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SELECTIVE DETECTION IN GAS CHROMATOGRAPHY

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19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The most popular method of separating a complex hydrocarbon mixture, such as jet propulsion fuel, into it's individual components is that of high resolution gas chromatography (HRGC) using a flame ionization detector (FID). However, neither the efficency of HRGC or the sensitivity of the FID lend any information as to the identity of the individual components.

This report looks at 24 different gas chromatographic detectors that respond selectively to heteroatom compounds such as those containing S,N,O,P, Halogens, and some metals. Recommendations for the use of these detectors for analyses of jet propulsion fuels are made.

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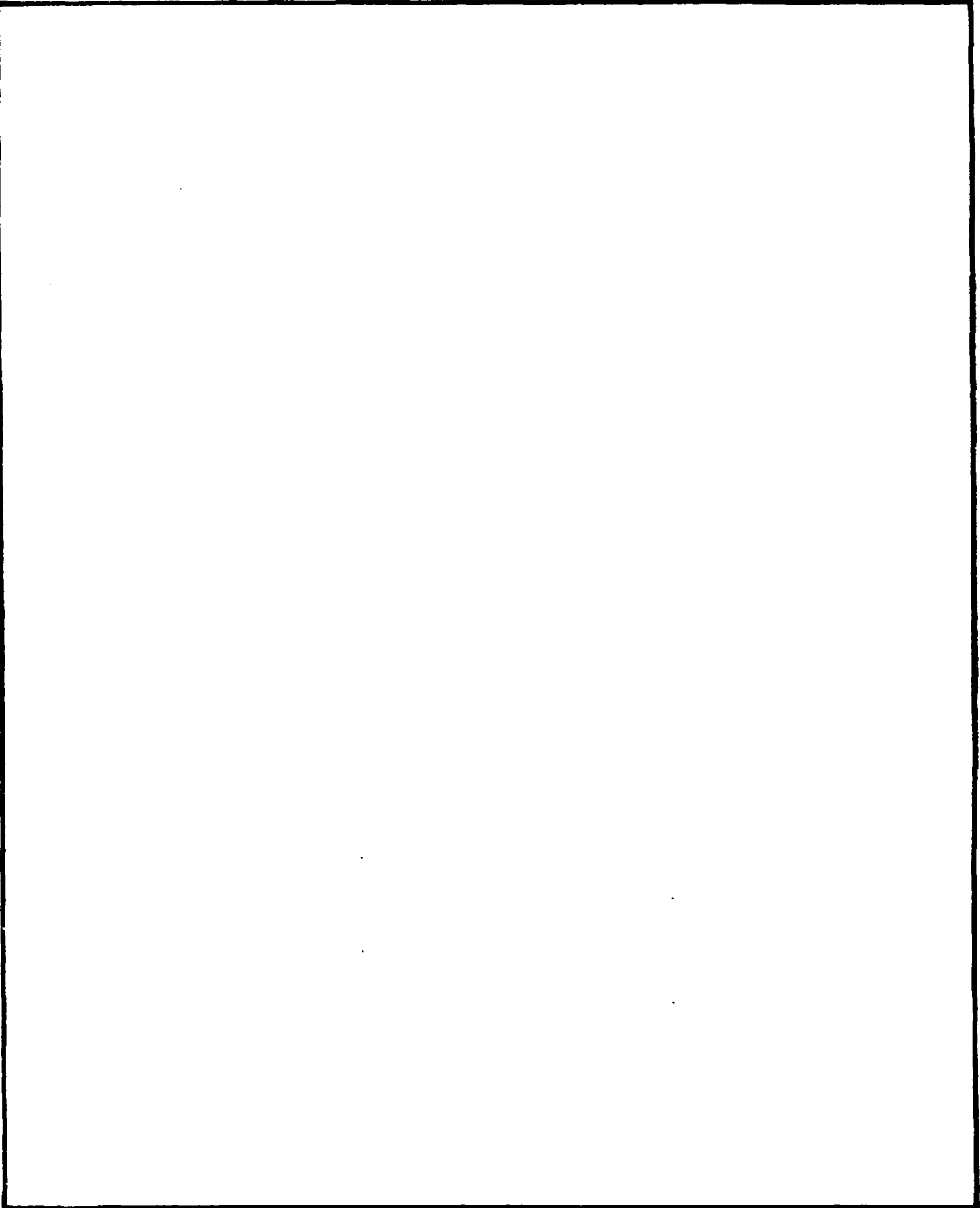SECURITY CLASSIFICATION OF THIS PAGE

TABLE OF CONTENTS   Page

iii

A-1

SECTION I

INTRODUCTION

High-resolution gas chromatography (HRGC) is capable of separating a very complex hydrocarbon liquid such as jet propulsion fuel into nearly all of its individual components. However, there is no guarantee that what appears to be a single chromatographic peak is in fact a single fuel component. The method of detecting these HRGC eluents is very often the flame ionization detector (FID), a very sensitive and universally responding hydrocarbon detector.

Neither the separating power of HRGC, or the sensitivity of the FID, however, lend information as to the identity of the eluting component. The need to specifically identify HRGC eluents, especially those containing heteroatoms such as N,S,P,O, halogens and some metals has been well-documented (5,11).

The purpose of this report is to review the progress in the area of selective gas chromatographic detectors and to recommend selective detectors for use in the HRGC analysis of jet propulsion fuels.

This report will present 24 different selective gas chromatographic detectors. These detectors, while not all directly applicable to the HRGC analysis of jet propulsion fuel, all show the concept of selective detection in gas chromatography.

The detectors presented herein range in complexity from simple modifications made to existing universal detectors or specific analyzers to detectors that are scaled down versions of high-technology, high cost spectroscopic techniques.

The applicability of these detectors to jet propulsion fuel analyses will be determined from a comparison of their complexity and cost versus their effectiveness as high-resolution gas chromatographic detectors.

1

SECTION II

TECHNICAL DISCUSSION

The most common method of chromatographing complex hydrocarbon mixtures such as jet propulsion fuel is with a high resolution gas chromatograph using glass capillary or fused silica columns. The sample is injected into a heated injector zone where it is vaporized. A large portion of this vaporized sample is vented, and the rest is routed into the column. Once inside the column, the sample partitions into a stationary liquid phase that coats the inside of the column. Different fuel components migrate down the column at different rates due to their individual partition coefficients with this stationary phase.

Once eluted from the column, compounds are then detected with any one of a number of available gas chromatographic detectors. The 24 detectors examined in this report are separated into four distinct categories: ionization detectors, absorption detectors, emission detectors, and conductivity detectors.

A. IONIZATION DETECTORS

Virtually any type of energy (electronic, radioactive, heat, etc.) can be used to ionize GC eluents. Selectivity is realized by certain compounds being susceptible to the type of ionization method used, or by ionization products being characteristic of the parent molecules.

