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Dick A. Mack, Craig D. Hollowell, and Ralph D. McLaughlin

July 1973

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TECHNIQUES FOR CONTINUOUS MONITORING

OF HYDROCARBONS*
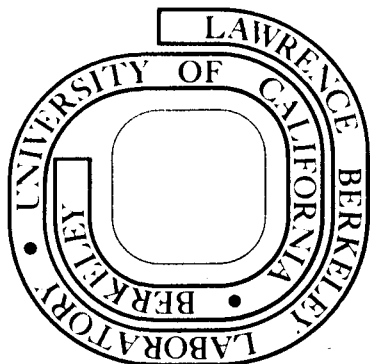
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ABSTRACT: Among the present methods for analyzing hydrocarbons to perform ambient air, stationary source and vehicular emission monitoring are flame ionization detection, gas chromatography, non-dispersive infrared spectroscopy, dispersive infrared spectroscopy and catalytic oxidation. Promising methodology includes ultraviolet spectroscopy, optoacoustic detection, along with others. Problems associated with the production of improved instrumentation are discussed and recommendations made for further research and development.

KEY WORDS: hydrocarbons, instrumentation, monitoring, environment, pollution

CONTENTS

I. INTRODUCTION

A. Hydrocarbons in the Atmosphere

Hydrocarbons may be viewed as both a blessing and a curse in the light of this country's energy resources and consumption problems. Hydrocarbons are a blessing in providing the largest fraction of our basic fuel and petrochemical resources; their curse is due to the manner in which they and their by-products are released into our environment. It should also be remembered that the most serious problems of hydrocarbons arise from the interactions with other pollutants in the photochemistry of the atmosphere. In this discussion we will only be concerned with gaseous hydrocarbons; particulates will be considered in another session. Although the primary emphasis at this Conference is on ambient air analysis, we will also consider stationary source and vehicular emission monitoring to provide a complete picture of hydrocarbon analysis.

A number of papers have been concerned with the sources of hydrocarbons, and with the technology of their utilization and control.[1,2,3,4] In this survey we will only deal with the detection and monitoring of hydrocarbons -- both as total hydrocarbons and their specific species. Although methane accounts for 60 to 90% of the atmospheric hydrocarbons, it is photochemically inert. Thus, the major interest will be devoted to the identification of the non-methane components present in the atmosphere.

We will describe the techniques that form the basis of present commercial instrumentation along with those ideas which appear to merit further investigation. More complete information on current instrumentation and operating principles will be found in Instrumentation for Environmental Monitoring, AIR.[5] It is realized that no survey can be exhaustive and complete; if commercial instruments have been omitted, we ask the indulgence of their manufacturers.

B. Classification of Instruments

Instruments suitable for hydrocarbon analysis may be divided into two classes: Manual and automatic.

Manual operation implies human involvement in order to progress from one step in the analysis to another; automatic operation implies that many of the operations are self-initiated. Automatic operation may be further subdivided into continuous and continual operation.

Manual operated analyzers will not be discussed in great detail here, in as much as the forward look of this Symposium is toward automated methods.

In continuous analyzing instruments the uninterrupted output response is a direct function of the concentration of the unknown constituent being analyzed; however, depending upon the detection technique certain integration times and chemical or signal processing delays may be involved. Flame ionization detection is an example of a continuous process.

Continual analyzing (sometimes referred to as semicontinuous) instruments are those where a representative fraction (sample) of the unknown is taken and analyzed and the process automatically repeated on a regular basis. In the ideal case the analyzing period is sufficiently short that no significant chemical changes take place before another sample is measured. Automated gas chromatographs may be considered continual instruments.

C. Gaseous Hydrocarbon Monitoring Systems

In this paper we are dealing with the instruments and techniques rather than the total monitoring system used for hydrocarbon analysis. Although the analyzer is necessary for monitoring, it is never sufficient by itself. A discussion of an entire monitoring system is beyond the scope of this discussion; however, the following general concepts are presented for discussion. Particular attention should be given to the role of each component in the system and how the system requirements change according to the application.

It cannot be overemphasized that considerable care must be exercised in designing a complete monitoring system. Depending upon the specific

application, systems vary widely in requirements and complexity. Nevertheless, in each system the following basic functions must be provided: Sampling, Analysis, Calibration, Data Acquisition and Reduction. Each function is important, and the entire monitoring system must be fully considered in order to realize the full operating capabilities of the system.

Gaseous monitoring systems can be classified as those suitable for any of three types of analysis: Ambient air monitoring, Stationary source monitoring and Vehicular emissions monitoring.

Ambient air instruments are those designed for monitoring in urban areas or industrial sites. They may be capable of mobile or portable operation in the field or be permanently located at suitable sites. The EPA Primary and Secondary National Air Quality Standards for Hydrocarbons corrected for methane are 160 $\mu g/m^3$ (0.24 ppm)[6] for a 3 hour averaging time and not to be exceeded more than once per year. Thus the sensitivity for monitoring hydrocarbons must be significantly better than 0.24 ppm. Table 1 lists a number of companies manufacturing ambient air monitors; the various detection techniques will be discussed in subsequent sections.

Stationary source monitors are those suitable for analyzing the effluents of flues, stacks and exhausts. Considerably less sensitivity is required for stationary source monitors typically 70 mg/m^3 ($\sim$ 100 ppm). Manufacturers supplying stationary source monitors are noted in Table 2.

Vehicular emissions monitors are those suitable for analyzing the exhaust from motor vehicles operating in the field or from vehicles brought to a laboratory. Manually operated instruments are most often used in certification testing of vehicles in the field; automatic monitors (usually with exhaust probe sampling) are for diagnostic purposes in automotive maintenance and surveillance. Table 3 lists commercially available vehicular emissions monitors.

Some instruments are sufficiently versatile and sensitive that they find application in more than one of the above categories.

Table 1 -- Commercially Available Continuous Ambient Air Monitors

Technique	Company
Flame Ionization Detection (FID)	Antek Beckman Bendix/PID Delphi Gow-Mac Meloy Mine Safety Appliances (MSA) Power Designs Process Analyzers Scott Aviation Scott Research Teledyne Thermo Electron
Gas Chromatography-Flame Ionization Detection (GC-FID)	Beckman Bendix/PID Byron Hewlett Packard

(Ref. 5)

Table 2 -- Commercially Available Continuous Stationary Source Monitors

Technique	Company
Flame Ionization Detection (FID)	Beckman
	Mine Safety Appliances (MSA)
	Process Analyzers
	Scott Research
	Teledyne
	Thermo Electron
	Wemco
Gas Chromatography-Flame Ionization Detection (GC-FID)	Beckman
	Byron
	Hewlett Packard
Non-Dispersive Infrared (NDIR)	Beckman
	Bendix/PID
	Ecological Instrument
	Horiba

(Ref. 5)

Table 3 -- Commercially Available Continuous Vehicular Emissions Monitors

Technique	Company
Catalytic Oxidation	Purad
Flame Ionization Detection (FID)	Beckman Delphi Gow-Mac Heath Horiba Intertech Mine Safety Appliances (MSA) Scott Research Thermo Electron
Gas Chromatography-Flame Ionization Detection (GC-FID)	Beckman Byron Carle Hewlett Packard
Non-Dispersive Infrared (NDIR)	Allen Autoscan Beckman Bendix/PID Bosch Chrysler Commercial Electronics Ecological Instrument Horiba Marquette Mine Safety Appliances (MSA) Peerless Scott Research Sensors Sun
Dispersive Absorption Spectroscopy	
(IR-UV)	Chrysler
(IR)	Wilks

(Ref. 5)

1. Multiparameter Capability

The trade-off between one instrument with multiparameter capability and a number of instruments each measuring a specific pollutant should be considered -- both with a view to the economics of procurement and the cost of operation and maintenance. In ambient air and vehicle exhaust monitoring one rarely encounters the situation where only hydrocarbons need to by analyzed. At the present time, however, the EPA reference method required by the National Air Quality Standards employs a different technology for each air pollutant. Our long-range view of the situation is that instruments capable of multiparameter capability will become more widely used.

