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SELECTIVE INFRARED DETECTORS FOR CHROMATOGRAPHY

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SUMMARY

Infrared absorption photometry has been investigated as a means for selective detection of gas chromatography effluents to facilitate identification of components in complex chromatograms. Results obtainable with different methods of instrumentation or operation are presented and discussed. New and simultaneous wavelength detection systems have been developed which provide separate multichannel chromatograms for components differentiated by molecular functional groups. The same principles can also be applied to other optical detectors such as ultraviolet, visible and fluorescence photometers.

Multiwavelength chromatography will add new dimensions to future qualitative applications for both gas and liquid chromatography.

INTRODUCTION

When Tswett[1], the originator of chromatography, made his first chromatograms, they were in some respect superior to those obtained today with our more sophisticated instrumentation: Tswett's chromatograms not only provided separation of components, but also their colorimetric identification. Hence the origin of the term "chromatography". Present-day gas chromatographic (GC) detectors provide very sensitive and precise component measurement, but the recorded chromatograms are relatively poor from the point of component identification. Retention time data and calibration techniques are widely used to this end, but are not always reliable and sometimes tedious for complex mixtures.

Optical detectors have the capability of measuring the color of components eluted from a chromatographic column and not just in the visible portion of the electromagnetic spectrum (which was Tswett's limitation) but in the infrared (IR) or ultraviolet (UV) regions as well. Absorption or fluorescence modes are equally suitable depending on the analytical requirements. Fixed (filter-type) or variable (spectrophotometer) wavelength systems are widely used for liquid chromatography (LC).

The use of IR absorption techniques as a GC detector would be particularly attractive since strong absorptions occur at molecular group frequencies that are useful for component structure analysis and, therefore, for identification. However, in spite of some early trials (see *e.g.*, Liberti *et al.*[2]), the application of IR or UV spec-

troscopy as a GC detector was found to be inadequate, owing mainly to sensitivity limitations. As stated by Freeman[3] "it can be fairly stated that no "on-the-fly" GC–IR combination is extant which approaches the utility of the many commercially available types of GC–MS unions". This statement was written about eight years ago and it is still true today, in spite of the various systems employing heated gas cells, interrupted elution or scanning systems which have been described by various researchers and introduced by companies specializing in spectroscopic instrumentation. The best indication of the lack of success in this field is the fact that none of the three authoritative books dealing with GC detectors[4–6] has any mentioning of UV or IR spectroscopy as detection technique.

This report describes some new systems that overcome the problems of the past. The results shown and discussed will illustrate that IR systems can be made sensitive enough to serve as detectors for most GC applications and can provide information for the identification of various classes of compounds presently impossible with other types of selective detectors.

THE INFRARED CHROMATOGRAPHY DETECTOR

Description of the system

A special non-dispersive photometer has been developed which has low noise of 0.0001 absorbance units at 0.3 sec response. The aperture of the optical system is such that it can pass radiation through a 1-cm heatable flow-through cell of 1 mm diameter (cell volume = 7 μl) without vignetting and without requiring a beam-condensing system. The filters are interchangeable to select specific wavelengths where strong functional group absorptions occur, which will selectively sensitize the detector for the chemical structure of components, thus making it possible to identify peaks as aliphatics, alkenes, alkynes, aromatics, esters, ketones, aldehydes, alcohols, phenols, halogen-, sulfur- or nitrogen-containing compounds, or special substances, etc. The system is equally suitable for GC and LC since the same cell can be used in both cases. LC applications are, however, subject to limitations to available solvents sufficiently transparent at the desired wavelengths.

