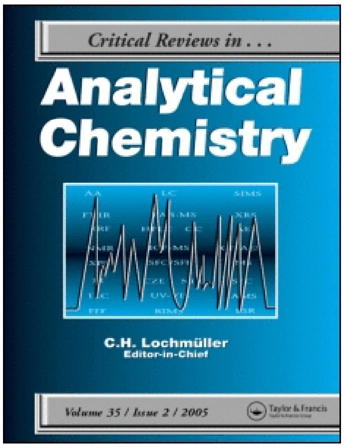

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Flame Photometric Detectors in Chromatography: A Review

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Flame Photometric Detectors in Chromatography: A Review

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ABSTRACT: This paper discusses the application of selective flame photometric detectors (FPD) in organic trace chromatographic analysis. Characteristics of modern FPD as well as procedures for the determination of sulfur-, phosphorus- and chloro-containing components and organometallic compounds are described. Further utilization of the procedures in different branches of science and technology are considered.

KEY WORDS: flame photometric detection, determination of sulfur-, phosphorus-, and chloro-containing compounds, determination of organometallic compounds.

I. INTRODUCTION

Presently, gas chromatography (GC) is the leading method for the determination of volatile chemical substances (see Reference 1). It is widely used in environmental analysis, medicine, industry, space research, and geology, among other fields. Furthermore, numerous analytical problems can be successfully solved using primarily selective gas chromatography detectors. Among them is the flame photometric detector (FPD). This is one of the seven most used detectors in gas chromatography.[1]

FPD utilization permits the selective detection of trace compounds containing sulfur, phosphorus, halogens, lead, etc., and can be successfully utilized to detect sulfur in motor fuels and natural gas, as well as hazardous substances like pesticides in air, water, and exhaust gases. In addition, various analytical procedures using FPD have been standardized in several countries.

FPD was first described by Brody and Chaney.[2] They demonstrated the potential of FPD as a highly sensitive and selective detector. Generally, papers published from 1967 to 1976 were devoted to the analysis of sulfur- and phosphorus-containing compounds as well as evaluations of the parameters of FPD permitting these analyses (e.g., pesticides). Hence, FPD has been widely applied to detect sulfur-containing compounds. Good results were obtained when FPD was used for determining sulfur-containing compounds in the petrochemical and oil-refining industry. Sulfur-containing compounds are known as sources of corrosion, environmental pollution, and catalyst poisoning. FPD has been used to a lesser extent for the selective monitoring of halogen-containing compounds and organometallics (containing tin, lead, selenium, tellurium, etc.). The last 2 to 3 years were marked by a growing interest in FPD usage in liquid chromatography (LC). In GC, FPD can be successfully used with both packed and open tubular capillary columns. Inert (helium, nitrogen, etc.) and nonideal (steam, ammonia) mobile phases can be used as carrier gases.

Unique FPD parameters, namely, high sensitivity (10^{-11} to 10^{-13} g of analyzed element), good selectivity with respect to hydrocarbons (10^4 to 10^7), satisfactory repeatability and reproducibility of results, and relatively simple design and handling led to wide FPD applications. Presently, FPD is one of the most widely used detectors. It can also be used in combination with other detectors, such as the flame-ionization detector, forming a multichannel high sensitivity detector

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system. Practically all major companies marketing gas chromatographs (e.g., Varian, Perkin Elmer, Carlo Erba, Hewlett-Packard, Tracor, Shimadzu, etc.) offer them with flame photometric detectors.

Unfortunately, data concerning the use of flame photometric detectors in GC and LC are scattered. In this respect, we have tried to systematize data concerning FPD applications in different analytical procedures.

II. GENERAL PRINCIPLES OF FLAME-PHOTOMETRIC DETECTION

A. Flame-Chemiluminescent Detection

Many chemical reactions proceed with the formation of excited products. The excited molecules emit photons while transferring to the ground state. This emission is of a chemical nature and therefore is called chemiluminescent emission. Chemiluminescence is possible[3] when: (1) the free energy of the reaction is sufficient to form excited products; and (2) preferable excited products form. The efficiency of excited products formation (E_E) can be defined as the ratio of the number of formed excited molecules to the number of the initial molecules. Furthermore, the efficiency of the luminescent molecules (E_l) can be defined as the ratio of the number of emitting molecules to the number of excited molecules. Hence, the chemiluminescence efficiency E_{Cl} can be defined as follows:

$$E_{Cl} = E_E \cdot E_l \qquad \text{(I)}$$

The E_{Cl} of chemical reactions is not higher than 0.01. However, chemiluminescent reactions are of great interest for analytical determinations since they are very selective. Modern equipment used to measure such emission intensities allows for simple and high selective determinations.

The chemiluminescent intensity I_{Cl} can be defined as follows:

$$I_{Cl} = E_{DE} \cdot E_D \cdot E_{Cl} \cdot \frac{dc}{dt} \qquad \text{(II)}$$

where E_{DE} is the detector quantum efficiency at a given wavelength (ratio of measured photons to photons directed to the detector), E_D is the ratio of photons directed to the detector to the photons formed, and dc/dt is the chemical reaction rate. The number of excited atoms or molecules formed during flame chemical reactions is much higher than with thermal excitation.

The chemiluminescent process can be given by the following reactions:[4]

$$A + B \xrightarrow{K_1} M^* \quad \text{(formation of excited particles caused by chemical reaction)} \qquad \text{(III)}$$

where A and B are initial reagents, M* is excited particles, and K_1 is the reaction rate coefficient; and

$$M^* \xrightarrow{K_2} M + h\nu \quad \text{(chemiluminescence of excited molecules } M^* \text{ is transferred into ground state M, emitting photon)} \qquad \text{(IV)}$$

where h is Planck's constant, ν is a frequency of emitted light, and K_2 is the rate constant of chemiluminescence. Simultaneously, deactivation of excited molecules M* without any emission takes place

$$M^* \xrightarrow{K_3} M \qquad \text{(V)}$$

where K_3 is the rate constant of nonemitting deactivation reaction.

Reaction (V) occurs via deactivation caused by quenching, internal deactivation, and energy transfer. This reaction weakens the chemiluminescence intensity. The quenching effect caused by different quenchers (more often, hydrocarbons) can be diminished by chromatographic separation of analyzed compounds and quenchers.

Different reactions accompanied by chemiluminescence can be used in chromatographic detection. For example, gas chromatographic detection based on the continuous measurement of sulfur compounds has been carried out by means of excited SO_2 chemiluminescence measurement at 300 to 400 nm, with SO_2 being formed as a result of sulfur-containing compounds oxidation in the presence of ozone.[5,6] However, the described procedure has not been widely adopted.

Sulfur-containing compounds were also determined by means of chemiluminescence intensity measurement due to reaction of the compounds with F_2.[7] The authors affirmed that the detectors used were comparable (with respect to their operation conditions) to flame photometric detectors.

Flame chemiluminescence detectors are widely used in GC being classified under the name of flame photometric detectors (FPD), with the latter name being more general. Diffusive hydrogen-air, hydrogen-oxygen, or hydrogen-air-oxygen flames are used in FPD, with the flame temperature being low (less than 1000°C).

Flame chemiluminescence detection is carried out by means of S_2-group intensity measurement in a low temperature hydrogen-air (oxygen) flame (with hydrogen access) at 394 nm, with background emission of OH and O_2 groups being excluded. The influence of functional groups emitting at similar wavelengths (e.g., CH at 390 nm, CN at 385 nm) is weakened.