In addition to analyzing more than one parameter one will usually need instruments to measure the temperature, pressure, humidity and the flow characteristics of both the sample and parent gas streams. Data from such instruments allow assessment of mass concentration, mass flow, and gas composition.

2. Operation Characteristics

Before discussing specific monitoring techniques it would be well to consider the factors one must take into account when selecting new instrumentation. Of primary concern are the reliability, durability and ruggedness of the complete system. The reliability of the measurement is determined by factors such as specificity, sensitivity and accuracy. It will often be necessary to settle for less than maximum reliability because of limitations in time available for inspection, maintenance and repair. This is especially true in stationary source monitoring in which the operating conditions may be quite hostile. Depending upon the desired frequency of data, available manpower and accessibility, one may also desire the capability of unattended operation for extended periods.

3. The Ideal System

Present-day instruments, although adequate in many respects, still have a number of shortcomings. Let us look into the future and list what would be the "ideal" instrumentation system for the next generation of environmental monitoring:

1. The detector or transducer should allow one to distinguish clearly the constituent of interest. That is, the detector should be specific and not subject to interferences. In addition, instruments that can identify a number of parameters should meet with more and more popularity.

2. The transducer should indicate the material present quantitatively as well as qualitatively.

4. Instruments should have a fast response so that the user can immediately take advantage of the information gained. A number of reactions are time dependent; samples held for many hours are always less desirable than samples from in situ monitoring.

5. Greater sensitivity is of particular importance. As the emission levels of contamination decrease, it is necessary that the instrumentation be able to cope with these lower levels.

6. Instruments should be capable of being read out both directly (e.g., for field use) and indirectly into data-handling facilities for stationary or laboratory use.

7. Sampling means should be provided as part of the equipment.

8. The system should be capable of accurate calibration either in the laboratory or in the field. Built-in calibration means are particularly desirable. Erroneous data are worse than no data at all!

9. Instruments should be rugged and thoroughly reliable.

10. Finally, any new analysis system must lead to cost benefits that are real and evident.

II. GENERALLY EMPLOYED DETECTION TECHNIQUES

The discussion here is confined to hydrocarbon analyzers that detect the pollutant in the gaseous phase. Each of the following brief descriptions applies principally to an analyzer. An analyzer, the heart of the monitoring system, is where the actual measurement of the pollutant concentration occurs. Depending upon its characteristics, a particular analyzer is usually intended for either ambient air, stationary source or vehicular emissions monitoring. As mentioned before, the analyzer by itself does not complete the monitoring system. Besides the analyzer, a system will need one or more of the following components: Probes to obtain the sample, lines to transport the sample, conditioning units to dry, heat, cool or otherwise pretreat the sample before analysis, selective filters to remove gases or particulates that can affect accuracy or operation, pumps to move the sample, calibration devices, readout means and data-handling peripherals such as strip-chart recorders or analog-to-digital convertors. Some or all of these components may be included as a part of the basic analyzer.

A. Flame Ionization Detection (FID)

Flame ionization detection is the most widespread hydrocarbon sensing method in use today. The FID technique as adapted to total hydrocarbon analysis was first reported by Andreatch and Feinland in 1960.[7] Its use in connection with GC separation will be discussed in the following section. With standard FID an air sample is introduced into a hydrogen flame. See Fig. 1.[8] The combustion of even a few ppb of a hydrocarbon produces measurable ionization which is a function of the number of carbon ions present. A collector surrounding the flame is positively polarized by an external power supply and the resulting ion current measured on an electrometer. Since pure hydrogen
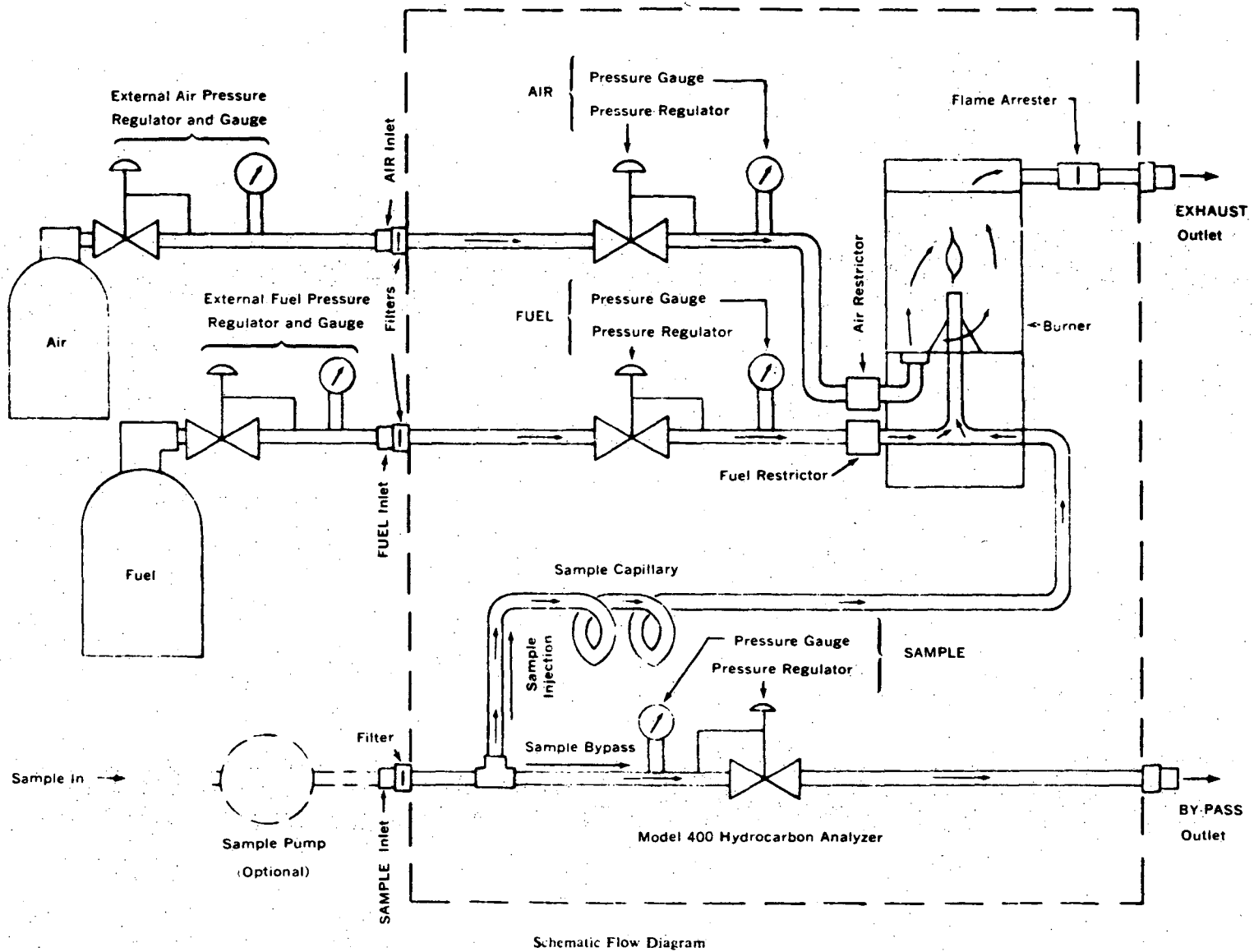
Fig. 1   An Example of a Flame Ionization Detection Analyzer (Ref. 8)