Fig. 1 is the functional schematic of the non-dispersive type IR detector designed for chromatographic applications. Radiation from a point source, 1 mm in diameter, is alternatively passed through one of the legs of the beam-switching optical system shown on the left. The intensities of both beams or filter transmittance can be equalized through either one of the trimmers T_1 or T_2. When operating the system in the single wavelength mode, one of the filters, F_A or F_B, is selected with a desired analytical wavelength and the other with a reference wavelength where no IR absorption is likely to occur, such as, *e.g.*, in the 4-μm region. This is similar to double-beam operation through the same sample cell and is best for short- and long-term stability, since source fluctuations are minimized. Another alternative for single wavelength operation is to place the analytical filter in position F_C and to use an opaque shutter in one of the beams, *i.e.*, at position F_A or F_B. A very narrow beam (3 mm for cells as long as 4 cm, or 1 mm diameter for the 1-cm-long flow-through cells used with open tubular columns) is passed through the cell which is connected to the effluent exit of either a gas or liquid chromatograph. Alternating radiation from the two wavelengths (either both analytical or one analytical and one reference) is transmitted

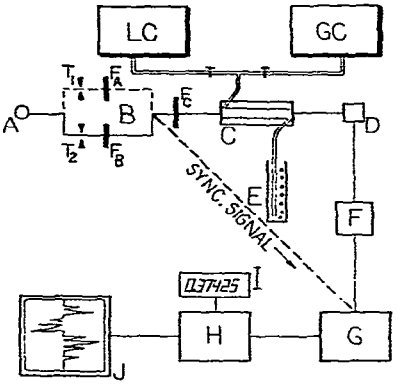

Fig. 1. Functional schematic of the gas chromatograph–IR detector system. LC = Liquid chromatograph; GC = gas chromatograph; A = IR source; B = beam switcher; C = flow-through cell; D = thermocouple; E = flow meter; F = pre-amplifier; G = lock-in amplifier; H = signal processor; I = digital meter; J = recorder; T_1, T_2 = trimmers; F_A, F_B, F_C = filters.

to the IR-sensitive thermocouple. As components pass through the cell, the radiation level passed is varied as a function of component concentration.

The thermocouple signal is first pre-amplified and then subjected to phase-sensitive rectification with synchronization from a signal generated from the beam-switcher, and further amplification in the lock-in amplifier. The resulting output is transferred to a signal processor for conversion of transmittance to absorbance (necessary for linear component concentration measurement), reference signal balancing in the "double-beam mode" and other output adjustments. A digital meter was

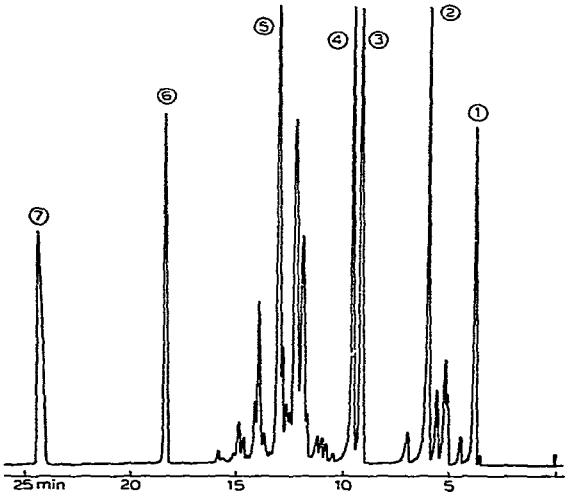

Fig. 2. Chromatogram of a hydrocarbon sample using IR detection. Column: 50 ft. × 0.50 mm I.D. SCOT prepared with a methylsilicone liquid phase; column temperature: 5 min isothermal at 40° then programmed at about 6°/min to 160°; sample volume: 0.2 μl, no inlet split; detector sensitivity: 0.1 a.u.f.s.; filter: 3.4 μm. Peaks: 1, *n*-pentane; 2, *n*-hexane; 3, 2,2,4-trimethylpentane; 4, *n*-heptane; 5, *n*-octane; 6, *n*-decane; 7, *n*-dodecane.