According to current thinking,[8] when introduced into a diffusive hydrogen-air (oxygen) flame at hydrogen excess, organic sulfur-containing compounds convert into H_2S (hydration) via:

$$\text{Sulfur-containing compounds} \rightarrow H_2S \qquad (1)$$

$$H_2S + H \rightleftarrows H_2 + SH \qquad (2)$$

$$SH + H \rightleftarrows H_2 + S \qquad (3)$$

$$SH + S \rightleftarrows H + S_2 \qquad (4)$$

$$SH + SH \rightleftarrows H_2S + S \qquad (5)$$

$$H_2S + OH \rightleftarrows H_2O + SH \qquad (6)$$

$$SO_2 + H \rightleftarrows OH + SO \qquad (7)$$

$$SO + H \rightleftarrows OH + S \qquad (8)$$

$$SO + H \rightleftarrows SH + O \qquad (9)$$

$$O_2 + H \rightleftarrows OH + O \qquad (10)$$

$$O + H_2 \rightleftarrows OH + H \qquad (11)$$

Several investigators considered that the energy required for the formation of excited S_2^* groups evolves from proton recombination, as

$$H + H + S_2 \rightleftarrows S^* + H_2 \qquad (12)$$

Others attribute this process to a recombination involving two or three atoms

$$S(^3P) + S(^3P) \rightarrow S_2^* \qquad (13)$$

$$S(^3P) + S(^3P) + Y \rightarrow S_2^* + Y \qquad (14)$$

where Y is a third atom (or molecule). It follows that the emission intensity of S_2 groups (and consequently, the FPD output signal) can be influenced by various factors affecting formation, excitation, and deactivation chemiluminescence processes. The S_2^* lifetime should be noted as being about 10^{-7} s.[8]

As a rule, flame photometry determinations of phosphorus-containing compounds are carried out by measurement of the HPO chemiluminescence intensity in a low temperature hydrogen-air (oxygen) flame at $\lambda = 526$ nm. The PO emission intensity is about 16 times lower than that of HPO; in addition, the characteristic phosphorus atomic lines are in the UV (177.5, 178.3, and 178.8 nm), and are quenched by air, flame gases, and optics.[9]

The excitation mechanism of HPO group can be given as follows:[9]

$$P_2 + O_2 \rightleftarrows P + PO \qquad (15)$$

$$P + OH \rightleftarrows PO + H \qquad (16)$$

$$H + PO \rightleftarrows HPO^* + Y \qquad (17)$$

$$H + PO \rightleftarrows HPO^* \qquad (18)$$

where Y is the third compound (e.g., an atom).

Hydrocarbons cause HPO chemiluminescence quenching, therefore high sensitivity is attained by chromatographic separation of hydrocarbons from phosphorus-containing compounds. To increase FPD sensitivity with respect to phosphorus-containing compounds, a flame was exposed to a modulated magnetic field at a frequency of 98 Hz and a magnetic field force varying from 0 to 0.45 T.[10] Associative noises (namely flame noises), OH, C_2, CH, S_2 emission, and dark current from the photoreceiver were not modulated, thus causing a fivefold selectivity increase.[10]

In a hydrogen diffusive flame, organic compounds of Se and Te also form chemiluminescence groups, Se_2^* and Te_2^*, respectively. However, because excited Se_2^* and Te_2^* groups are easily quenched by the presence of carbon atoms, the complete chromatographic separation of Se and Te from hydrocarbons seems necessary.[11,12]

The FPD also has been used to determine tin organic compounds. Determinations are based on the SnH chemiluminescence measurement, with chemiluminescence being weakened in the presence of hydrocarbons. The latter phenomenon takes place when the methane (i.e., carbon) concentration is higher than 5%.[13]

B. Flame-Emission Detection

When chemiluminescence in hydrogen-air (oxygen) flames is not possible, analytes can be detected with respect to the thermal emission or adsorption of their oxides. Other analytes can be determined by products formed by their interaction with a sensitizer in a hydrogen-air flame having a temperature optimal for thermal emission. Several halogen derivatives were analyzed quite successfully by using different sensitizers such as Cu and In.[14,15]

Lead organic compounds were detected by measuring the Pb thermal emission intensity in a high temperature hydrogen-air flame at a wavelength of 460 nm.[16]

Flame-emission detectors with an operational wavelength equal to 4.3 nm were used to detect hydrocarbons in both GC and LC.[17] The chosen band 4.3 nm has an asymmetrical shape due to CO. In contrast to other detectors (thermal conductivity or flame ionization detectors), the described method ensures a selective sensitivity with respect to CO, with a detection reproducibility of about ±3%.[18]

III. FPD DESIGN AND OPERATION CONDITIONS

FPD used in chromatography can be classified as follows:

1. With respect to the field of application:
   - PD for GC
   - FPD for LC
2. With respect to the number of photometry channels:
   - One-, two-, and multichanneled detectors
3. With respect to the number of burners used in FPD:
   - Single burner FPD
   - Double burner FPD

A. Single Burner FPD for Gas Chromatography

Figure 1 shows a standard single burner FPD (SSD 250 "Carlo Erba"). The chemiluminescence (thermal emission) chamber is installed in the body of the burner (1), a light-proof unit for the removal of burned products is installed in the body (2). To equalize the temperature of the photoreceiver (7), a narrow-band optical interference filter (6) and two optical windows (5) are installed, the windows being separated with air. The photoreceiver (7) is thermostated at normal ambient conditions.

Sometimes a localized mirror is installed in the burner body to increase the sensitivity by two to five times. Optimal thermal conditions of the optical filter and photoreceiver can be attained with the use of optical pipes. To decrease the detector time constant (especially in the case of open tubular columns), the chemiluminescence chamber volume is decreased by installation of a glass (fused silica) tube.[19] This is also of importance for preventing exposure of the optical system to combustion products.