1. Mass Spectral (MS)

Compact mass selective GC detectors are now commonly available for use. The Ion Trap Detector (Finnigan Mat) is an excellent example of one such detector.

The eluents of a GC are transferred to the detector via a heated fused silica transfer line where they are ionized by electron impact. The ions are then ejected from the ion storage region sequentially from low to high mass and then detected by an electron multiplier. The resultant mass spectrum for any given mass-to-charge ratio can then be matched to existing mass spectrum in a library by computer searching techniques. This detector is capable of universal mass spectrum scanning and specific mass spectrum searching.(See Fig.1.)

2. Fourier Transform Mass Spectral (FTMS)

The use of Fourier Transformation with mass spectral data greatly enhances the mass resolution of GC/MS data. For example, the GC-FTMS system referenced here is capable of collecting 8,192 data points every 100 ms. This fact combined with the background separation capability of Fourier Transformation makes GC-FTMS an extremely powerful GC peak identification technique (2).

3. Oxygen-Flame Ionization (O-FID)

The Oxygen Flame Ionization Detector obtains selectivity for O2 containing compounds by utilizing two microreactors in line between the column outlet and the flame. The first, a cracking reactor operated at 1500-K, forms CO from the O2 compounds. The second reactor operated at 620-K, hydrates the CO to form CH4. The CH4 is then detected by normal flame ionization (20).(See Fig.2.)

4. Hydrogen Atmosphere Flame Ionization (HAFID)

The Hydrogen Atmosphere Flame Ionization Detector realizes selectivity for Si, P, Cl and Fe by merely altering the type and flow rates of gases to the detector. The normal 300 ml/min air and 30 ml/min H2 is changed to 130 ml/min O2 and 1600 ml/min H2. This results in suppressed responses to normal hydrocarbons and selective responses to the above-mentioned compounds (19).
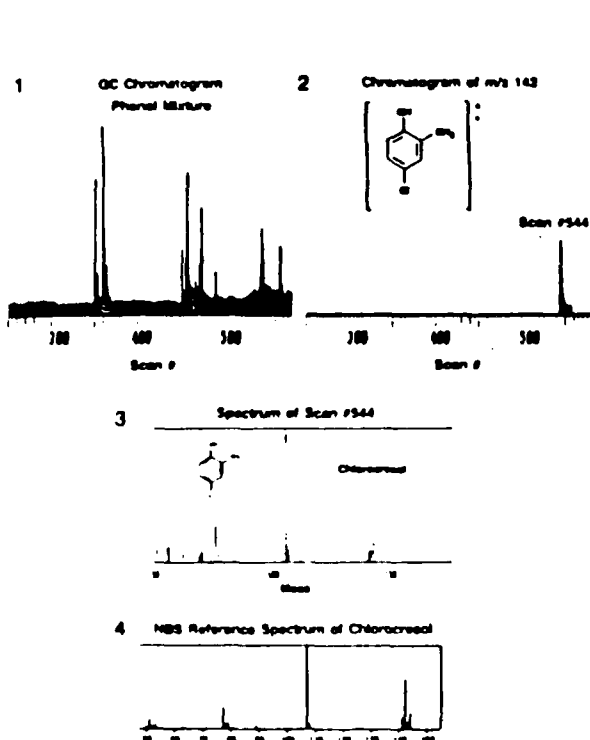
3

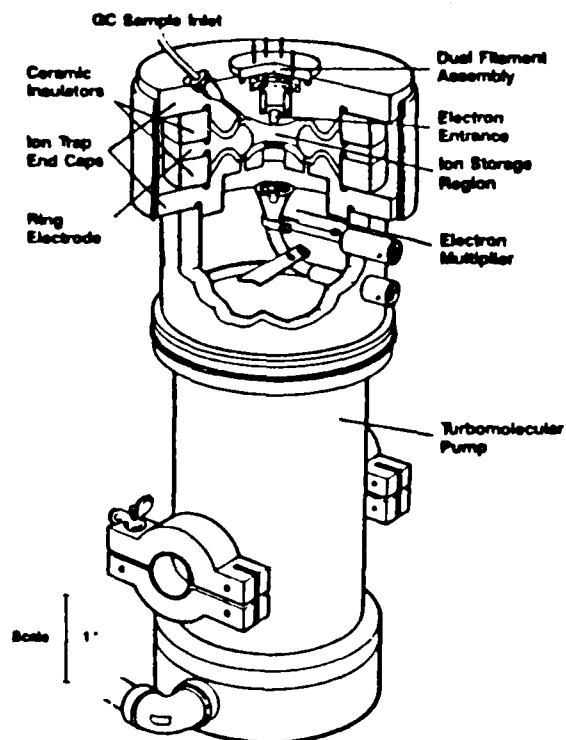Figure 3 *Procedure for compound identification using the ITD.*

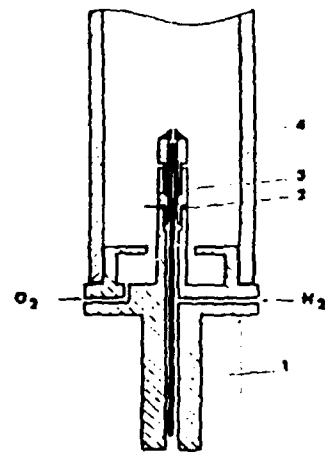Figure 2 *Schematic diagram of ion trap detector.*

Table 3

Compound classes with masses generally characteristic of them*

Compound class	Characteristic mass
Paraffins	43, 57, 71, 85
Aliphatic carboxylic acid methyl esters	74, 87
Alkenes	41, 55, 69
Triterpanes	191
Steranes	217
Siloxanes	73
PCBs	256, 290, 324, 358, 392

*For a more detailed list of masses common for compound classes, see Ref. 3.