burning in air produces very little ionization, the effects of background sub-traction are minimized. The output current calibrated in ppm (or percentages) is read on a panel meter or chart recorder.

Hydrocarbons containing nitrogen, oxygen or halogen atoms give a reduced response. Thus FID hydrocarbon analyzers are almost universally calibrated in terms of a gas such as methane or hexane and the output read in ppm of carbon measured as methane or hexane.

It is important to note that nitrogen, CO and CO_2 do not produce inter-ferences.[9] Patterson and Henein point out that although there is a very low sensitivity to water vapor, condensed water vapor may block the sample entry tube and give erratic readings.[10] Also when oxygen is present in excess of 4%, a significantly lower output reading may occur.[10] Beckman Instruments report the relative response of the Model 400 Hydrocarbon Analyzer to various hydrocarbons, including those with attached oxygen, chlorine and nitrogen atoms in Table 4.[11] The response is given in effective carbon numbers (ECN) where

$$ECN = \frac{\text{Instrument response caused by atom of given type}}{\text{Instrument response caused by aliphatic carbon atom}}$$

In order to detect the non-methane portion of total hydrocarbons King has reported two methods based on a selective catalytic combustor.[12] In the first method the selective combustor is operated in the cold condition and methane plus other hydrocarbons are measured; next the combustor temperature is in-creased so that all hydrocarbons except methane are consumed. A signal sub-traction between the two measurements yields the non-methane component. This technique is employed in the Gow-Mac analyzer.

In the second method the hydrogen content of the hydrocarbon is measured. The selective combustor is followed by a water-sensing sorption detector. Thus, the water of combustion is a measure of the hydrocarbon present. An air dryer is placed ahead of the combustor to keep atmospheric water vapor from swamping the analyzer.

Table 4 -- Approximate Effective Carbon Numbers

Type of Atom	Occurrence	Effective Carbon Number
Carbon	In Aliphatic Compound	+1.0
Carbon	In Aromatic Compound	+1.0
Carbon	In Olefinic Compound	+0.95
Carbon	In Acetylenic Compound	+1.30
Carbon	In Carbonyl Radical	0.0
Carbon	In Nitrile	+0.3
Oxygen	In Ether	-1.0
Oxygen	In Primary Alcohol	-0.6
Oxygen	In Secondary Alcohol	-0.75
Oxygen	In Tertiary Alcohol, Ester	-0.25
Chlorine	As two or more chlorine atoms on single aliphatic carbon atom	-0.12/each
Chlorine	On Olefinic Carbon Atom	+0.05
Nitrogen	In Amine	Value similar to that for oxygen atom in corresponding alcohol

$$\text{Effective carbon number} = \frac{\text{Instrument response caused by atom of given type}}{\text{Instrument response caused by aliphatic carbon atom}}$$

(Ref. 11)

Poli and Zinn have described a dual FID analyzer to continuously monitor the methane and non-methane components in ambient air.[13] One part of the air sampling stream is fed to the first flame ionization detector to measure the total hydrocarbons present; the other part is fed to a Hopcalite catalyst that selectively combusts all hydrocarbons except methane. The efficiency of the catalytic separation is evidenced by the following example. At 260 C approximately 98% of ethane and virtually all of the heavier hydrocarbons are oxidized, while the methane component is unaffected. A second FID at the output of the catalytic convertor measures the methane content. Electronic circuits provide the necessary signal subtraction to indicate the non-methane fraction. Mine Safety Appliances market an analyzer using this principle.

B. Gas Chromatography (GC)

Gas chromatographs have been used manually to monitor hydrocarbons for many years. The great power of this technique is the unique ability to separate hydrocarbons into a number of individual compounds. In principle GC is a method for physically separating a gaseous mixture into its components by passing it through a column with a high surface-to-volume ratio. See Fig. 2.[14] The surface area consists of a solid material or a liquid dispersed on a solid. The segregation of the various components depends upon their selective absorption into the column material. An inert carrier gas moves the sample through the column. If the gas sample consists of different hydrocarbons, the different components will require different times to pass through the column. The weakly absorbed components are the first to emerge from the column. The selective process is highly temperature sensitive and thus requires that most of the components of the chromatograph be housed in a temperature controlled oven. As the various components emerge from the column their identification and concentration are determined by an appropriate detector. For hydrocarbons flame ionization detection, described in the previous section, is almost universally employed.
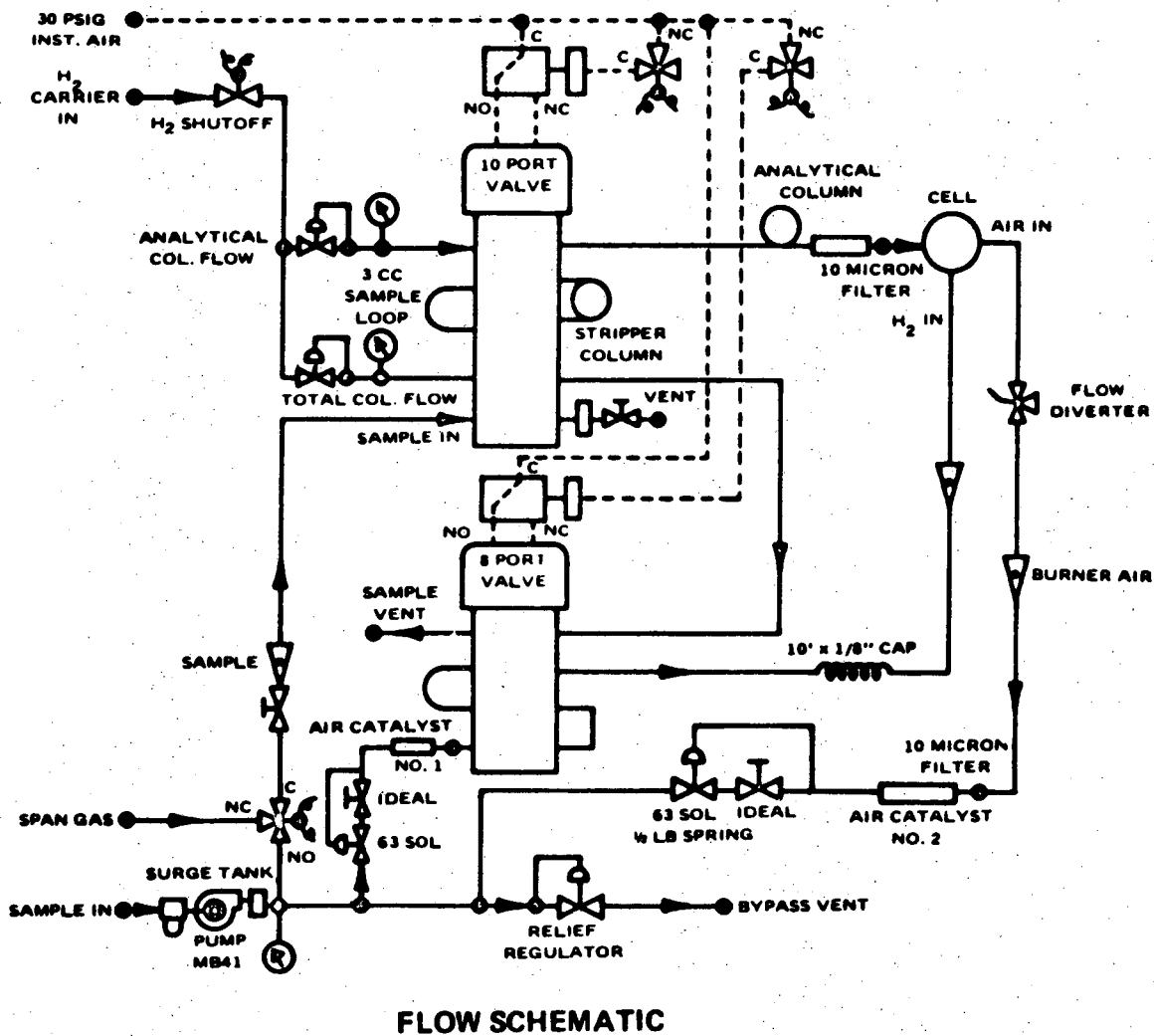
FLOW SCHEMATIC