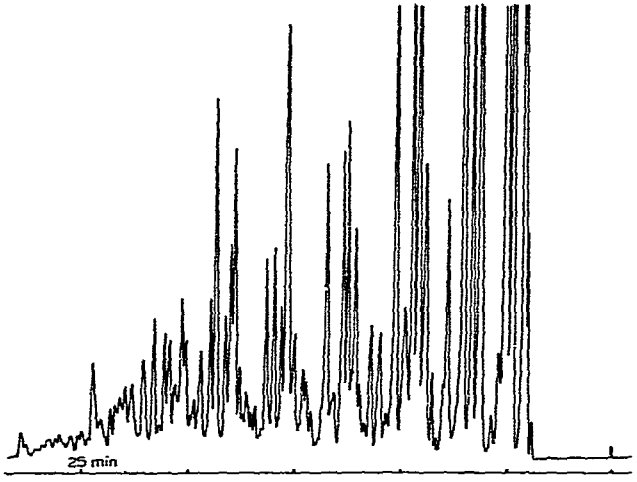

Fig. 3. Chromatogram of a gasoline sample using IR detection. Column and conditions as in Fig. 2. Sample volume: 0.3 μl, no inlet split.

used for setting up the parameters and observing the intensity of strong peaks which are off recorder scale. This is a convenience accessory and is not strictly necessary for the operation of the photometric detector. The signal processor output is connected to either a one- or a two-pen recorder for recording the chromatograms.

Performance of the IR detector

A typical IR gas chromatogram is shown in Fig. 2 with a mixture of hydrocarbons serving as the sample. This chromatogram was obtained using a support-coated open tubular (SCOT) column[7,8] with 0.2 μl sample injection, without any inlet split. Fig. 3 shows a chromatogram obtained when analyzing a 0.3-μl gasoline sample. Fig. 4 is another chromatogram of a gasoline sample with an injected sample volume of only 0.2 μl at a higher sensitivity of 0.05 a.u.f.s.

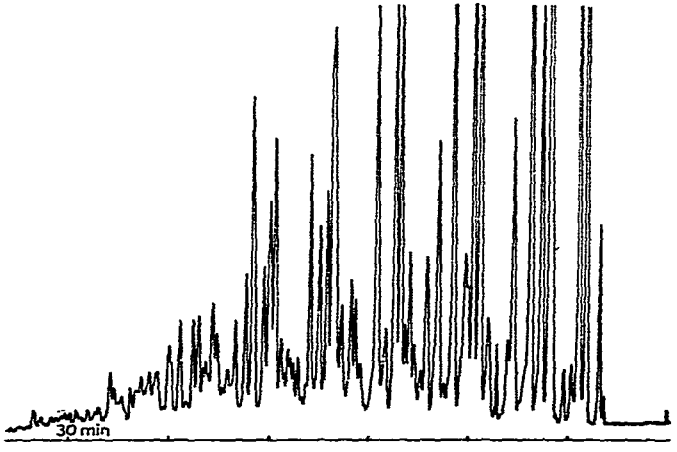

Fig. 4. Chromatogram of a gasoline sample using IR detection. Column and conditions as in Fig. 2. Sample volume: 0.2 μl, no inlet split; detector sensitivity: 0.05 a.u.f.s.

The sensitivity of this detector for aliphatic compounds is about two orders of magnitude inferior to the highly sensitive flame-ionization detector (FID); however, it is significantly better than that of most thermal conductivity detectors. As for any selective detector, the sensitivity is different for each class of compounds. For optical absorption detectors it is a function of the extinction coefficient at the selected wavelength for a particular functional group. For lower-molecular-weight carbonyl, hydroxyl and halogenated substances, these extinction coefficients are very strong and for these substances the IR sensitivity is only one order of magnitude inferior to the FID. For alkenes and aromatics, increasingly with higher molecular weight, IR sensitivities are about three orders of magnitude lower. A UV detector offers somewhat better sensitivities for these, although single and group-specific wavelengths are more difficult to select.

The IR detector is ideal for the detection of small amounts of water, which are difficult or impossible to detect with the FID. It would also be ideal for separating deuterated compounds.