4

12 = CRACKING REACTOR

13 = HYDROGEN REACTOR
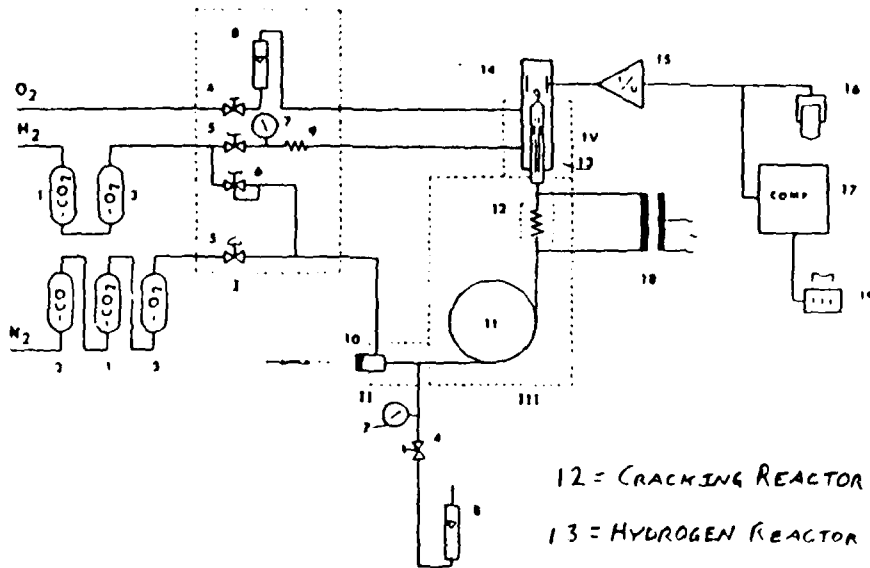
HYDROGEN REACTOR

CRACKING REACTOR

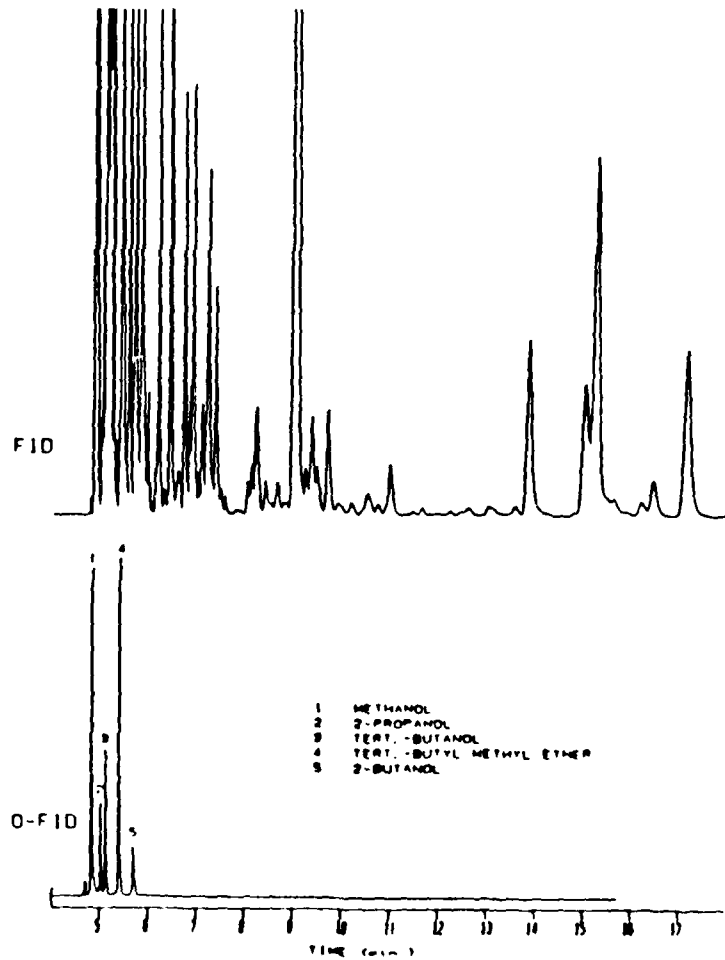|		
1	METHANOL	
2	2-PROPANOL	
3	TERT.-BUTANOL	
4	TERT.-BUTYL METHYL ETHER	
5	2-BUTANOL	
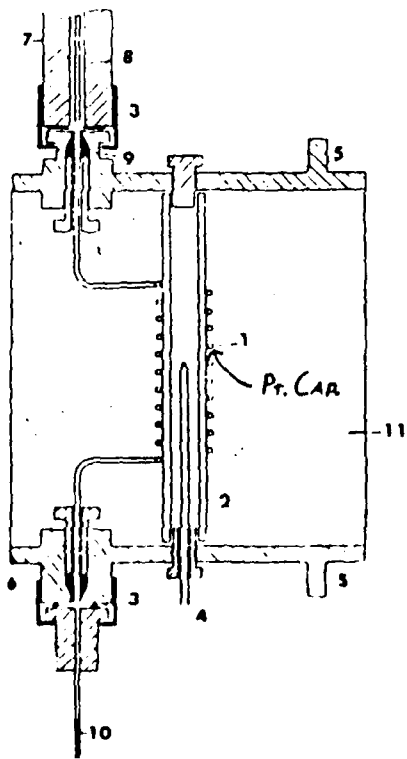
FIG 2: Selective detection of 02 compounds in starting fluid by GC/O-FID.
(Reproduced by permission from ref. 20 , Copyright Elsevier Science
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5

5. Thermionic Specific (TSD)

The thermionic emission of charged particles from the surface of a hot bead consisting of alkali metal embedded in a ceramic matrix provides highly specific responses to compounds containing N and P as well as halogenated compounds. To a small extent the detector is selective to aromatic compounds in hydrocarbon fuel samples (17) (22).

6. Ion Mobility (IMD)

Ion Mobility Spectrometry is a method closely related to the Electron Capture Detector where organic compounds are ionized by charge transfer reactions in the presence of a constant electric field gradient. Product ions drift down this field at different rates, dependent on mass, charge and ion size. By doping the detector with oxygen, increased selectivity and sensitivity are gained for halogenated compounds. (13).

7. Electron Capture Detector (ECD)

The constant signal of a radioactive electron source, commonly Ni-63, in an inert gas flow is interrupted by the introduction of molecules with "capture free" electrons, such as halogenated compounds, which generate a negative response. The eluents are ionized but the response is read as the reduction of the ion current (5).

8. Photoionization (PID)

The Photoionization Detector selectively detects gases such as H2S, NH3, AsH3, and I2. A U.V. lamp irradiates the GC eluents. Any compound with an ionization potential less than the U.V. lamp will be ionized. The resultant ion current is measured by a sensitive electrometer system (11).

6

9. Catalytic Ionization

When organic compounds are oxidized on the surface of a heated platinum filament only certain compound types yield an ion current comparable to that of the flame ionization detector. Specifically, these compounds are highly branched hydrocarbons such as alkanes and alcohols (17).

B. ABSORPTION DETECTORS

Comparing the absorption characteristics of an eluting GC compound to known standards in some region of the electromagnetic spectrum truly defines the nature of that compound. This technique is used either by scanning a specific region of the spectrum or at a set wavelength specific to the compound of interest.

1. Infrared (IR)

Eluting GC components are trapped or isolated in a GC/IR cell through which a dispersive I.R. spectrophotometer provides an I.R. spectrum of the component. This is not a continuous analysis, and is limited by the I.R. scan time (3).(See Fig.3.)

