improve if we use the inverse variant of this type of detector. For example,[87-90] the selectivity of the hydrogen FID is increased if the reverse flame is used. This is the hydrogen-atmosphere FID, where the flame of oxygen exists in a hydrogen atmosphere.

In conclusion, we should like to note that the use of detectors with nontraditional flame-forming agents has not been sufficiently studied. The field has, in our opinion, many "blank spots".

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