Generally speaking, the sensitivity of a non-dispersive IR detector is sufficient for most applications with packed and SCOT columns. It is a concentration-type detector and, therefore, flow-rates have to be kept at about 2 ml/min for SCOT columns and at a relatively low rate with packed columns. At the present stage of development the sensitivity of the IR detector is somewhat marginal for 0.25 mm I.D. wall-coated open tubular columns which require very small sample introductions. Also, for some very difficult trace analyses it cannot compete with the FID or the electron capture detector, but it is not intended for such applications.

A very interesting aspect of IR detectors used in GC is that almost anything can be used as the carrier gas, as long as it does not have absorption at the selected analytical wavelength. Compressed air is the obvious choice for economic reasons since oxygen and nitrogen have no absorption in the IR. Small and very inexpensive minicompressors are available; coupled with a small lecture gas bottle they are very convenient as portable carrier gas supplies. This could eliminate the bulky hydrogen, helium, oxygen and air tanks usually found in a GC laboratory, if only an IR detector is to be used with the chromatograph. This is also advantageous for portable systems, especially for plant air pollution control devices.

The unlimited choice of carrier gases or vapors may lead to improvements in separations. Viscosity, polarity and chemical structure are known to have effects on component elutions. In LC, gradient elution and reversed-phase chromatography are powerful techniques for achieving better and faster separations. It will be worth investigating in the future whether these techniques can be applied to GC when using optical detectors, "desensitized" to the mobile phase.

IR detectors are insensitive to flow, pressure and temperature. Thus, good baseline stability can be obtained even if these conditions are varied, which simplifies many instrumental requirements. This is best illustrated by the fact that most of the chromatograms shown in this paper were obtained with a home-made gas chromatograph consisting of a heated tee serving as the injection port, a small heated box serving as the column oven and a flow meter connected to the cell. Temperature programming was achieved through fixed variac settings.

The heated interface (flow-through cell and capillary) is located after the light-modulation system, because otherwise cell emission will also be detected, which

causes baseline shifts with temperature. Commercially available low- and medium-cost IR spectrophotometers were found unsatisfactory in this connection since for most of these the chopper is located after the sample space. Their sensitivity for GC detection is also considerably inferior to a filter photometer specifically designed for chromatography. At 0.3 sec or 1 sec response full scale, most commercial IR spectrophotometers have noise of 0.5–1 % transmission which corresponds to about 0.004 absorbance units. This is 40 times higher than the noise level of this photometer.

Of course, wider slit settings will improve the signal-to-noise performance of spectrophotometers; however, it then becomes apparent that at low absorbance levels the sensitivity of the nulling attenuator (optical wedge) in the reference beam becomes limiting. True ratio systems have better performance capability for this reason but are more expensive.

Since the flow-through cell must have very small volume for open tubular column GC or for LC, and yet decent path lengths are required for sufficient sample absorption (1–2 cm), it can be calculated that the cell diameter must be of the order of 1 mm or less. When using such cells in conventional spectrophotometers, they will only pass a few percent of incident radiation. Except for smaller pathlength cells, with resulting lesser component sensitivity, beam condensers will only yield marginal improvement because of the wide apertures of their optical system. This is also an additional expense. Conventional spectrophotometers further require an additional absorbance readout accessory since a detector must necessarily measure component concentration. Thus, the performance-to-cost ratio of available dispersive IR instrumentation is relatively unattractive when compared with a filter photometer gas chromatographic detection system.

APPLICATIONS OF THE SELECTIVE INFRARED GC DETECTOR

Single-wavelength mode

Selective detector response is obtained for each available filter placed into the photometer for specific functional groups. Thus different chromatograms for the same sample are obtained with each filter or analytical wavelength. When chromatograms are superimposed or compared, qualitative assignments by functional groups of individual peaks is made possible. When retention time and column characteristics are taken into account, it is then possible in most cases to identify the sample components. Relative peak height for a given component, as recorded with different filters, is also informative for chain-length, as will be discussed later.

Changing filters is very easy and takes only a matter of minutes allowing for filter warm-up (stabilization) time. Interference filters are commercially available for most desirable wavelengths and relatively inexpensive for small sizes, which are entirely adequate for such a microphotometer.