2. Fourier Transform Infrared (FTIR)

By use of a interferometric system allowing the infrared to scan eluting chromatographic compounds at a rate of up to 10 scans per second, the Fourier Transform Infrared system can produce a spectrum of a single chromatographic peak while it is eluting. The spectrum is then compared to a library of infrared spectrum for peak identification. Absorbance versus time can also be plotted to produce a more traditional chromatogram (4).
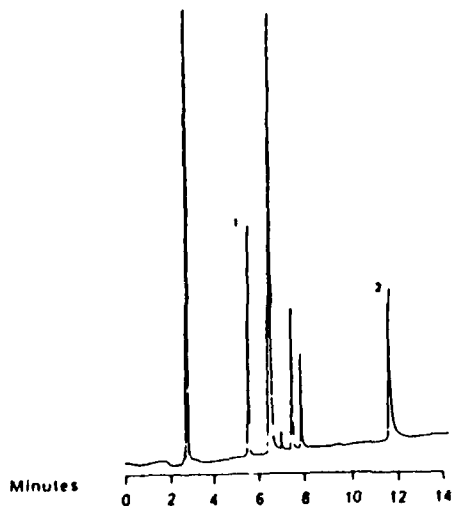
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Figure 12 Chromatogram of a fragrance mixture, recorded as in Figure 1. Chromatographic conditions are the same as for Figure 1, except the oven was programmed from 90°C to 220°C at 10°C/min.
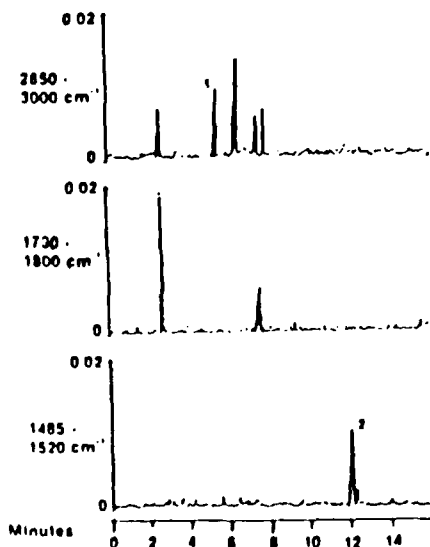
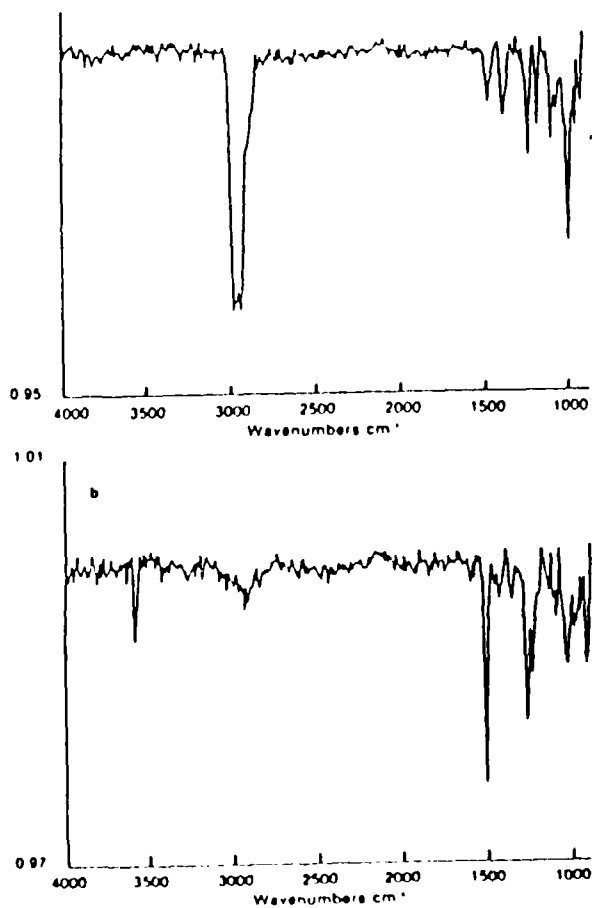Figure 13 Infrared chromatograms of the fragrance mixture in Figure 11, obtained on an IBM IR/85 GC/IR system

Figure 14 a) Eucalyptol and b) eugenol are infrared spectra in transmittance of peaks 1 and 2 (Figures 12 and 13), respectively

FIG 3: Selective detection of eucalyptol and eugenol by GC/IR. (Reproduced by permission from ref. 4, Copyright International Scientific Communications.)

8

3. Atomic Absorption Spectrometry (AAS)

Through the simple interfacing of a high resolution gas chromatograph to an atomic absorption spectrophotometer organomercury (II) compounds can be selectively analyzed at trace levels in organic mixtures. The background interference from the organic molecules is minimal for two reasons. The AAS is not particularly sensitive to organic molecules and these molecules are mostly cracked in the 600 Deg.-C decomposition furnace used to convert the organomercurials to elemental mercury (9).

4. Ultraviolet (UV)

GC column eluents are directed to a sample cell with a quartz window. Through this window, the sample is irradiated by U.V. light at a fixed wavelength. The choice of this wavelength determines the compound-type sensitivity. Typically, a setting of 250 nm renders the detector very sensitive to aromatic hydrocarbons and insensitive to aliphatic or naphthenic species (5).(See Fig.4.)

C. EMISSION DETECTORS

Eluting GC compounds are converted to an excited state and allowed to relax yielding characteristic emissions. These detectors combine the advantages of ionization and absorption detectors in that the type and amount of energy applied is controllable and the emissions are characteristic in the electromagnetic spectrum.