Presently, hydrogen fuel gas and column

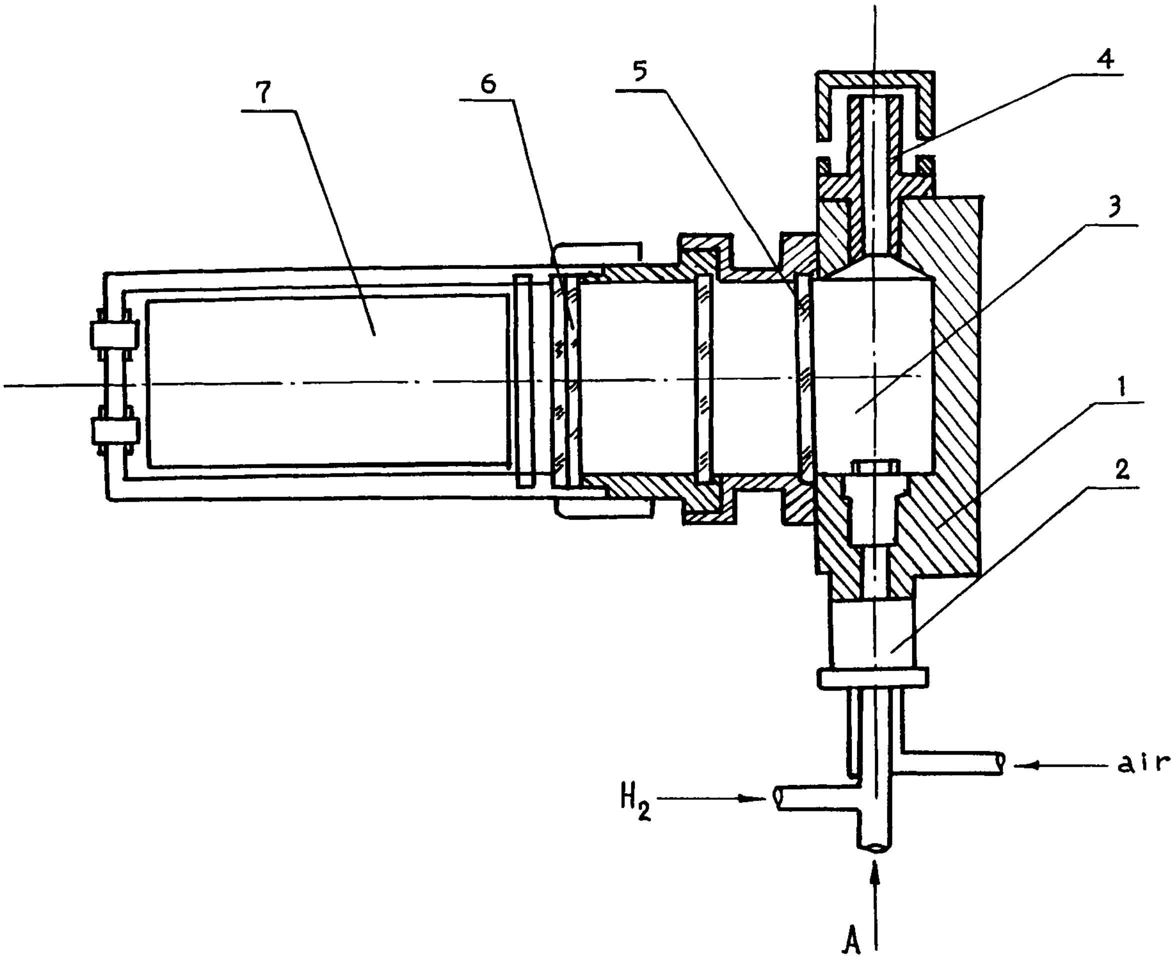

FIGURE 1. Single burner flame photometric detector.[22] (1) burner body; (2) burner; (3) chemiluminescent chamber (4) exhaust; (5) optical windows; (6) interference filter; (7) photoreceiver; (8) air; (9) eluent.

eluent are injected into a central burner nozzle while air is injected into an annular peripheral nozzle. This scheme permits laminar diffusive hydrogen-air (oxygen) flame formation, providing a high flame stability.

The FPD optical system includes a quartz window (converging lens), an optical interference filter, and a photoreceiver. As a rule, multipliers are used as photoreceivers, however, other types of receivers are also permissible. To increase FPD selectivity, narrow-band optical interference filters having band widths equal to 4 to 8 nm and luminous transmission 20 to 70% are used. When conditions are optimal, such as for FPD with selective sensitivity to tin compounds, optical filters are not necessary. The principal parameters of both foreign and domestic single burner FPD systems are given in Table 1.

To prevent the condensation of steam and other products in the FPD, the burner body should be maintained at 100 to 250°C. The body temperature can influence FPD operating parameters significantly. Dressler[20] showed that in the case of LFD-4 (Special Design Bureau of Estonian Academy of Sciences, USSR), varying the FPD body temperature in the range of 80 to 200°C led to a three- to fourfold decrease in output signal and a two- to threefold increase in background noise; in addition, the power index (n) of the detector decreased from 1.7—1.9 to 1.2—1.4. Hence, FPD temperature optimization should be performed. Chemiluminescence quenching in the presence of hydrocarbons is well known. Therefore a high FPD sensitivity can be attained if

TABLE 1
Characteristics of Some FPD Systems

					Gas flow rate (cm^3/min)					
Detector	**Number of channels**	**Operation wavelength (nm)**	**Sensitivity limit (g/s)**	**Selectivity with respect to hydrocarbons**	**H_2**	**Air**	**O_2**	**Carrier gas**	**Sensitizer**	**Ref.**
LFD 51	2 (S or P)	394 526	$4.6 \cdot 10^{-11}$(S) $2.0 \cdot 10^{-13}$(P)	10^6 10^7	40	40	—	36	No	21
SSD 250	1 (S or P)	394 526	$2 \cdot 10^{-11}$(S) $1 \cdot 10^{-12}$(P)	10^4	—	—	—	—	No	29
Tracor/ Meloy Melpak	1 (S)	394	8.10^{-12}	—	109	60	16.3	—	No	23
Melpak 100 AT	1 (S)	394	—	—	120	70	10.0	N_2,30	No	24
SSD 250	1 (Sn)	485 and 611	6.10^{-9} g/l	—	250	30	—	40	No	25
Tracor	1 (Sn)	610	6.10^{11} g	10^6	250	30	—	40	No	26
FPD	1 (P)	406	1.10^{-9} g	800	52	150	—	65	No	27

sulfur phosphorus compounds and organometallics of interest are separated from hydrocarbon contaminants.

As follows from the results given in Reference 28, S_2, HPO, or SnH chemiluminescence is not quenched by steam, permitting one to use water as a mobile phase.[29] Furthermore, contemporary single burner FPDs provide an opportunity for the injection of large sample volumes (10^3 to 50^3 mm) and the use of both packed and open tubular GC columns. These improvements were achieved by changing the FPD gas injection scheme and burner design, and by decreasing the "dead volume" of the chemiluminescence chamber. All this can be attributed to design developments. However, single burner FPD systems selective to sulfur have a disadvantage: the calibration plot steepness depends on the nature of the analyzed sulfur-containing compound. This drawback can be somewhat overcome, however, using modern microprocessor techniques.

B. Double Burner FPD

The necessity of developing sulfur-sensitive FPD systems for which calibration graphs steepness would not be dependent on component structure was precipitated by the fact that FPDs used previously were characterized by strong dependence of their parameters on the nature of the analyzed compound ("n" varying from 1.10 to 1.96). Presently, double burner FPDs that are highly selective and sensitive to sulfur-containing compounds are produced by several companies, namely, IBM Instruments (DANI model 68/7)[8] and Varian.[30] Some characteristics of the Varian double burner FPD and its operation parameters are given in Figure 2 and Table 2. The sensitivity and selectivity of double burner FPDs are the same as those of single burner FPDs, with its design being more complex. Double burner FPDs sensitive to bromine-, chlorine-, and iodine-containing compounds have been described.[31]

C. FPDs in Liquid Chromatography

In the late 1970s, attempts were made to use traditional GC FPD systems in LC. However, acceptable results were only recently obtained. To connect a FPD to an LC, two types of interface principles are widely used: supersonic and thermal. A scheme of a supersonic interface permit-