The selective IR detector is an ideal informative supplement to the most commonly used FID or thermoconductivity detectors in conventional chromatographs. Signals from both detectors (IR and FID) are fed into a two-pen recorder. It is best to use high split ratios in favor of the IR detector since the FID has plenty of sensitivity and requires splitting in most cases anyhow. Some care has to be taken to adjust the system for equivalent flow-rates through each detector, in order to ensure reasonable peak synchronization on the recorder. This is accomplished with restrictors or back-

pressure valves. Split ratios of 100 to 10/1 are best for maximum IR detector response. However, in this study, a 1:1 split ratio was deliberately used (although it is unfavorable), in order to make absolute response comparison easier.

Figs. 5 and 6 show two examples of FID–IR recordings obtainable in this manner. The sample analyzed for Fig. 5 was a gasoline for which the IR detector was used to pinpoint aromatics and alkenes. The sample for Fig. 6 was a naphtha and the IR response was selected to record aliphatics. In this case the aromatics can also be sorted out by difference as indicated by the black dots over the FID chromatogram.

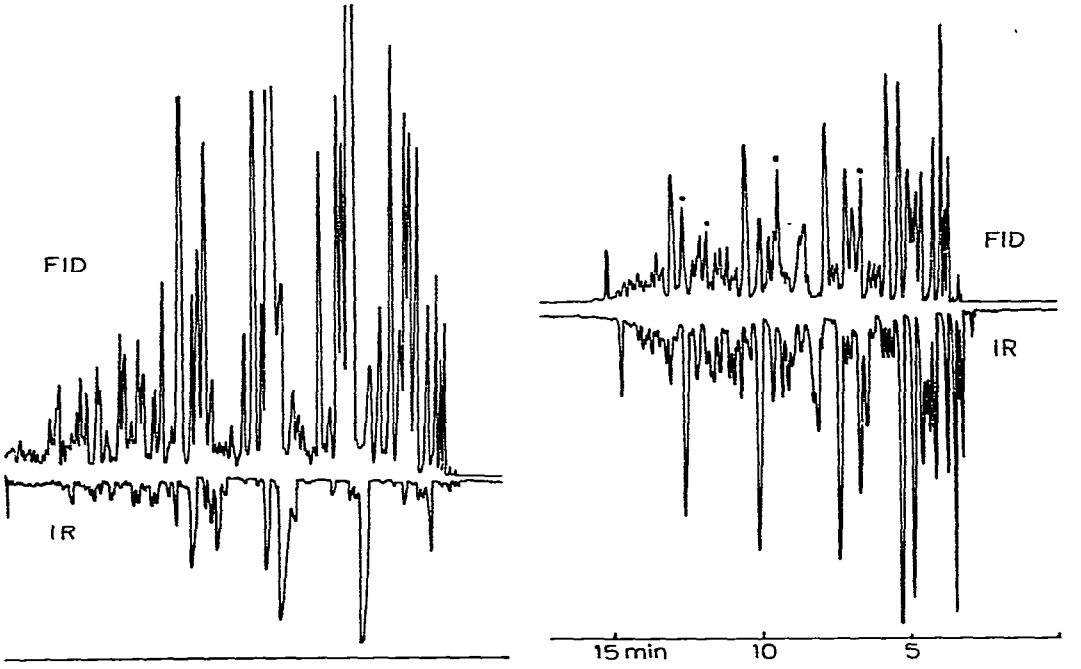

Fig. 5. Determination of aromatics and alkenes in gasoline. Column: 50 ft. × 0.50 mm I.D. SCOT prepared with Carbowax 20M liquid phase; column temperature: programmed from 40 to 150° at about 16°/min; sample volume: 0.3 μl, no inlet split; column effluent split 1:1 to the two detectors; IR detector sensitivity: 0.05 a.u.f.s.; filter: 3.3 μm.

Fig. 6. Determination of aliphatic and aromatic compounds in a naphtha sample. Column and conditions as in Fig. 5. IR detector sensitivity: 0.1 a.u.f.s.; filter: 3.4 μm.