1. Rotationally Cooled Laser-Induced Fluorescence (RC-LIF)

GC eluents are excited by a high-intensity laser beam and caused to fluoresce. By taking advantage of the fact that any compound will fluoresce at least one wavelength unique to that compound, RC-LIF is virtually unsurpassed in selectivity. However, at present, the system is restricted to scanning for a particular compound at it's unique wavelength (8).(See Fig.5.)
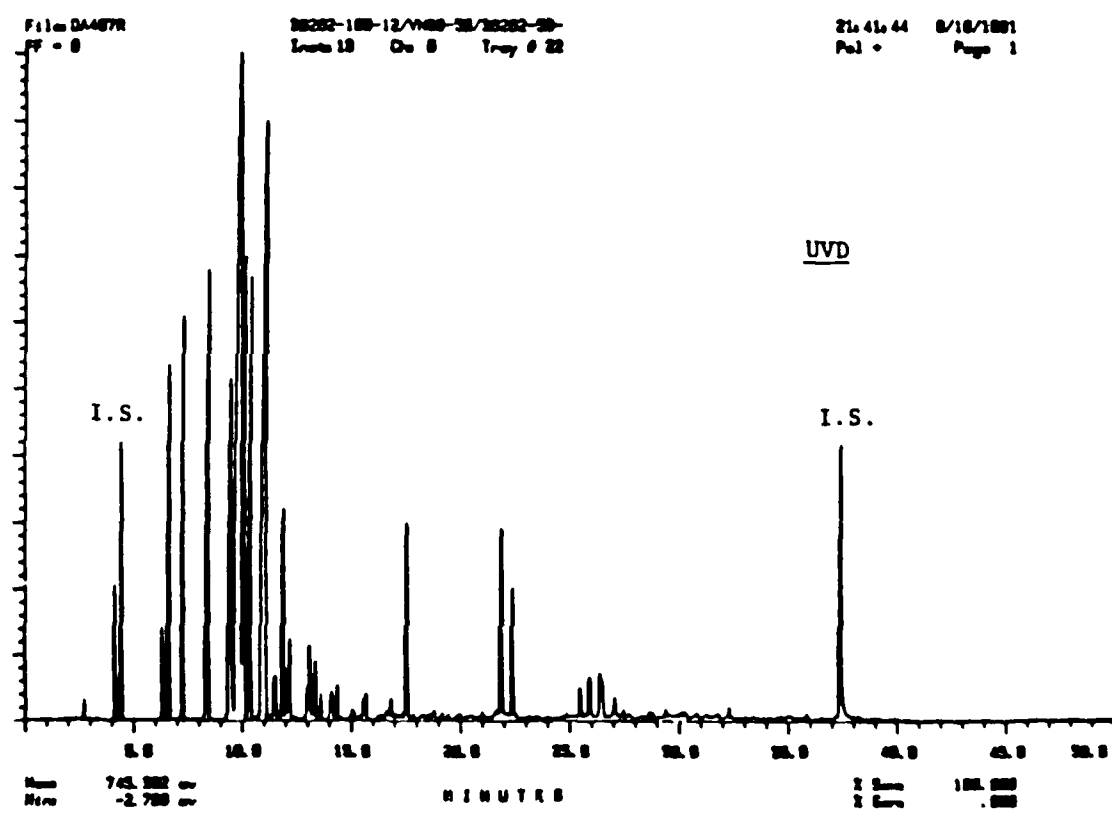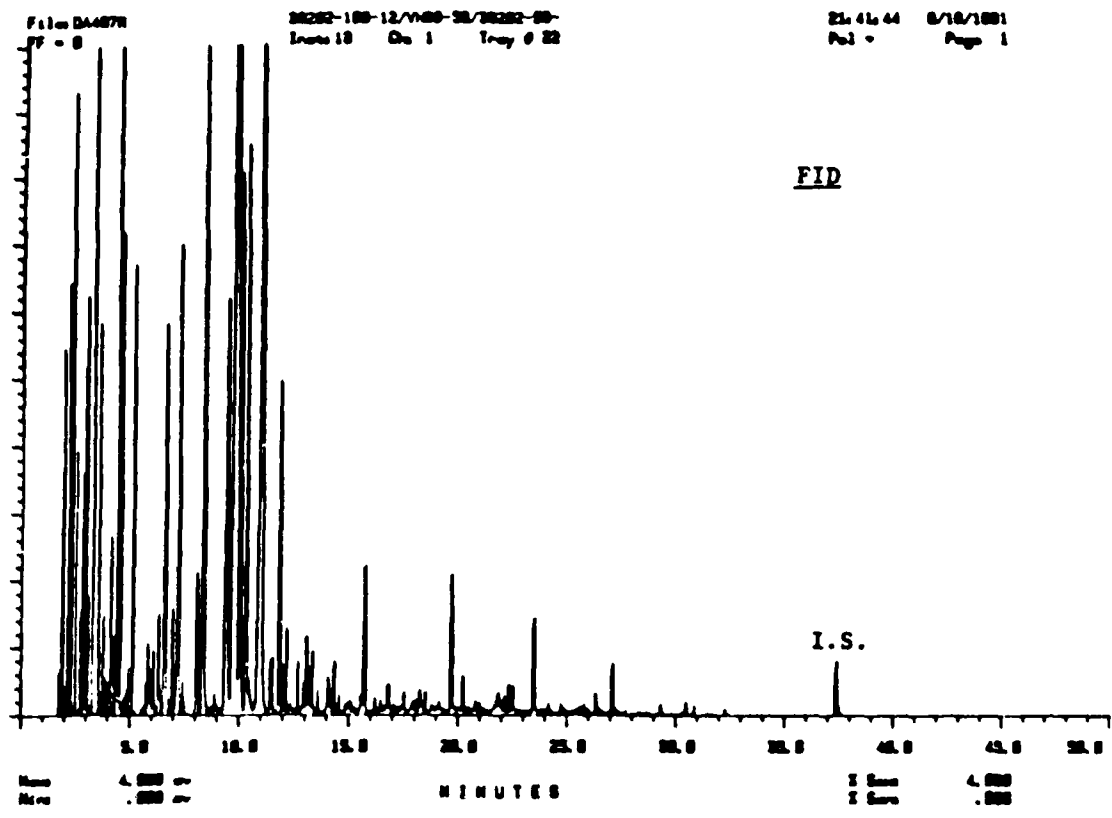
FIG 4: Selective detection of aromatics in a jet propulsion fuel by GC/UV. (25)

10
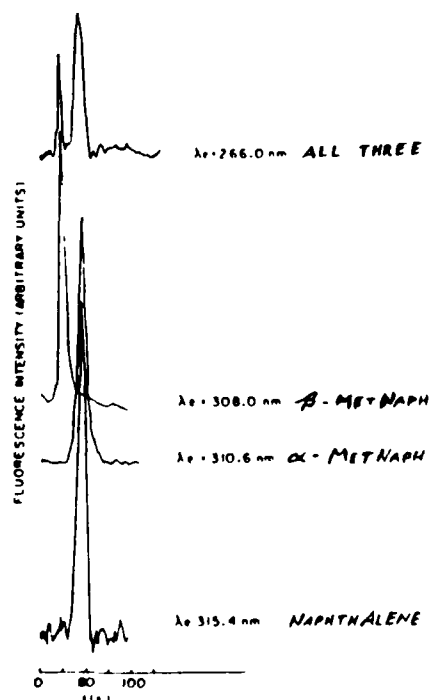
Figure 2. Chromatograms of an equimolar mixture of naphthalene, α-methylnaphthalene, and β-methylnaphthalene. Excitation wavelengths used for each injection are indicated.
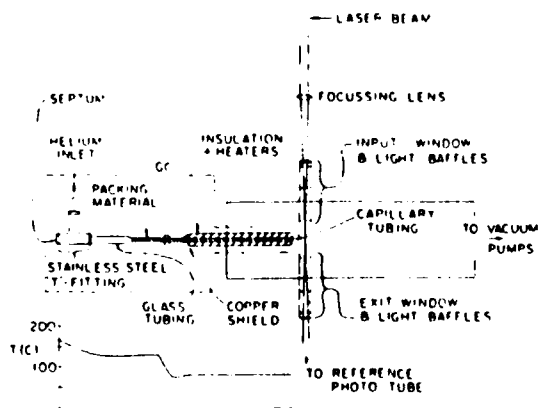
Figure 1. Diagram of the RC-LIF/GC apparatus. The portion enclosed by the dotted line forms a simple GC. Temperature variation along the column is shown below.
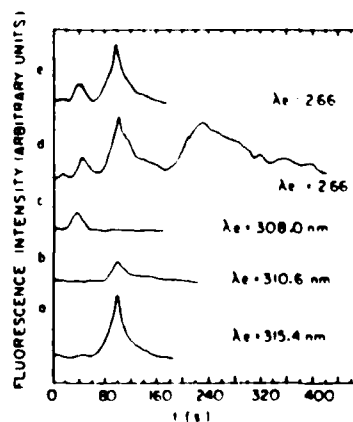
Figure 3. Chromatograms of a Wilmington Crude Oil sample: (a-d) chromatograms of the crude oil excited at the wavelengths indicated; (e) a laboratory prepared mixture of naphthalene, α-methylnaphthalene, and β-methylnaphthalene at the concentrations determined for the crude oil sample.