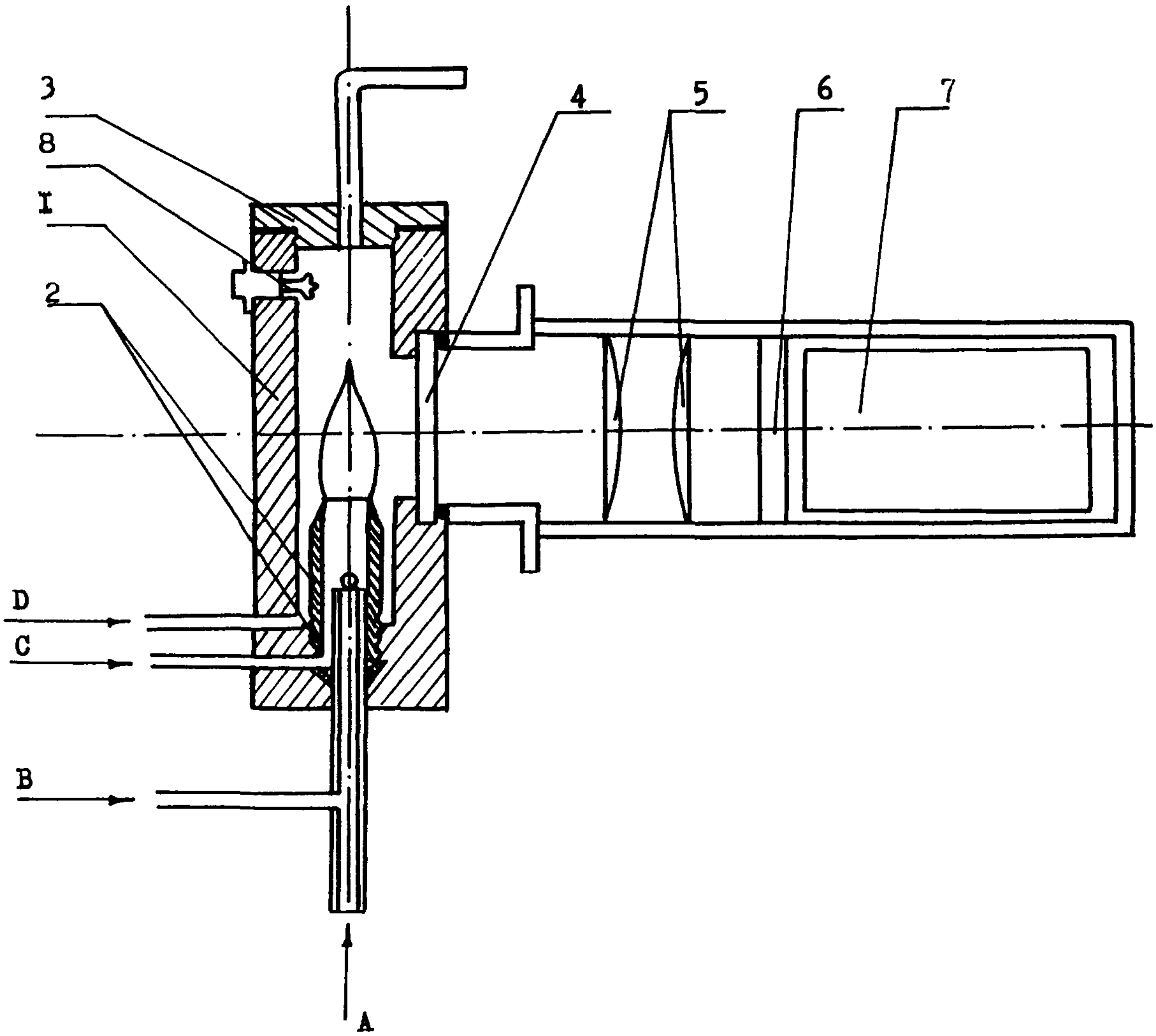

FIGURE 2. Double burner flame photometric detector.[30] (1) burner body; (2) double flame burner; (3) exhaust; (4) quartz window; (5) lenses; (6) interference filters; (7) photomultiplier; (8) eluent, (9) air 1; (10) hydrogen; (11) air 2.

ting high FPD sensitivity is shown in Figure 3.[32] The supersonic interface consists of a supersonic microsprayer, transforming the eluate into a fine spray which contains particles of d_p <10 μm. Nonsprayed eluate residue is removed from the interface with a wick. About 50% of the spray misses the tube connecting the supersonic interface and the FPD inlet. Electric power consumed by the supersonic interface is 5 to 15 W. To provide an increased coefficient of efficiency, the supersonic source is cooled by circulating water. Components of an LC system containing a GC-FPD selective to phosphorus-containing compounds and a supersonic interface are listed in Table 3.

Operating conditions of a Varian FPD used for GC and for LC in combination with a supersonic interface are compared in Table 4.A decrease in FPD sensitivity for LC-FPD systems is caused by a fivefold increase in background noise due to the supersonic sprayer and HPO chemiluminescence quenching by hydrocarbon solvent. Optimal gas flow rates for such systems differ greatly.

A GC-FPD system selective to chlorine-containing compounds was used for microcolumn LC with a thermal interface.[32,33] Quartz tubes with fused silica capillaries are used as thermal interfaces (Figure 4). The tubes are installed in an electric oven, maintained at 1000°C. The inlet

TABLE 2
Characteristics of Varian's Double Burner FPD[30]

Operation parameters	g/s
Sensitivity limit	10^{-11}
Selectivity with respect to hydrocarbons	10^3—10^6
Dynamic range	10^3
Gas flow rate (cm^3/min)	
Hydrogen	140
Air 1	80
Air 2	170
Carrier-gas flow rate cm^3/min	
Helium	30

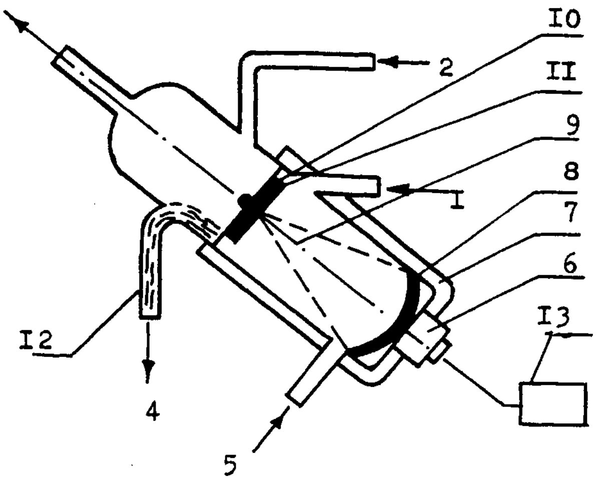

FIGURE 3. Supersonic interface FPD-LC.[32] (1) eluate; (2) carrier gas; (3) spray exit; (4) liquid drain; (5) cooling water; (6) electric disconnection; (7) air; (8) supersonic emitter; (9) supersonic field; (10) glass trap; (11) spray point; (12) wick; (13) supersonic generator.

thermal interface temperature is about 300°C. Scheme b is preferable because it excludes the adsorption of nonvolatile compounds on the quartz fibers. In addition, with scheme b, temperature control is possible, with the operating temperature being 250°C.

Figure 5[33] shows a schematic of a GC-FPD burner with an interface of a type used in LC. This detector is intended for the selective determination of chlorine-containing compounds. These components are determined with respect to InCl emission intensity in a hydrogen-air flame. The detector can be used in microcolumn LC. The LC column eluate (20 to 70 μl/min) is injected into the heated detector system through the thermal interface. The sensitivity limit is 9.10^{-2} g Cl/s, with a signal-to-noise ratio equal to three (with respect to 1,1,2-trichloroethane), water being used as a mobile phase, and the linear range is 16.

A mobile phase flow rate of less than 20 μl/min deteriorates stability, giving a nonhomogeneous evaporation. When the flow rate is higher than 75 μl/min, the chromatographic peak shape is distorted. When hydrocarbons are also present, InCl emission quenching takes place (as well as in GC). For example, when a mixture of methanol:water of 15:85 is used as a mobile phase, the sensitivity limit is 10 times higher than in the case of pure water, providing a response of 115.10^{-12} g Cl/s and a linear range of 0.3 to 4.3.[33]

IV. MAIN FEATURES OF CHROMATOGRAPHY DETECTION USING FPD

A. Determination of Sulfur-Containing Compounds

The high reactivity of sulfur-containing compounds demands much of chromatography columns and materials used in FPD in both GC and LC chromatographs. Adsorption of the analyzed compounds in the chromatography system should be excluded. In addition, separation conditions should be chosen to avoid hydrocarbon and overlapped peaks and provide complete separation of the components. Under these conditions, maximum sensitivity and selectivity can be obtained. High sensitivity can be achieved if large sample volumes are injected (10 to 50 μl for packed columns). Chromatography parameters of GC and LC systems containing an FPD selective to sulfur-containing compounds are presented in Table 5.