Fig. 2   An Example of a Gas Chromatograph (Ref. 14)

Early GC's were, of course, manually controlled. During the past few years numerous attempts have been made to automate GC analysis. These developments are still being evaluated. Stevens, O'Keeffe and Ortman described what they termed "second generation" air pollutant monitors in 1968.[15] At that time these NAPCA (now EPA) scientists developed an automated procedure for the gas chromatographic analysis of carbon monoxide and methane in concentrations between 10 ppb and 200 ppm. Carbon monoxide was converted to CH_4 using a catalytic convertor. Although methane was not of primary interest, subtracting this component from the total hydrocarbons yielded a rough indication of the reactive hydrocarbons remaining.

The first commercial automatic gas chromatograph following the above developments was produced by Mine Safety Appliances. Another automated GC was developed by Union Carbide Corp., and reported by Fee[16]. This unit analyzed three parameters: CO , CH_4 and total hydrocarbons at a maximum rate of 12 cycles per hour. The range of sensitivity was from 0 - 1 ppm to 0 - 1000 ppm in several steps. Ambient air was continuously drawn into the analyzer through a two-section particulate filter. A timer activating an injection valve transferred an 8 ml air sample directly into the FID. This operation measured the total hydrocarbons present. About 38 seconds later another 8 ml sample was taken. A pre-column stripper removed CO_2, water vapor and non-methane hydrocarbons. The sample was then separated into methane and CO components in the GC column; the CO portion was catalytically converted to methane, and the two components, arriving about 15 seconds apart, analyzed by FID. It is our understanding that these units are no longer in commercial production.

Villalobas and Chapman describe the Beckman adaptation of the work of Stevens, <u>et al</u>., to measure methane, ethylene, acetylene, carbon monoxide and total hydrocarbons in ambient air.[17] Individual components are measured

with 1 ppm sensitivity while total hydrocarbons are analyzed at 200 ppb sensitivity. Improvements include the elimination of a separate inert carrier gas by the use of suitably purified air, and the hydrogen gas for the FID flame may be derived electrolytically.

It should be noted that only automated GC's have been included in Tables 1, 2 and 3. GC instruments made by Beckman, Bendix, Byron and Hewlett-Packard fall into this category. The Carle GC is capable of automated operation when used with additional options supplied by the manufacturer.

C. Non-Dispersive Infrared Absorption (NDIR)

Non-dispersive infrared spectrometry is a technique based upon the broadband absorption characteristics of certain gases in the wavelength region of a few micrometers. Infrared radiation is directed through two separate absorption cells -- a reference cell and a sample cell. See Fig. 3.[18] The sealed reference cell is filled with non-absorbing gas, such as nitrogen or argon. The sample cell is physically identical to the reference cell and receives a continuous stream of the gas being analyzed. When the particular hydrocarbon is present, the IR absorption is proportional to the molecular concentration of that gas. The detector consists of a double chamber separated by an impermeable diaphragm. Radiant energy passing through the two absorption cells heats the two portions of the detector chamber differentially. The pressure difference causes the diaphragm to distend and vary a capacitance which is measured electronically. The variation in capacitance is proportional to the concentration of the component of gas present. By optically chopping the IR radiation, the capacitance may be made to change periodically and as a result, the electronic readout problems are facilitated.

Beckman, Horiba and Mine Safety Appliances all manufacture NDIR analyzers based on the above principles, and use two IR sources. Ecological Instruments
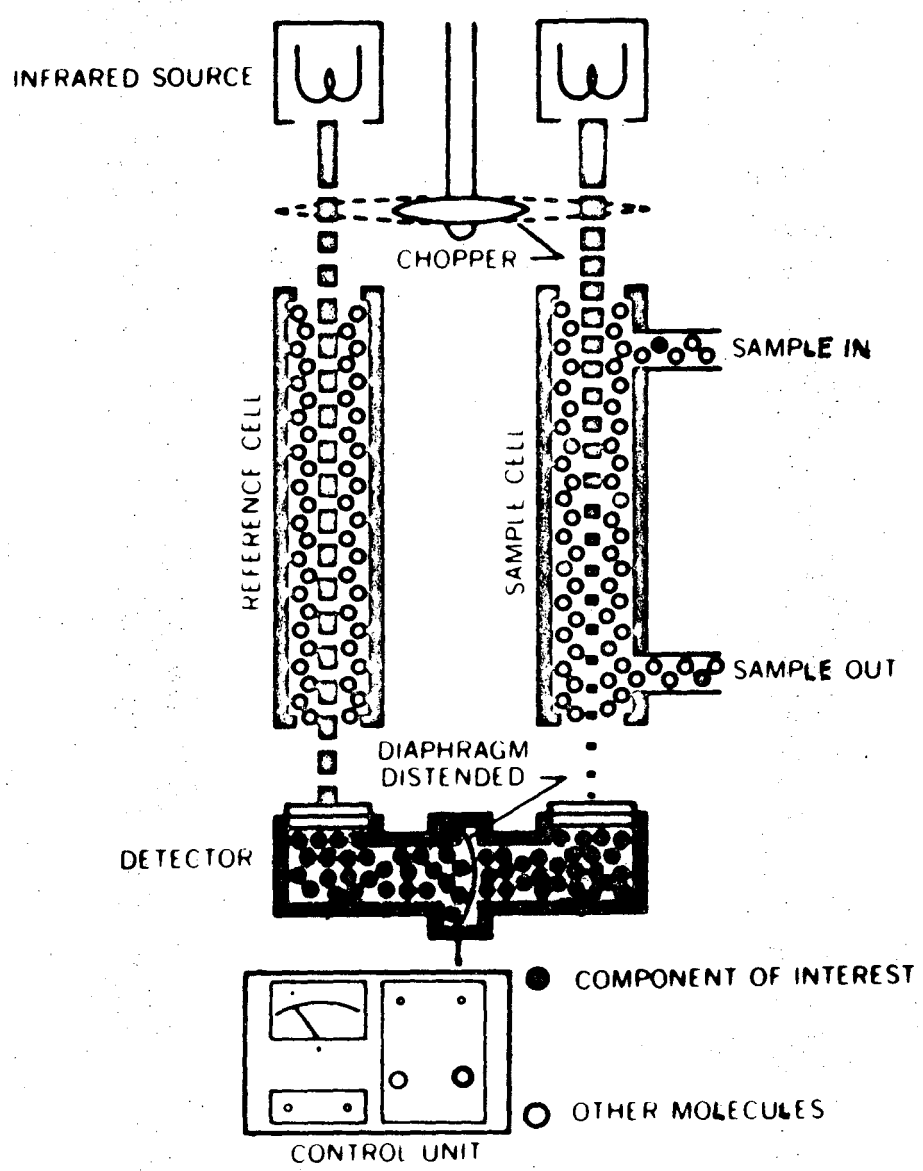
Fig. 3   An Example of a Non-Dispersive Infrared Absorption Analyzer (Ref. 18)