Figs. 7 and 8 show a very important application the solution of which was up to now impossible: the selective detection of various oxygen-containing compounds, in this case those with carbonyl and hydroxyl groups. The sample was peppermint oil, and only a very small amount, 0.04 μ, was injected. A carbonyl (Fig. 7) and subsequently a hydroxyl filter (Fig. 8) were used with the IR detector to pinpoint peaks that contained these functional groups. This example illustrates the convenience of this selective detector for the identification of components in such a complex sample.

In this mode of operation, the FID serves as a monitor indicating every component that can be separated by the column.

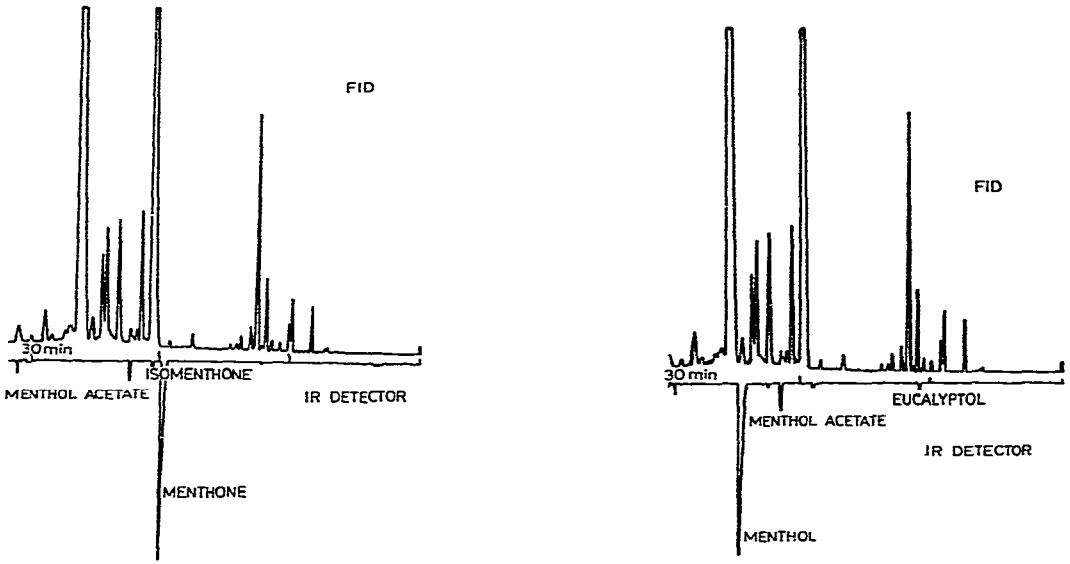

Fig. 7. Determination of compounds containing carbonyl group in a sample of peppermint oil. Column: as in Fig. 5; column temperature: programmed from 75 to 150° at about 4°/min; sample volume: 0.04 μl, no inlet split; column effluent split 1:1 to the two detectors; IR detector sensitivity: 0.05 a.u.f.s.; carbonyl filter (5.6 μm).

Fig. 8. Determination of compounds containing a hydroxyl group in a sample of peppermint oil. Column and conditions as in Fig. 7; hydroxyl filter (9.8 μm).

Although the IR detector is quite linear at low and medium concentrations, the FID is probably better for accurate quantitative work and has a higher sensitivity in trace analysis. Calibration of a democratic detector is also easier, specially with internal standard methods. Thus, quantitative analysis may be best obtained from the FID output.

Dual-wavelength mode

The special photometer used for this work with its beam-switching configuration makes it possible to use simultaneously two filters or different analytical wavelengths. As a result, the detector's response is of opposite polarity for components belonging to the corresponding functional groups.

Fig. 9 illustrates this effect with a 1:1 mixture of benzene and *n*-hexane. The chromatogram on the left was obtained in the single wavelength mode with an alkane filter (3.4 μm). Benzene response is just barely noticeable, in spite of close proximity of the alkane and alkene analytical wavelengths which are 0.1 μm or a frequency of 100 cm^{-1} apart. The chromatogram on the right shows the peaks of benzene and *n*-hexane in opposite direction when using two filters.