Chromatograms of sulfur compounds determined in casing head gas obtained using a combination of a packed precolumn and capillary col-

TABLE 3
Characteristics of System: LC-FPD[32]

Units	Model	Company	Operation conditions
HPLC	5560	Varian	Split mode, solvent flow rate 2—20 μl/min
Injector	7520	Rheodyne	1 μl
Supersonic generator	185	Wavetek	3.25—3.45 MHz
Supersonic multiplier	2402	E.N.I.	
FPD		Varian	
Gas flow rate			
Hydrogen			105—175 ml/min
Air			135 ml/min
Helium			105—175 ml/min

TABLE 4
Characteristics of Varian FPD for LC and GC[32]

Parameters	GC system	LC system
Sensitivity limit (gP/s)	1×10^{-12}	50×10^{-12}
Selectivity with respect to hydrocarbons	10^6	—
Linear range	10^4	10^3
Determination error at signal to noise ratio equal to 5	—	2—6%

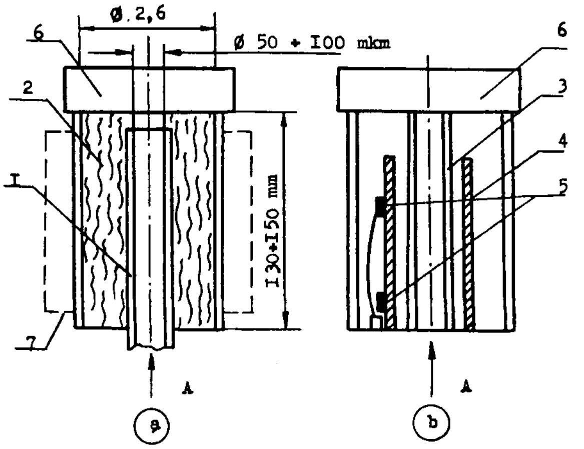

FIGURE 4. LC-FPD interfaces.[33] (1) quartz capillary; (2) quartz fibers; (3) fused silica capillary; (4) stainless steel capillary; (5) electric contacts; (6) FPD burner inlet; (7) electric oven; (8) eluate.

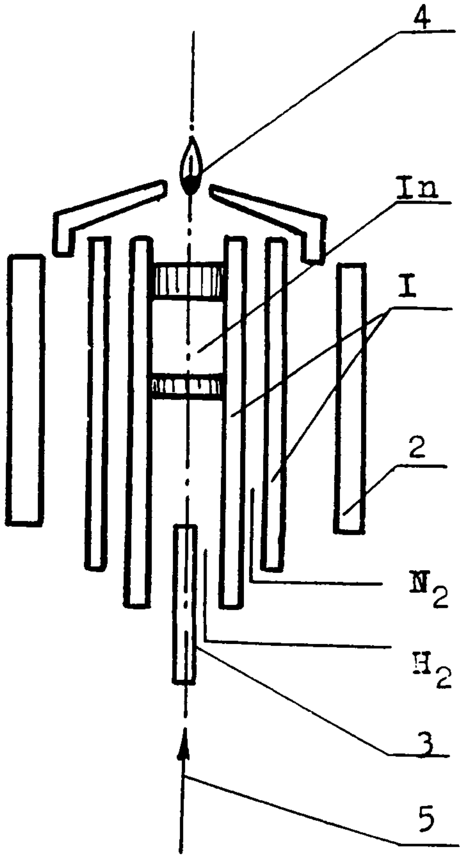

FIGURE 5. LC-FPD with thermal interface.[33] (1) quartz tubes; (2) detector oven; (3) capillary; (4) emission area; (5) LC eluate input.

umn system and an FPD are given in Figure 6. Figure 7 shows sulfur determination in light hydrocarbons using a combination of capillary open tubular chromatography and FPD. One of the features of contemporary GC for sulfur deter-

TABLE 5
Main Characteristics of Parameters of Chromatography Methods for GC and LC Systems

Column material	Column dimensions Length (m)	Column dimensions Inner diameter (mm)	Solid support	Stationary liquid phase	Column temperature (°C)	Carrier gas	Carrier gas flow rate (cm^3/min)	FPD producer	Sensistivity limit	Ref.
Sulfur GC Determination with FPD										
Stainless steel	2.5	3.0	Chromaton N-AW 0.20—.315 mm	5% XE-60	110	Water steam	25	—	5.10^{-10} g^s/x	29
Pyrex glass	3.0	4.0	Chromaton 0.25—0.315mm	5% SE-30	Program 30 → 100°c	Helium	75	—	$7.10^{-11}{}_g$ S/s	34
PTFE (Teflon)	2.0	4.0	Polychrom 0.16—0.250 mm	10% PEG-400 + 0.1 Triton X-305	20	Helium	40	—	2.510^{-4}% vol.	35
PTFE + fused silica	0.6 40.0	0.2 0.53	Porapak QS 40—60 mesh	0.5% H_3PO_4 50% phenyl methyl silicone, film thickness 0.53 mm	65 Program 15°/min +0ra120°C	Nitrogen	17 2.13	Hewlett-Packard	5.55 ppm respect to ethylmercaptan	36
Stainless steel	3.0	6.0	Supelcoport 80/100 mesh	3% SP-2100	Program 8°/min 0ldg→350°C	Nitrogen	30	Melpar 100AT	1.10^{-9} g S/	37
PTFE	6.0	2.2	Chromosorb T 40/60 mesh	12% polyphenylester and 0.5% H_3PO_4	105	Nitrogen	16	Meloy 100 AT	1.0 μg/l dimethylsulfide in 4% C_2H_5OH in H_20	38 39
PTFE	4.0	3.0	Teflon powder	6% polyphenyl ester	50	Air	50	XN-1	3 ppm with respect to H_2S	40
Quartz	30.0	0.53	—	DB-1	Program 30°C/min −20→120°C	Helium	6	Tracor	3 ppm with respect to H_2S	41
Fused silica	50.0	0.32	—	OV-351	Program 2°C/min 40ra240°C	Helium	3	Carlo Erba SSD 250	0.01 ppm with respect to diethylsulfide	42
Fused silica	30.0	0.53	—	GS-Q	Program 5°C/min 80→180°C	Helium	5	—	—	43
Glass	4.0	2.50	TZ K 0.25 0.30mm	10% Apiezon M	Program 80→200°C	Nitrogen	40	—	1 × 10^{-11} g	44
Phosphor and Chlorine Determination with FPD										
Fused silica	17	0.2	—	SP-2100	Program 100→230°C	Helium		Siemens	0.2 × 10^{-9} g/μl	45
Glass	20	0.32	—	OV-225	Program 100→230°	Helium				
Glass	2.0	3.0	Chromosorb WAW DMCS 80/100 mesh	2% OV-17	Program 150ra290°C	Nitrogen	40	Hitachi	1 × 10^{-9} g P	23
Stainless steel		1.0	Micropak Sp1P-5	Mobile phase: 10 m*M* octylamine +0.5 m*M* potassium perchlorate +0.1 m*M* hydroammonium phosphate +0.5 m*M* potassium acetate; flow rate, 2 μl/min; room temperature				Varian (+ supersonic interface for LC)	$5.10^{-11}{}_g$ ^{P}/S	32
Stainless steel	0.25	1.0	Nucleosil OH 7 μm	Mobile phase: 20% acetonitrile in H_20; flow rate, 3 μl/min; room temperature					(0—115) × 10^{-12} g/s	33
GC Determination of Pb and Sn Organometallic Compounds										
Glass	3.00	3.0	Chesasorb N 0.25—0.36 mm	10% PEG 6000	175	Helium	45	—	6.10^{-9} g $(C_2H_5)_4$ Pb in gasolines	27
Glass	2.00	2.0	Chromosorb WHP, 80/100 mesh	3% OV-225	220	Nitrogen	25	Melpar	(6—15) × 10^{-11} g	46 54
Glass	20.0	0.3	—	Pluronik 464 (film thickness I 0.15 μm) or PS 225 (film thickness 0.5 μm)	Program room temperature →200°C 4°C/min	Helium	5	SSD 250	(1—9) × 10^{-9} g/l	56