uses a single radiation source. Infrared Industries uses two concave mirrors, thus allowing a single source arrangement. See Fig. 4.[19] Bendix produces an analyzer with the two detector chambers in series; both detectors are filled with the gas under measurement. The gas in the forward chamber is heated by the center of the absorption band; the gas in the rear chamber by the edges of the band. Hydrocarbon gas in the sample will absorb primarily in the center of the band and thus cause the front chamber to become cooler. The pressure change is detected as a change in capacitance and read out as previously described.

D. Dispersive Infrared Absorption

A dispersive absorption spectrometer is an instrument which can be set to pass any small wavelength interval within its range and differs from a non-dispersive type instrument which looks at a broad spectral region.[20]

In one version of a DIR spectrometer IR radiation is directed through a 10 Hz optical chopper, a 13 cm absorption cell and an adjustable narrow band-pass filter. Detection is by means of a thermistor bolometer mounted at the focus of a concave mirror.[20] The relative sensitivity of this instrument for hydrocarbons closely resembles NDIR.

Another DIR spectrometer employs a mirror chopper and a concave grating to reflect the appropriate wavelengths of IR radiation onto several different detectors. See Fig. 5.[21]

The Chrysler Vehicle Exhaust Analyzer in addition to monitoring hexane hydrocarbons is capable of measuring CO and CO_2. In the dispersive ultra-violet mode it can also monitor NO and NO + NO_2 read as NO_x.
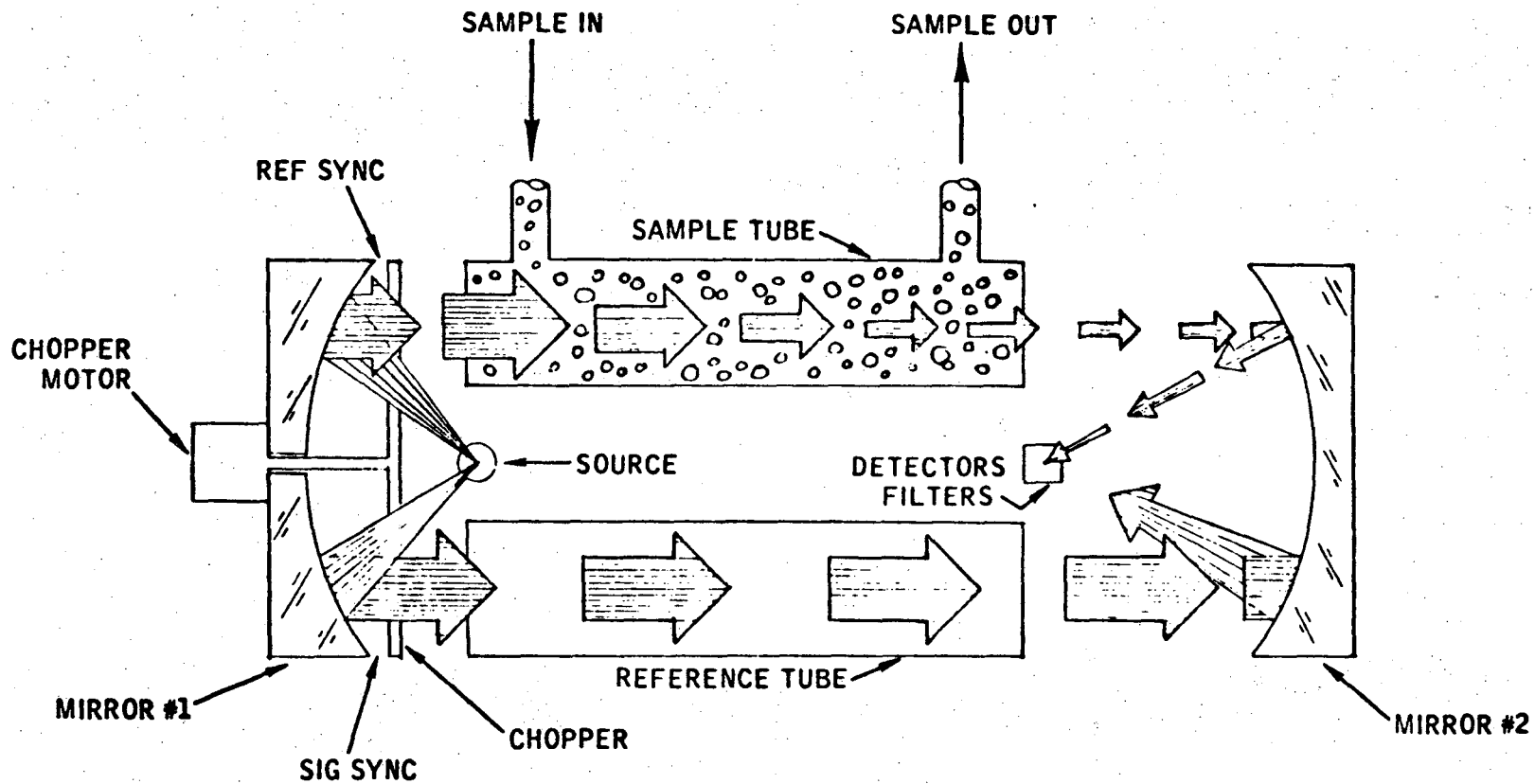
Fig. 4   Non-Dispersive Infrared Absorption Analyzer with Single Source (Ref. 19)