FIG 5: Selective detection of naphthalene isomers by GC/RC-LIF. (Reproduced by permission from ref. 8 , Copyright American Chemical Society.)

11
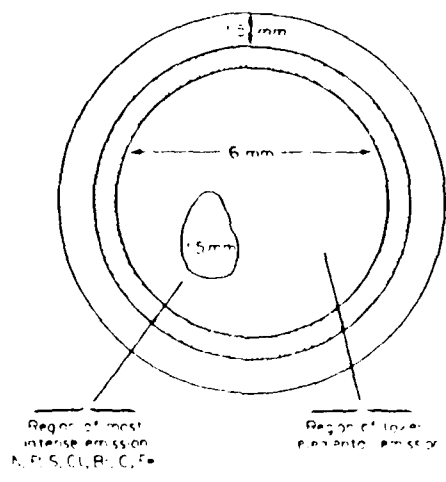
Fig. 3 Helium plasma image as projected on the spectrometer entrance slit for a 1.0 mm i.d. quartz capillary tube
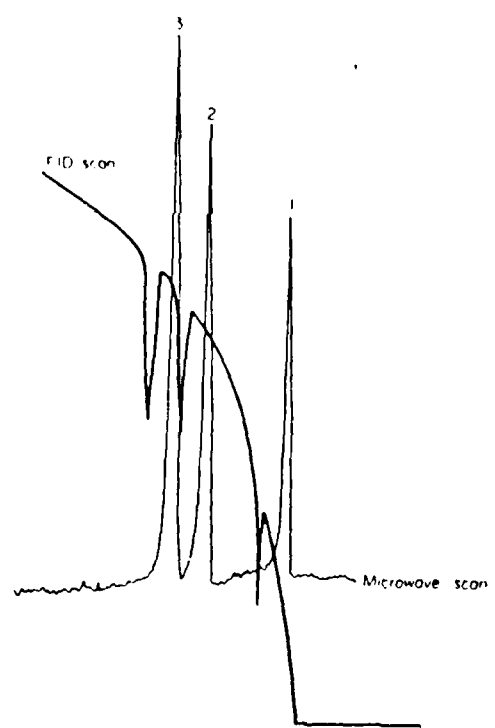
Fig. 13 Separation of a monochlorobiphenyl isomer mixture and subsequent detection by a helium microwave plasma. Peak concentrations are (1) 18.4 µg g⁻¹ ortho; (2) 32.5 µg g⁻¹ para; and (3) 44.8 µg g⁻¹ meta. Chlorine response is at 481.0 nm with 2 µl injections being made of the mixture. The column is the same as that used in Fig. 12. Note absence of matrix response compared to Fig. 12.

FIG 6: Selective detection of monochlorobiphenyl isomers by GC/MIP. (Reproduced by permission from ref. 10 , Copyright Pergamon Press, Inc..)

12

2. Microwave-Induced Plasma (MIP)

The use of emission spectroscopy by an atmospheric pressure microwave induced helium plasma (MIP) has been proven to be a specific detection technique for N, P, S, Cl, Br, C and Fe. A small portion of the plasma image, slightly off-center of the microwave cavity, was found to exhibit intense elemental emissions for the compounds mentioned while the rest of the plasma showed no emissions for those compounds. By varying the helium flow and power to the microwave cavity, optimum responses for each of the above mentioned compounds were obtained (10).(See Fig.6.)

3. Oxygen-Inductively Coupled Argon Plasma (O-ICAP)

Use of inductively coupled argon plasma to excite non-resonance atomic emissions from oxygen in the red and near infrared regions is used to quantitatively and selectively determine oxygen in permanent gas mixtures and volatile organics (6).

4. Chemiluminescent (CLD)

The Chemiluminescent Detector provides very sensitive, very selective responses to bound nitrogen in hydrocarbon matrices. The sample is combusted to form nitric oxide. The nitric oxide is detected photometrically by it's reaction with ozone to form the chemiluminescent species NO2*. Similarly, the detector can be used to specifically detect volatile polyhalogenated hydrocarbons by utilizing the halogenated compounds' reaction with sodium vapors and the resultant chemiluminescent sodium species (14) (23) (11).

5. Glow Discharge Detector (GDD)

A quartz tube, using axially mounted platinum wire electrodes, provides the spectrum for this optical emission detector. Use of a very stable power supply is necessary to maintain the tuning at the emission wavelength of choice.The detector is used primarily to indicate the presence of halogens, S, P, C and metals in GC effluents (7) (15).

13

6. Atmospheric Pressure Active Nitrogen (APAN)

Atmospheric Pressure Active Nitrogen sources have been used to selectively

detect organo- Hg, Pb, and Sn as trace GC eluents. These compounds react with

metastable atoms and molecules of nitrogen from the active nitrogen source. In

these reactions the fragmentation and excitation of species lead to

characteristic atomic and/or molecular emissions (16).

7. Flame Photometric Detector (FPD)

Emissions from a flame burning chromatographic eluents are viewed through

appropriate bandpass filters by a photomultiplier. The maxima of the

characteristic filters are 394 nm for sulfur and 526 nm for phosphorus.

Filters of other wavelengths are available for other compound types (5)   (17).

8. Thermal Energy Analyzer (TEA)

The Thermal Energy Analyzer can be used as a GC detector to selectively

detect N-nitroso compounds in organic matrices. The sample is pyrolyzed and

converted to nitrosyl and organic radicals. The organic fragments either

decompose or rearrange to stable forms. The nitrosyl radical is converted to

NO2* through ozonolysis. The NO2* decays rapidly with an emission in the near

infrared region of the spectrum (18) (21).