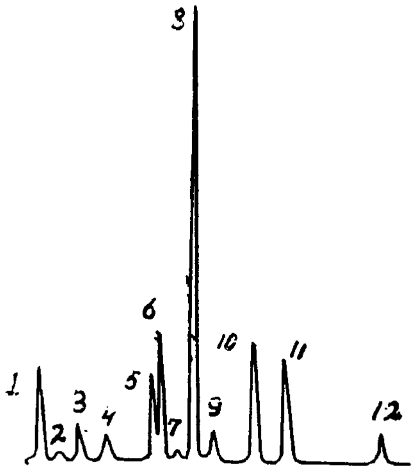

FIGURE 6. Sulfur-containing compounds in natural gas.[36] Separation conditions are given in Table 5. (1) methane; (2) ethane; (3) hydrogen sulfide; (4) COS; (5 and 6) hydrocarbons; (7) methylmercaptan; (8) ethylmercaptan; (9) isopropylmercaptan; (10) *n*-propylmercaptan, (11) secbutylmercaptan; (12) dimethylsulfide.

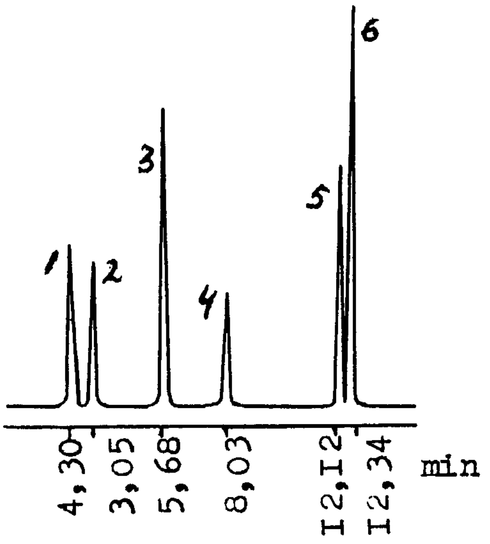

FIGURE 7. Sulfur-containing compounds in light hydrocarbons.[42] Separation conditions are given in Table 5. (1) H_2S; (2) COS; (3) SO_2; (4) MeSH; (5) CS_2; (6) Me_2S.

mination with FPD is the use of wide-bore capillary columns. As a rule, fused silica columns are used.[55] Therefore, FPD burner "dead volumes" should be diminished. This could be achieved by inserting fused silica tubes into the inlet part of an FPD burner. The FPD time constant can be diminished by fused silica tube installation, permitting burner chamber reduction and shortening of the time needed to pass an eluate through the detection unit. Inert gases (namely, helium, nitrogen, and argon) are widely used in GC-FPD systems, while air is rarely used because of some design peculiarities of FPD burners. It is known that steam and ammonia used as mobile phases can improve chromatography separations, permitting shortening of the analysis time for high molecular weight, polar substances, and water impurities. We carried out experimental verifications and showed that GC-FPD could be successfully used to analyze sulfur-containing compounds using water, steam, and ammonia as mobile phases[29] and an FPD sensitive to sulfur compounds (as described in Reference 47). We used a GC with a unit specially designed to carry out the chromatography using steam as a carrier gas.[48] To increase sensitivity, the flow rates of the gases were optimized.

Figure 8 shows GC chromatograms of the

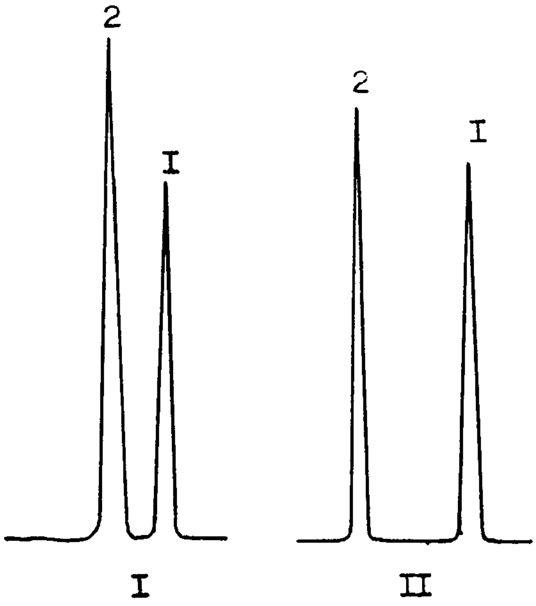

FIGURE 8. Di-*n*-butylsulfide and benzene separation.[29] Mobile phase: I — nitrogen (scale $5 \cdot 10^{-10}$ Å), II — steam (scale $50 \cdot 10^{-12}$ Å). (1) benzene; (2) di-*n*-butylsulfide (5 μl; 0.001% mass). Mobile phase flow rate: nitrogen 55 cm^3/min, steam 25 cm^3/min. Separation conditions are given in Table 5.

analysis of di-*n*-butyl-sulfide in benzene using nitrogen or steam as the mobile phase. Using steam, the sensitivity of the sulfide analysis is significantly reduced. This can be explained as a reduction in the number of chemiluminescence S_2 groups due to deactivation with steam. However, the use of steam significantly improves the separation.

These data show that steam can be used as a mobile phase for the GC determination of polar sulfur-containing components. They also can be determined in high molecular compounds and water, the sulfur concentration being equal to 10^{-1} to 10^{-4}% by weight, and the water content in the overall gas flow not being higher than 22%.

Figure 9 shows FPD output signal vs. the properties and quantity of mobile phase in FPD gas stream. When microamounts of water are introduced directly before GC analysis, the signal amplitude becomes 12 to 25% higher (see for example, Reference 23). The data were obtained with 0.4 μl of distilled water introduced 20 s before the elution of the sulfur-containing compound. Due to the low level of water, quenching of S_2 groups did not occur. The output signal increase is due to the suppression of active absorption sites by the steam.

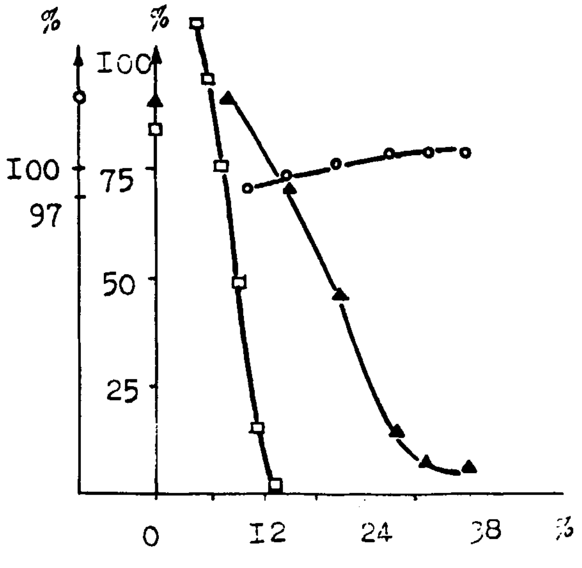

FIGURE 9. Decrease FPD response (R) as function on mobile phase composition in detector gas flow.[29] ○ — nitrogen; ▲ — steam (H_2O); □ — ammonia. Test sample 0.001% mass di-*n*-butylsulfide in benzene. Separation conditions are given in Table 5.