EXIT SLITS WITH DETECTORS

CONCAVE GRATING

ENTRANCE SLIT

SHIELD

REFERENCE PATH

SOURCE

COLLIMATING MIRRORS

FOLDING MIRROR

IRIS DIAPHRAM

FOCUSING MIRROR

GAS OUTLET

GAS INLET

SAMPLE PATH

SHIELD

MIRROR CHOPPER

SAMPLE CELL
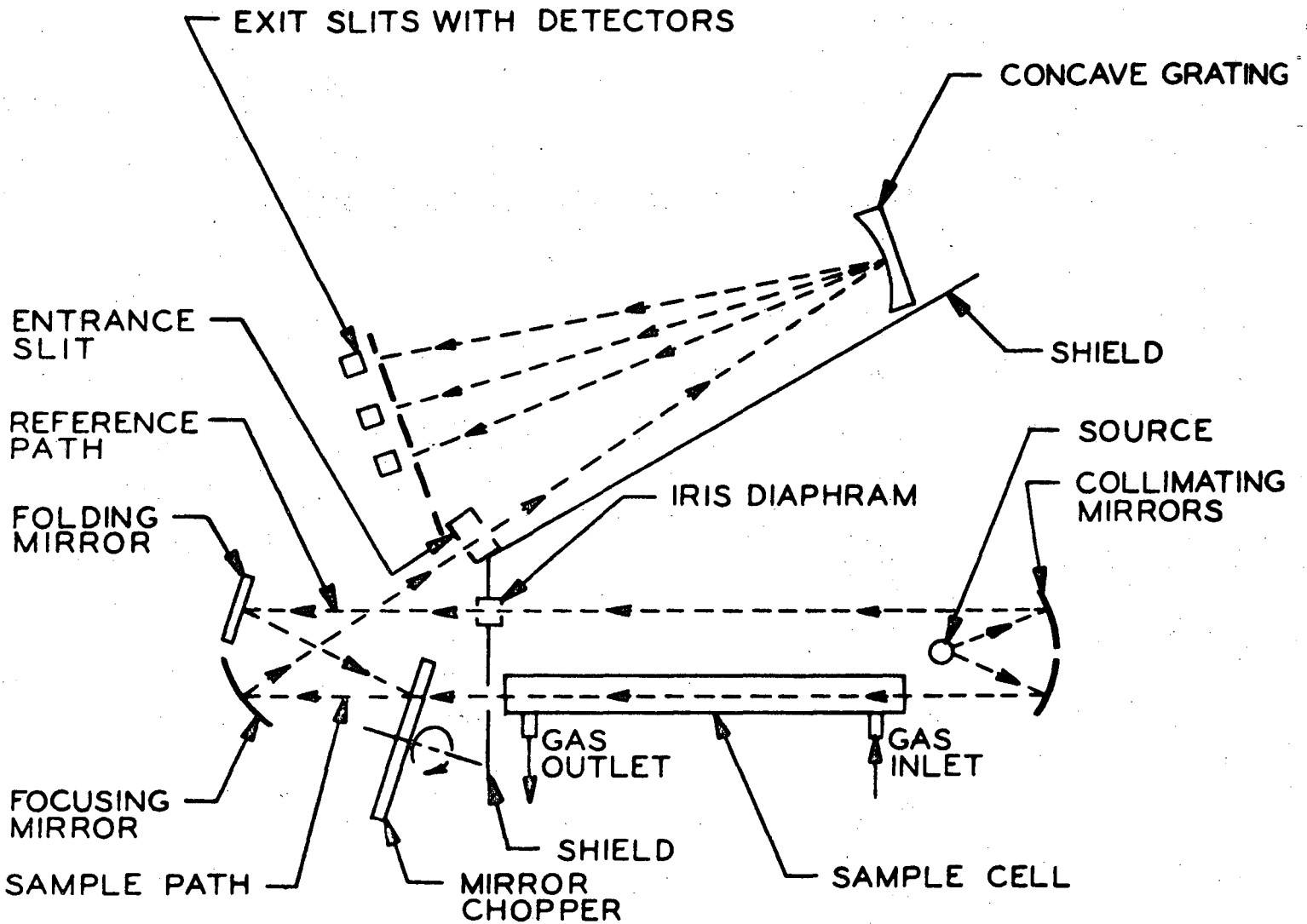
THESE OPTICAL COMPONENTS ARE FIXED TO AN ALUMINUM JIG PLATE 19" X 36" X 3/4" AND COVERED BY .060 ALUMINUM SHEET- METAL HOUSING.

Fig. 5   An Example of a Dispersive Infrared Detection Analyzer (Ref. 21)

E. Catalytic Oxidation

Catalytic oxidation has been employed to measure total hydrocarbons in vehicle exhaust gases.[22,23,24] The temperature rise from a slug sample is injected into an air stream with a constant rate of flow and a vanadia-alumina catalyst; the temperature rise gives a linear measure of the total hydrocarbons present. See Fig. 6.[25] Incidentally, with a Hopcalite catalyst the carbon monoxide content in exhaust gases may be measured simultaneously. In the Purad analyzer the air sample flows through the catalytic reactor element by suction. The temperature rise is detected by temperature probes measuring the difference between the reactor housing and the oxidation occurring in the catalyst bed. A lower detectable limit of 5 ppm of HC as butene is reported.

F. Comparison of Methods

The selection of the most appropriate method for monitoring hydrocarbons depends on many factors. A few of the most obvious factors are the following:

    a) The need to monitor total hydrocarbons, or identify individual species.

    b) The maximum sensitivity required -- of the order of 0.1 ppm or 1000 ppm.

    c) Equipment cost.

Ambient air monitoring requires a lower detectable limit of at least 0.1 ppm. Total hydrocarbons may be analyzed by flame ionization detection and gas chromatography; however, only GC is able to identify individual hydrocarbon components. Manufacturers using the catalytic oxidation process claim a lower detectable limit of 5 ppm. Two non-dispersive infrared analyzers (Infrared and Horiba) have reported sensitivities of 1 ppm as Hexane.
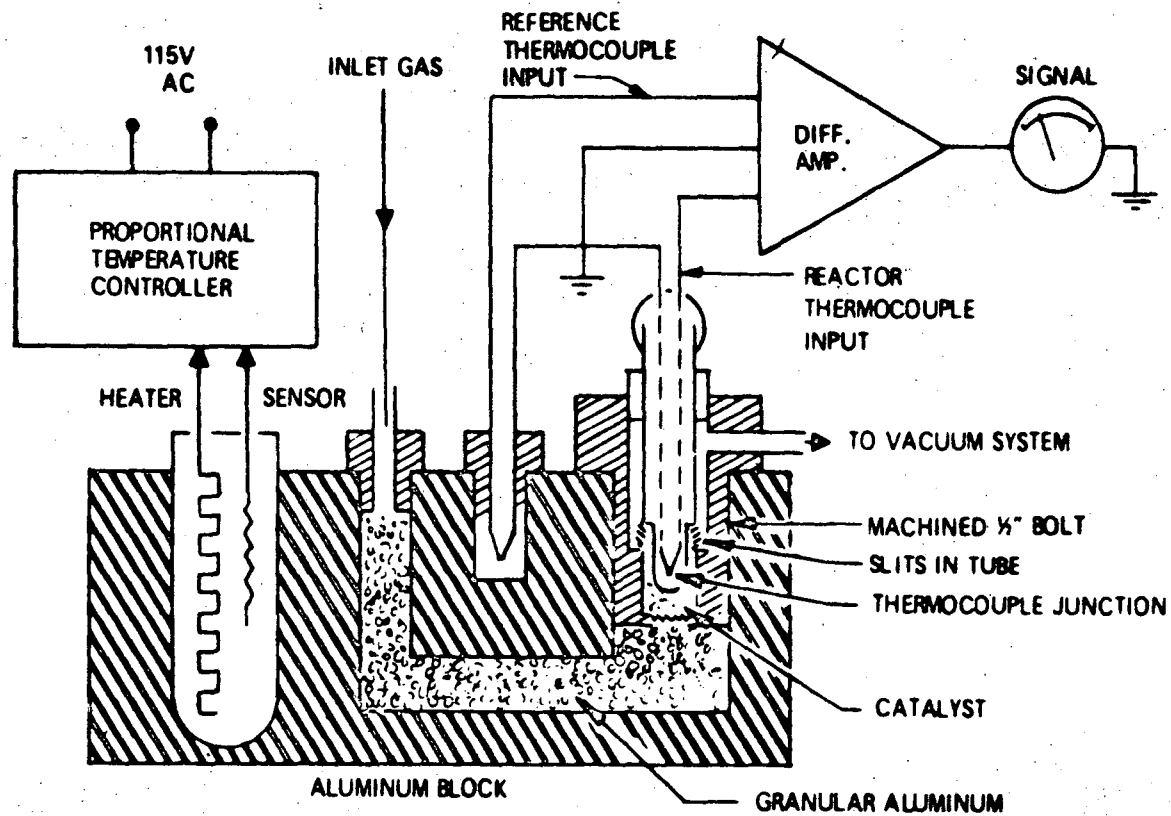
Fig. 6   An Example of a Catalytic Oxidation Analyzer (Ref. 25)