Fig. 10 is another example for dual functional group analysis. In this case, the sample consisted of hydrocarbons mixed with halogenated compounds. The recording on the left with a single wavelength shows only the hydrocarbons while the one on the right obtained with dual filters shows both types of components, but now in opposite directions. In this manner it is easy to determine which peaks in a mixture relate to halogenated substances.

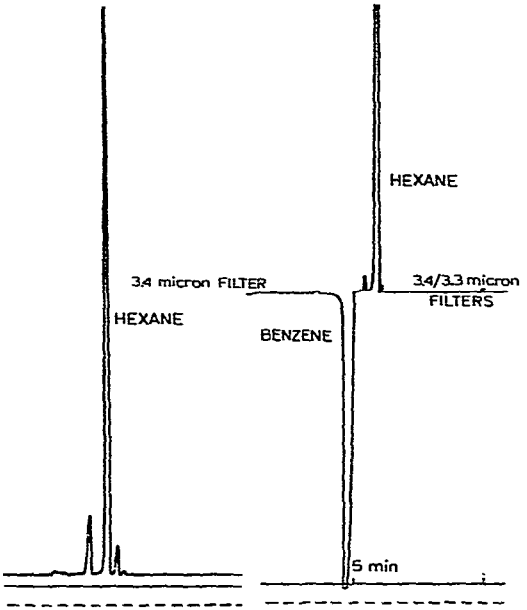

Fig. 9. Simultaneous determination of aromatic and aliphatic compounds. Sample: a 1:1 mixture of *n*-hexane and benzene; column: as in Fig. 2; column temperature: 80°, isothermal; sample volume: 0.1 μl, no inlet split; IR detector sensitivity: 0.2 a.u.f.s.; IR filters: left 3.4 μm, single wavelength mode; right 3.4 μm (peaks upward) and 3.3 μm (peaks downward), dual wavelength mode.

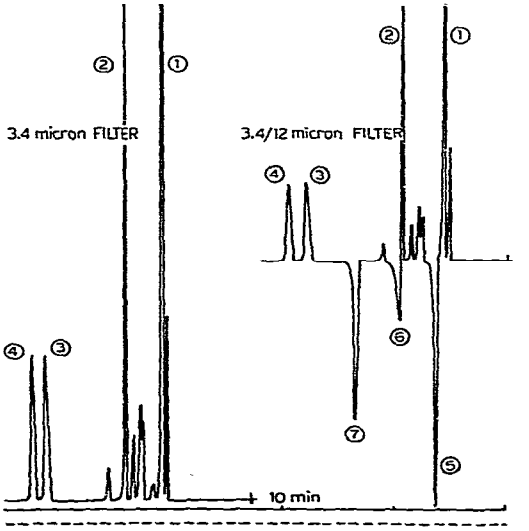

Fig. 10. Simultaneous determination of aliphatic and halogen-containing compounds. Column: as in Fig. 2; column temperature: 50°, isothermal; sample volume: 0.1 μl, no inlet split; IR filters: left 3.4 μm, single wavelength mode; right 3.4 μm (peaks upward) and 12 μm (peaks downward), dual wavelength mode. Peaks: 1, *n*-pentane; 2, *n*-hexane; 3, 2,2,4-trimethylpentane; 4, *n*-heptane; 5, freon; 6, chloroform; 7, carbon tetrachloride.

An application of considerable industrial significance is the determination of aromatics in gasoline. Since several hundred components are present in most gasolines, it is with present techniques quite tedious to determine what all the peaks are or where the significant ones are located in the chromatogram.