The use of ammonia as a mobile phase to determine small amounts of sulfur-containing components was tested using a laboratory gas chromatograph equipped with an FPD and a separate gas preparation unit. This unit was installed to carry out additional ammonia purification and prepare the gas dosage. The chromatography column and analysis conditions were similar to those used in the case of steam. When the ammonia content in the gas flow is increased, the output FPD signal decreases. This can be explained by action of CN groups at λ_{max} at 398 nm overlapping the S_2 group emission. CN groups can be formed by incomplete separation of di-*n*-butylsulfide from benzene, or by hydrocarbon impurities in the flame-forming gases. Therefore, the determination of sulfur-containing compounds based on S_2 group chemiluminescence intensity in a low temperature hydrogen-air flame with ammonia as a mobile phase can be carried out, providing that hydrocarbons are absent in all gases and complete separations of sulfur-containing compounds from hydrocarbons can be achieved.

We showed that FPD sensitivity and selectivity to S can be used to analyze small amounts of sulfur (10^{-1} to 10^{-3}% by weight) using ammonia as a mobile phase (provided that its content in gas flow stream does not exceed 9 to 10% by volume.[29]

B. Determination of Phosphorus- and Chlorine-Containing Compounds

During the last 5 years, FPD utilization for the selective determination of phosphorus-containing compounds was supplanted by the use of thermal spray detectors since the latter are easier to use. Thermal spray detectors are most widely used in LC. FPD systems are used more often in simultaneous S and P determinations (double channel mode). For example, they can be used to identify pesticide residues containing both S and P atoms. To simplify complex mixture identifications, the P/S ratio (%) in a compound is determined.

To characterize quantitatively pesticides containing both P and Cl heteroatoms, parallel GC analysis is conducted using two selective detectors: the FPD for P, and the electron-capture detector (ECD) for Cl.[45] A multicolumn system consisting of two switchable columns differing in polarity can be used. The characteristics of such a system are given in Table 5. This procedure has been used to identify numerous pesticide residues. Determinations were based on retention time measurements. The same results can be obtained using two or more GC systems.

A GC-FPD supplied with a supersonic interface was used in LC (see earlier discussion). This system has been used to determine phosphorus compounds in phospholipids and phosphates in sugar derivatives. Operating conditions are presented in Table 1, with the chromatogram given in Figure 10.

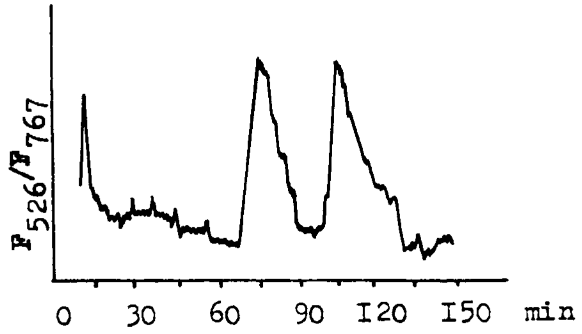

FIGURE 10. Sugar phosphate chromatogram obtained in the system LC-FPD-supersonic interface.[32] (1) 1 μg glucose-6-phosphate; (2) 1.5 μg glucose-1-phosphate. Operation conditions are given in Table 5. Note: FPD response ratio of 526 to 767 nm.

When water solutions of potassium salts are used as the mobile phase, the FPD noise increases and, consequently, the sensitivity decreases. To avoid this drawback (or to decrease the FPD noise), a double beam mode is used. In particular, this procedure is based on the simultaneous measurement of the emission intensity at 526 nm (HPO emission) and at 727 nm (potassium salt emission), with the ratio of F_{526}:F_{727} being registered. This procedure has some distinct advantages: (1) a sufficiently high sensitivity and high selectivity (note: LC procedures based on thermal conductivity or refractometry detection are nonselective); and (2) a relative simplicity (in contrast to LC procedures using different post-column reactors). In addition, GC-FPD systems with proper interfaces can be used in multidetector LC arrangements since physicochemical principles of FPD and their design permit such a combination.

During the last 10 years, FPD methods that were selective to chlorine were not employed, due to the improvement of operating conditions, and technical and metrological parameters of ECD systems for GC analysis. However, many attempts were made to evaluate the selectivity of GC FPD selective to Cl in LC. Microcolumn reversed-phase LC, with an FPD equipped with a thermal interface is of special interest. The characteristics of this system are given in Table 5.

Figure 11 shows LC chromatograms of chlorinated components obtained with an LC equipped with a Cl-sensitive GC FPD, a thermal interface, and a UV-detector operated at different wavelengths. The sensitivity, selectivity, and linear range of this system permits the analysis of ultratrace amounts of chlorinated compounds in different substances.

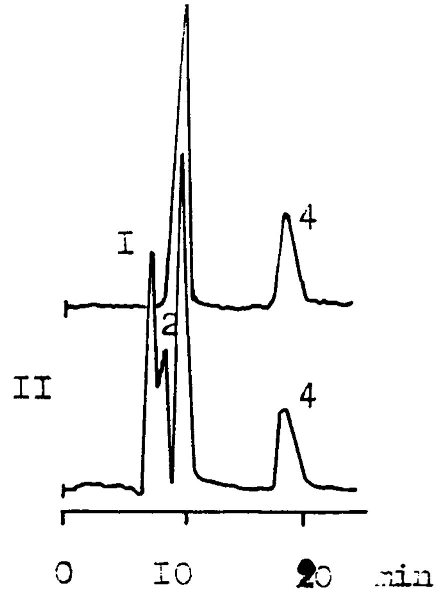

FIGURE 11. LC separation of chlorophenols.[33] I — chromatogram obtained with FPD; II — chromatogram obtained with UV-detector at 280 nm; (1) phenol; (2) o-cresol; (3) chlorophenol; (4) 2,5-dichlorophenol. Operation conditions are given in Table 5.

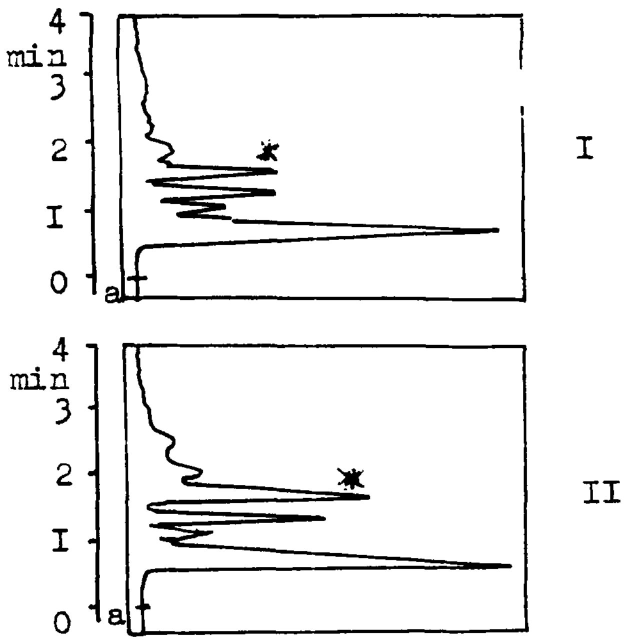

FIGURE 12. Tetraethyl lead in automobile gasolines A 76 (I) and A 93 (II).[27] (a) sample injection; (*) tetraethyl lead $10 \cdot 10^{-12}$. Other conditions are given in Table 5.