For analyzing stationary sources and vehicular exhaust all of the above methods are applicable. Jackson has compared the relative response of FID and NDIR methods of analyzing vehicular exhausts.[26,27] It was noted that the FID readings were taken with pure hydrogen fuel at a 15.4 to 1 air-to-fuel ratio which is near optimum. Table 5 indicates that both NDIR and FID agree when monitoring the paraffin hydrocarbons, but when olefins, acetylenes or aromatics are present in the sample, NDIR is much less sensitive.

Dispersive infrared absorption detection is employed for vehicular exhaust monitoring. The Chrysler DIR analyzer has a 0 - 100 ppm sensitivity scale range for low N-Hexanes and 0 - 2000 ppm for high N-Hexanes. The DIR principle suffers much less from interferences, such as CO, CO_2 and water vapor, than NDIR.[20]

III. DEVELOPING DETECTION TECHNOLOGIES

Among the most promising instrumental developments for hydrocarbon monitoring are those techniques which are based on well-known spectrographic methods.

A. Ultraviolet Spectroscopy

Konosu, Mashiko and Sato have described a non-dispersive vacuum ultraviolet spectrometer for continuously recording the concentration of two-component gaseous systems.[28] The analyzer measures the relative intensities of a reference gas (N_2 or air) and the sample in the region of 165 - 200 nm. The light source is a deuterium discharge tube and the gas cell has an 0.2 m absorption length. A sodium salicylate plate is employed as a detector. Table 6 lists the maximum detection sensitivity for several hydrocarbons, along with the maximum measurable concentrations.

Table 5 -- Average Relative Hydrocarbon Responses (Carbon Basis)

Hydrocarbon	NDIR (5.25" Sample Cell)	FID (Pure Hydrogen Fuel, 15.4:1 Air/Hydrogen Radio)
Paraffins	Hexane=100	Hexane=100
Methane	30	104
Ethane	100	103
Propane	103	103
i-Butane	101	-
n-Butane	106	102
i-Pentane	99	101
n-Pentane	104	102
n-Hexane	100	100
n-Heptane	97	100
Olefins		
Ethylene	9	104
Propylene	31	104
1-Butene	53	-
1-Hexene	61	-
Acetylenes		
Acetylene	1	95
Methylacetylene	16	96
Ethylacetylene	32	96
Aromatics		
Benzene	2	105
Toluene	13	105

(Ref. 26 & 27)

Table 6 -- Maximum Detection Sensitivity and Maximum Measurable Concentrations
of Several Hydrocarbons by NDUV

Compound	Maximum Sensitivity (ppm)	Maximum Concentration (ppm)
Ethylene	2	1200
Propylene	1	900
Acetylene	18	13000
Propane	830	6×10^5
Benzene	0.3	500
Benzene in Air	0.7	150
Toluene	0.3	300

(Ref. 28)

B. Optoacoustic Detection

Optoacoustic detection of several hydrocarbons has been reported by scientists from Bell Telephone Laboratories.[29] The absorption of various wavelengths from CO and CO_2 molecular gas lasers was measured by a chopper-modulated beam directed through a gas sample. The absorbed energy caused a pressure increase in the sample cell which was detected by means of an internal microphone. Table 7 lists the sensitivities, type of laser and the wavelength of emission for different hydrocarbon pollutants.

C. Chemiluminescence Detection

Chemiluminescence is well known for the detection of oxidants; recently the chemiluminescent reactions between atomic oxygen and a number of reactive hydrocarbons, namely methane, ethane, propane, ethylene, propylene, trans-butene, acetylene and formaldehyde were reported as well.[30] Intense emission spectra were observed in the region of 700 to 900 nm at pressures of 1 torr. Intensity peaks at 760 nm projected above the continuous NO + O spectrum so that with appropriate optical filtering reactive hydrocarbons should be capable of identification without interference from NO. Spectra were obtained from a photomultiplier viewing a flow tube excited with 2450 MHz microwaves.

D. Other Methods

Mass spectrometers have been employed for organic analysis for many years. Interest is now in evidence for MS applied to air monitoring. Both quadrapole focusing and time of flight spectrometers might be employed with the former having a greater sensitivity and the latter yielding shorter analysis time.

Remote sensing of environmental pollutants has excited considerable interest. Prengle et al. have reported on the measurement of a number of

Table 7 -- Sensitivities for Detecting Various Pollutants by Optoacoustics

Gas	Sensitivities (ppb)	Laser	Wavelength μm
Benzene	3	CO_2	9.6392
1,3-Butadiene	1	CO	6.2153
1,3-Butadiene	2	CO_2	10.6964
1-Butene	2	CO	6.0685
1-Butene	2	CO_2	10.7874
Ethylene	0.2	CO_2	10.5321
Methanol	0.3	CO_2	9.6760
Propylene	3	CO	6.0685
Trichoroethylene	0.7	CO_2	10.6321

(Ref. 29)

pollutants in gas plumes including CH_4 plus saturates and C_2H_4 plus unsaturates.[31] Field measurements were made at a distance of 65 meters from several power plant plumes; temperatures were determined to within ±10 K and gas concentrations to within ±28%. The system consisted of a custom-designed, 25 cm Cassegrain telescope and a Block Engineering 2.8 to 15 μm interferometer spectrometer.

Early transistors were plagued with atmospheric contaminants affecting the surface characteristics of the semiconductor wafers. If the contamination could be identified and its effects controlled, a pollutant sensor might be developed. The results of a thin-film indium sesquioxide detector produced for NASA by General Electric has been reported.[32] The sensor exhibited a change in resistance when exposed to hydrogen or hydrocarbons in concentrations greater than 500 ppm. Difficulty in producing and calibrating these devices make their present utility questionable.