D. CONDUCTIVITY DETECTORS

By converting GC eluents to the appropriate inorganic forms their specific

electrical nature can be detected. This detection can be accomplished either

by direct measurement of electrolytic conductivity or by titration with

electrolytically generated reactive ions.
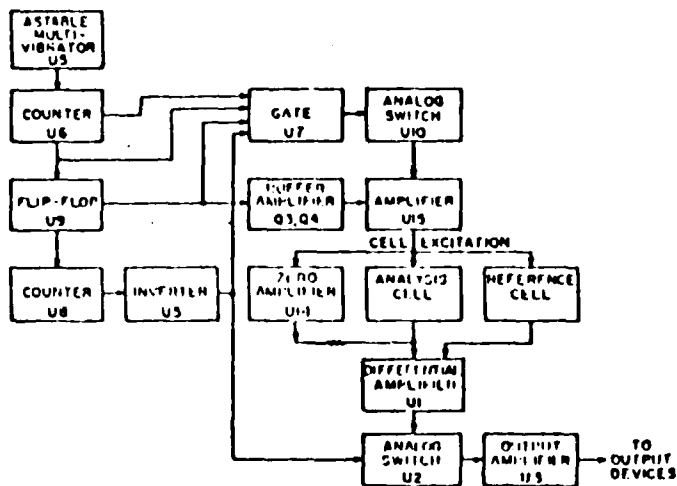
Figure 2 Block diagram of bipolar pulse, differential conductivity circuit.
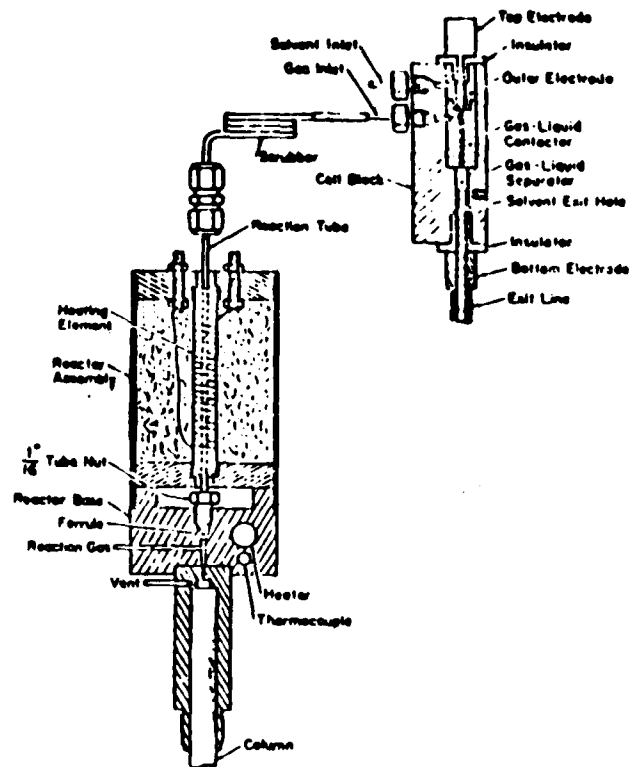
Figure 3 Cross section of microreactor and differentia.

A
2 μl, 10 ng Arochlor 1254 Standard

B
2 μl, 5ml MeOH/2ml Blank Oil

C
2 μl of 5ml MeOH/2ml of Oil with 1ppm Arochlor 1254

D
2 μl of 5ml MeOH/2ml Oil with 40ppm Arochlor 1254

RESPONSE

TIME, minutes

Figure 18 Arochlor 1254 in transformer oil, extracted with methanol.

FIG 7: Selective detection of chlorinated compounds in transformer oil by GC/HECD. (Reproduced by permission from ref. 12 , Copyright Preston Publications, Inc..)

15

1. Hall Electrolytic Conductivity (HECD)

The Hall Electrolytic Conductivity Detector can be operated with different modes of selectivity for halogen-, sulfur-, carbon-, nitrogen-, or nitrosamine-containing compounds. The species of interest are converted to stable inorganic forms by combustion or hydrogenolysis. Upon dissolving these converted species in water or alcohol they can be detected by measuring the resultant electrolytic conductivity (12).(See Fig.7.)
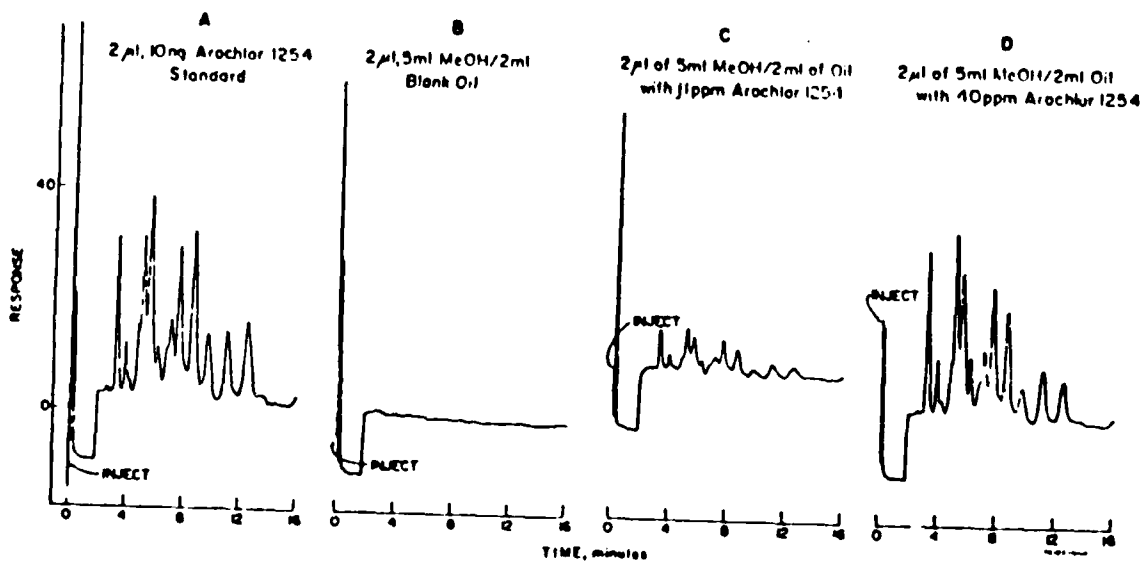
2. Microcoulometry (MC)

Microcoulometry has been successfully used as a specific GC detector for S, N and Cl. The elements in question are converted to the inorganic forms SO2, NH3, and HCL respectively. The species are then titrated by electrolytic generation of reactive ions. For example, SO2 is titrated with electrogenerated I2 via a redox reaction. The quantity (ie microcoulombs) of electricity required for this generation is the area under the GC-MC peak. GC-MC peaks are broad with delayed response times and some tailing (11).