C. Organometallic Compounds of Lead and Tin

During the past 5 to 7 years, GC FPD systems selective to tin or lead were used by several investigators. This is probably due to the fact that FPD systems highly selective to Pb or Sn are not produced commercially. The reported procedures are based on the use of modified FPD systems. There were no reported data on FPD applications in LC for Pb and Sn analysis. The main parameters of the reported GC systems are listed in Table 5. One of the most important organometallic compounds is tetraethyl lead (TEL), widely used as an antidetonator in automobile gasolines. The GC method for TEL analysis is based on FPD utilization.[32] Figure 13 shows chromatograms of commercial ethylated gasolines. When TEL determinations were carried out, sulfur compounds present did not influence the detector signal. This can be explained by the fact that the flow rates and ratios of the flame-forming gases are far from optimal with respect to sulfur FPD analysis. Furthermore, hydrocarbons affected the FPD signal if the separation of TEL and the hydrocarbons was incomplete; led to a decrease in the detector sensitivity compared with that obtained at calibration. The application of this technique permits a reduction in the analysis time compared with the chemical methods, with the former being 50 to 60 times faster.

The analytical identification of Sn in waste waters, air, and food became a pressing problem because Sn organic compounds are widely used as polyvinylchloride stabilizers and fungicides. Therefore, many researchers reverted to GC determinations with FPD selective to Sn. The operating conditions are given in Table 5, while a typical chromatogram is given in Figure 13.[56] Figure 13 shows a chromatogram of a water extract taken from Zurich Lake (Spring, 1986). Hence, GC FPD systems can be successfully used for the laboratory monitoring of the described compounds in both research institutions and industrial laboratories.

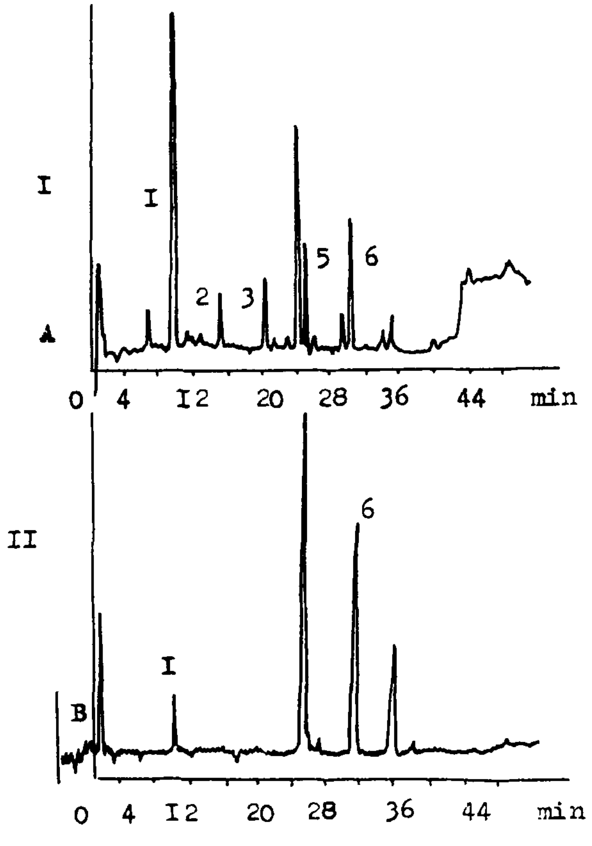

FIGURE 13. Chromatogram of water extract taken from the Lake Zürich in 1986 (GC-FPD selective to Sn).[56] I — column coated with Pluronic-64; II — column coated with PS 228. (1) $SnEt_4$ ($1—10^{-9}$ g/l); (2) $BuSnEt_3$ ($12 \cdot 10^{-9}$ g/l); (3) Bu_2SnEt_2 ($6 \cdot 10^{-9}$ g/l); (5) Bu_3SnEt ($7 \cdot 10^{-9}$ g/l); (6) internal standard, alkyl tin.

V. PECULIARITIES OF THE CALIBRATION PROCEDURE USING FPD

Special features of FPD calibration are caused by inherent peculiarities of the FPD, namely, nonlinearity in response, and variations in detector sensitivity. The slope of a response curve depends on the nature of the analyzed compound. This is most typical in the FPD response to sulfur compounds. Therefore, absolute calibration with respect to individual compounds is widely practiced. Other procedures use a calibration with respect to an internal standard.

A large variety of standards are used to calibrate FPD chromatography systems. As a rule, high purity individual compounds are used as standards, although sometimes standard mixtures are also used. Standards which can be used to calibrate FPD chromatography procedures discussed herein are given in Table 6.

Liquid standards for chromatography are available in ampules of 1 to 3 ml, while gas standards are available in compressed gas cylinders (0.1 to 4.0).

A relatively narrow linear dynamic range is known to be one of the disadvantages of sulfur-containing compounds detection by FPD. Usually, this range is about 10^2 to 10^3. To increase the linear dynamic range, methods of electronic linearization are usually used. The exception to this is the broad FPD linear dynamic range shown for SO_2.[2] A system employing electronic linearization of the FPD vs. the flow of a sulfur-containing compound entering the detector ("dilution method") has been suggested.[53] According to this "dilution method", after an increase in the concentration of the sulfur-containing compound entering the FPD causes the FPD signal to approach the limit of its linear response range, the eluate entering the detector is diluted 10 to 100 times (e.g., dilution can be carried out by means of a splitter). As a result of this stepwise dilution, the detector continues working in a linear range, and its linearity can be increased by two orders of magnitude.

VI. CONCLUSIONS

Chromatographic procedures for the selective determination of compounds containing S, P, Cl, Pb, and Sn using FPD are very popular among researchers working in both GC and LC. A number of publications devoted to these problems have been published during the past 3 to 5 years. Different aspects as well as numerous applications have been discussed. Much attention was given to procedure developments as well as detector design.

Some attempts have been made to use commercially available GC-FPD systems in LC. Different interfaces for this purpose have been used and interesting results have been obtained. Much attention was given not only to FPD sensitivity and selectivity to hydrocarbons, but also to technical parameters such as the dynamic range, time constant, and "dead" volume of the detector, and the influence of the mobile phase flow rate on the output of the FPD signal amplitude. It is also noted that capillary columns in combination with FPD have become popular. Capillary columns, however, demand refined dynamic detection parameters.

Finally, it is concluded that FPD systems are worth utilizing for selective analyses of sulfur-bearing, phosphorated, chlorinated compounds as well as of organometallic compounds present in a variety of materials.

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TABLE 6
Sulfur-Containing Standard Samples

Company, country, catalog number, or NBS number	Standard sample	Certified	Parameter	Ref.
1616 (NBS, U.S.)	Sulfur in oil	Mass concentration S, % mass	0.719	49
1620a (NBS, U.S.)	Sulfur in oil		4.504	
1621c (NBS, U.S.)	Sulfur in oil		1.040	
1622c (NBS, U.S.)			2.012	
1623 a (NBS, U.S.)			0.240	
1624a (NBS, U.S.)	Sulfur in oil distillate		0.141	49
1636b (NBS, U.S.)	Pb in standard fuel	Mass concentration Pb, mg/g	11.200 18.800 25.100 764.000	49
1818 (NBS, U.S.)	Cl in lubricants of oil nature	Mass concentration Cl, mg/g	29 63 78 231 558	49
4-4597 Supelco (U.S.)	Chlorinated insecticides (16 components)	Mass concentration, Cl	—	50
4-4598 Supelco (U.S.)	Phosphorated insecticides (15 components)	Mass concentration of P-containing compounds	—	50
31.901-3 Aldrich (U.S.)	Standard Pb solution	Mass concentration, Pb	—	51
14-20-54...14-20-111 Interethalone (U.S.S.R.)	Analytical samples of pesticides	Mass concentration	—	52

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