Microwave rotational spectroscopy depends upon the selective absorption of microwave energy by some gases at low pressure.[33] In practice microwave radiation is swept over the frequency range of interest, and the power transmitted through the sample is observed. Only molecules with permanent dipole moments lend themselves to this method of measurement. For example, benzene does not have a permanent dipole moment, but propane and propylene do. The detection sensitivity is a function of the absorption coefficient of each particular gas; for hydrocarbons the method is not expected to compete with GC-FID for sensitivity.

IV. NATIONAL STANDARDS

No discussion of monitoring is complete without a brief review of the present air quality and emission standards. Federal powers to protect and enhance the quality of the nation's air resources and to promote public health and welfare are contained in the Clean Air Act Amendments of 1970. Under this act the Environmental Protection Agency (EPA) is charged with setting national air pollution standards. The national standards are only highlighted here, and one should refer to the Federal Register for the complete texts of these regulations.

"National Primary and Secondary Air Quality Standards" were published in the Federal Register on April 30, 1971. Primary standards to protect public health and secondary standards to protect public welfare (against effects on vegetation, animals and materials) were promulgated for sulfur oxides (measured as sulfur dioxide), particulate matter, carbon monoxide, photochemical oxidants, hydrocarbons, and nitrogen dioxide. The primary air quality standard for hydrocarbons (corrected for methane) is 160 $\mu g/m^3$ (0.24 ppm) averaged over a 3-hour period. This National Standard is not to be exceeded more than once per year. The reference method described by EPA is Flame Ionization Detection using Gas Chromatography. An "equivalent method" means any method of sampling and analysis which can be demonstrated to the EPA to have a "consistent relationship to the reference method."

The ASTM Standard Method of Test for C_1 through C_5 Hydrocarbons in the Atmosphere by Gas Chromatography, D 2820-72, covers the measurement of the concentrations of individual hydrocarbons by GC with FID.[34] The procedure is employed for the analysis of both grab samples and integrated samples. The lower limit of measurement is 10 ppb by volume.

The Tentative Method of Analysis for Methane and Carbon Monoxide Content of the Atmosphere (Gas Chromatographic Method by Reduction to Methane) by the

Intersociety Committee describes the procedure for separating CH_4 and CO in a stripping column.[35] Hydrocarbons other than methane are also rejected in the stripper. Detection is made by FID.

"Standards of Performance for New Stationary Sources" were published in the Federal Register on December 23, 1971. These standards are for five categories of new stationary sources starting construction as of August 17, 1971. The five categories and their emissions standards do not include references to gaseous hydrocarbons.

On June 11, 1973, the EPA published in the Federal Register proposed standards of performance for seven new categories of stationary sources. The only category dealing with hydrocarbons was "Storage Vessels for Petroleum Liquids." The regulations for stationary source performance standards include sampling and analysis methods for determing emissions.

Regulations covering 1972 through 1975 model year light duty vehicles and heavy duty engines were collected in a compendium and published in the Federal Register on November 15, 1972. Gasoline-fueled light duty vehicle emission standards are summarized in Table 8. These regulations cover emissions of hydrocarbons. Carbon monoxide and oxides of nitrogen have also been included for completeness. Standards of emission for heavy duty gasoline-fueled and diesel-fueled engines beginning with the 1973 model year were collected and published in the Federal Register on November 15, 1972. On July 6, 1973, the EPA promulgated standards for control of air pollution from aircraft and aircraft engines. A summary of the status of exhaust emission standards for mobile sources is presented in Table 9. On July 16, 1973, EPA

> "proposed emission standards for low emission vehicles. Under the Clean Air Act, the Federal government will pay premium prices for motor vehicles whose emissions control performance is signifi-cantly better than required by the Federal standards in effect for regular production vehicles.

Table 8 -- Federal Gasoline-Fueled Light Duty Vehicle Exhaust Emission Standards

Model Year	Test Method	HC (g/mile)	CO (g/mile)	NO_x (g/mile)
1970	7-Mode Cycle	2.2	23	-
	*	4.1	34	-
1971	7-Mode Cycle	2.2	23	-
	*	4.1	34	-
1972	CVS-I	3.4	39	-
	*	3.0	28	-
1973	CVS-I	3.4	39	3.0
	*	3.0	28	3.1
1974	CVS-I	3.4	39	3.0
	*	3.0	28	3.1
1975 (original standards)	CVS-II	0.41	3.4	3.1
(interim "49 State" standards)	CVS-II	1.5	15	3.1
(interim "California" standards)	CVS-II	0.9	9.0	2.0
1976	CVS-II	0.41	3.4	0.4

*Standards shown through 1974 are equivalent standards based on the 1975 Federal test procedure (CVS-II technique). (See text.)

Table 9 -- Federal Mobile Source Exhaust Emission Standards

Mobile Source	Initial Year of Standards	Status	Exhaust Emissions
Gasoline-Fueled Light Duty Vehicles	Current	Promulgated	HC,CO,NO$_x$
Diesel Light Duty Vehicles	1975	To be proposed	-
Gasoline-Fueled Light Duty Trucks	1975	To be proposed	-
Gasoline-Fueled Heavy Duty Engines	1973	Promulgated	HC, CO
	1974	Promulgated	HC,CO,NO$_x$
Diesel Heavy Duty Engines	1973	Promulgated	Smoke
	1974	Promulgated	Smoke, HC, CO, NO$_x$
Aircraft Turbine Engines	1974	Promulgated	Smoke
	1979	Promulgated	Smoke, HC, CO, NO$_x$
Aircraft Piston Engines	1979	Promulgated	HC,CO,NO$_x$

(See text.)

"To be eligible for these premium prices, a motor vehicle must first be classified as a low emission vehicle by EPA, and then approved by the Inter-Agency Low Emission Vehicle Certification Board as a suitable replacement for some class or model of vehicles that the Federal government is purchasing. To date, no vehicles have received this designation by the Board.

"EPA intends the low emission standards to be at a level that requires advanced technology or production techniques. The proposed standards are: 1975 Light Duty Vehicles, hydrocarbons .08 grams per mile (gpm), carbon monoxide .7 gpm, and nitrogen oxides .3 gpm. 1976 Light Duty Vehicles, hydrocarbons .08 gpm, carbon monoxide .7 gpm, and nitrogen oxides .16 gpm. 1975 and 1976 Heavy Duty Vehicles, hydrocarbons plus nitrogen oxides 2.1 gpm per brake horsepower-hour, and carbon monoxide 1 gpm per brake horsepower-hour."[36]

V. CONCLUSIONS

The presently available hydrocarbon monitors allow the user to identify total hydrocarbons; in the case of non-methane hydrocarbons one must use a subtraction process. A direct method for determining the latter component would be particularly useful.

Individual species are readily identified only by means of a gas chromatographic separation column. The minimum time to analyze one sample usually runs at least 5 minutes. There is no method on the horizon which appears to be competitive with GC for individual hydrocarbon gas analysis.

With respect to on-going developments both the IR and UV portions of the spectrum appear promising for dispersive spectroscopy technology.

VI. ACKNOWLEDGEMENTS

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