3. Molecular Weight Detector

By directing GC eluents to one of two carrier gas flow paths which are legs of a Wheatstone Bridge the density changes caused by the eluents can be used as a detector signal. While this method is not specific to eluent types, the use of two of these systems in parallel, each using a different carrier gas, can be used to determine molecular weights of eluting compounds. The molecular weight is calculated by the simultaneous solution of the gas density balance equations for the two systems (17).(See Fig.8.)

Table 1 is a listing of the detectors covered in this report by their types of selectivity. Table 2 lists performance data for some of the detectors covered in this report as available in the references listed herein.
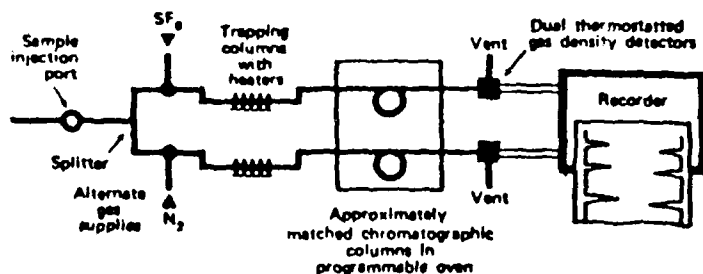
16

Figure 3 (Ref. 3). Chemalytics molecular weight chromatograph splits sample between two columns, uses two carrier gases.

The basis for the method can be seen by examining the basic equation for the gas density balance:

$$\rho_x = k\left(\frac{MW_x}{MW_x - MW_{CG}}\right) \quad (1)$$

where $\rho_x = W/V = W/A$ and A is the peak area, MW is molecular weight, and CG denotes carrier gas. For a system with two gas density balances with different carrier gases,

$$\rho_x = \frac{W_1}{A_1} = k_1\left(\frac{MW_x}{MW_x - MW_{CG_1}}\right) \quad (2)$$

$$\rho_x = \frac{W_2}{A_2} = k_2\left(\frac{MW_x}{MW_x - MW_{CG_2}}\right)$$

The two weights are related to the total weight by the split flow ratio:

$$W_1 = C_1 W_{total} \qquad W_2 = C_2 W_{total} \quad (3)$$

where C_1 is the fraction of sample through detector 1

and C_2 is the fraction of sample through detector 2 and $C_1 + C_2 = 1$.

$$W_{total} = \frac{W_1}{C_1} = \frac{W_2}{C_2} \quad (4)$$

Substituting Equation 2 in Equation 4

$$W_{total} = \frac{k_1 A_1}{C_1}\left(\frac{MW_x}{MW_x - MW_{CG_1}}\right)$$

$$W_{total} = \frac{k_2 A_2}{C_2}\left(\frac{MW_x}{MW_x - MW_{CG_2}}\right) \quad (5)$$

Simplifying, we obtain

$$\frac{k_1 C_2 A_1}{k_2 C_1 A_2} = \frac{MW_x - MW_{CG_1}}{MW_x - MW_{CG_2}} = \frac{KA_1}{A_2} \quad (6)$$

where

$$K = \left(\frac{k_1}{C_1}\right)\left(\frac{C_2}{k_2}\right)$$

Let

$$Y = K\frac{A_1}{A_2} \quad (7)$$

Then

$$Y MW_x - Y MW_{CG_2} = MW_x - MW_{CG_1} \quad (8)$$

$$MW_x = \frac{Y MW_{CG_2} - MW_{CG_1}}{Y - 1} \quad (9)$$

Equation 6 is first used to determine K using a standard material whose molecular weight is known. Substituting for MW_x, and the measured areas A_1 and A_2, K can be determined after which Y is determined from Equation 7, and is then used in Equation 9. Typical results are shown in Table I.

FIG 8: Molecular Weight Detector system and density balance equations. (Reproduced by permission from ref. 17 , Copyright John Wiley and Sons, Inc. Publishers.)

17

TABLE 1 : DETECTOR SELECTIVITY BY COMPOUND CLASS

DETECTOR	TYPE	ELEMENT
Mass Spectral	Ionization	Various
Infrared	Absorption	Various
Rotationally Cooled-Laser Induced Fluorescence	Emission	Various
Molecular Weight	Conductivity	Various
Ion Mobility	Ionization	Various
Chemiluminescent	Emission	N, X
Thermionic Specific	Ionization	N, P, X
Microcoulometry	Conductivity	N, S, X
Hall Electrolytic	Conductivity	N, S, X
Microwave Induced Plasma	Emission	N, P, S, X, C, Fe
Thermal Energy Analyzer	Emission	N-Nitroso
Electron Capture	Ionization	Electrophores
Flame Photometric	Emission	S, P
Glow Discharge	Emission	S, P, C
O-Flame Ionization	Ionization	O
O-Inductively Coupled Argon Plasma	Emission	O
Atomic Absorption	Absorption	Metals
Hydrogen Atmosphere Flame Ionization	Ionization	Si, P, Cl, Fe
Atmospheric Pressure Activated Nitrogen	Emission	Hg, Pb, Sn
Photoionization	Ionization	H2S, NH3, PH3, AgH3
Ultraviolet	Absorption	Aromatic HC's
Catalytic Ionization	Ionization	Branched HC's

18

TABLE 2 : COMPARISON OF AVAILABLE PERFORMANCE DATA OF SELECTIVE DETECTORS (1,11)

DETECTOR	SENSITIVITY (g/sec)	DYNAMIC RANGE	SELECTIVITY (g-x/g-c)	ELEMENT
MS	10^{-10}	10^{4}	------	Various
TSD	10^{-13}	10^{5}	5×10^{4} (N/C)	N,P,X
HECD	10^{-12}	10^{4}	$>10^{6}$ (N/C)	N,S,X
MC	10^{-10}	---	$>10^{6}$ (N/C)	N,S,X
CLD	10^{-10}	---	$>10^{6}$ (N/C)	N,X
PID	10^{-12}	---	------	H2S,NH3, PH3,AgH2
FPD	10^{-12}	---	10^{5} (S/C)	S,P
ECD	10^{-13}	10^{3}	10^{5} (Cl/C)	Electrophores

19

SECTION III

CONCLUSIONS

A chromatographer with a specific G.C. detection problem clearly has two choices, either to attack the problem with a high-technology detector such as the GC-FTMS, or to approach the problem with a novel device such as the O-FID.

High technology, high cost detectors such as the GC-FTMS and GC-FTIR have advantages over even the most novel element specific detectors in that they are "universally specific." However, one cannot afford to overlook the phenomenal achievements made over the last two decades in the development of element specific detectors.

For the purpose of analyzing heteroatom constituents of jet propulsion fuels, the following detectors are recommended : the O-FID for the detection of oxygen-containing compounds, the FPD for the detection of phosphorous and sulfur-containing compounds, either the CLD or TSD for the detection of nitrogen-containing compounds. A system containing either MSD, FTIR, or both capabilities is also highly recommended for these analyses.

SECTION IV

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