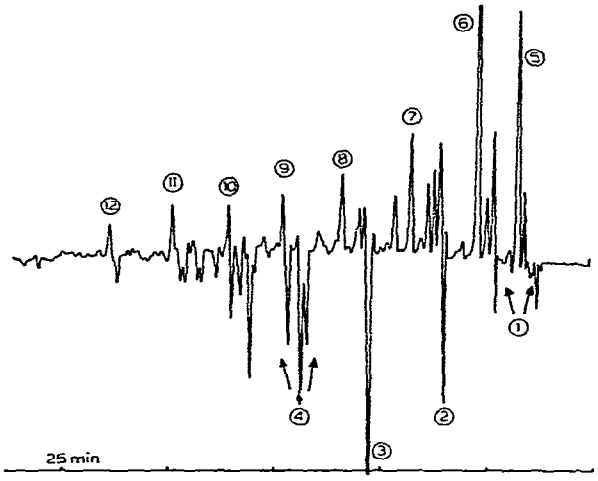

Fig. 11. Determination of aromatic compounds in gasoline. Column: as in Fig. 2; column temperature: 5 min isothermal at 45° then programmed at about 6°/min to 160°; sample volume: 0.2 μl, no inlet split; IR detector sensitivity: 0.05 a.u.f.s.; filters: 3.4 μm (upper peaks) and 3.3 μm (lower peaks); dual wavelength mode. Peaks: 1, alkenes; 2, benzene; 3, toluene; 4, xylenes + ethylbenzene; 5, *n*-pentane; 6, *n*-hexane; 7, *n*-heptane; 8, *n*-octane; 9, *n*-nonane; 10, *n*-decane; 11, *n*-undecane; 12, *n*-dodecane.

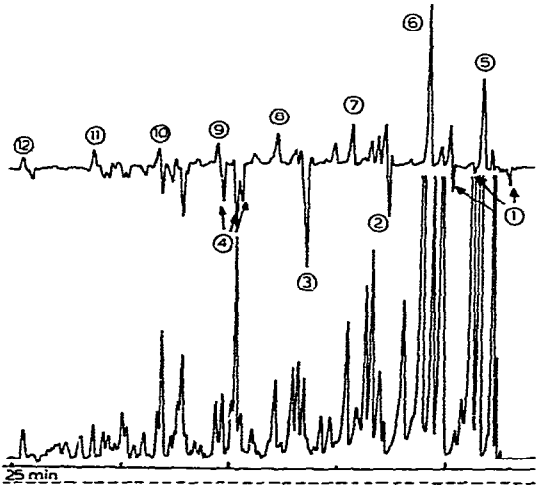

Fig. 12. Determination of aromatic compounds in gasoline. Column: as in Fig. 2; column temperature: 5 min isothermal at 40° then programmed at about 6°/min to 160°; sample volume: 0.2 μl, no inlet split; IR detector sensitivity: 0.1 a.u.f.s.; upper chromatogram: dual wavelength recording with 3.3 and 3.4 μm filters; lower chromatogram: single wavelength mode. Peaks, as in Fig. 11.

Fig. 11 shows a dual-wavelength chromatogram of gasoline where the aromatics peaks point downwards and the aliphatics upwards. There are a few small peaks before benzene that correspond to alkene absorption in this same filter region. Alkenes can be separated from aromatics at longer wavelengths in the IR or through UV absorption photometry if necessary. It should be noted as a curiosity that in this fashion the normal C_5–C_{12} alkanes stand out from the upward portion of the chromatogram and can be easily spotted.

Fig. 12 shows a more convenient presentation of the analysis of aromatic compounds in a gasoline sample. Here the dual-wavelength recording, which is somewhat less sensitive for reasons given later, is superimposed or rerecorded on a normal single-wavelength run. The upper trace is then helpful for determining which peak from the lower chromatogram belongs to which functional group category. This technique is very useful for differentiating between different types of gasoline, because their aromatic contents vary significantly and for each aromatic component. It should therefore also be possible to apply this technique to the categorization of oils, *e.g.* in the investigation of oil spills in water pollution.

Multiwavelength tandem mode

IR or other optical detectors are non-destructive, except for flame emission. It is therefore possible to operate two or more in series or tandem. The exit of the first flow-through cell merely has to be connected to a second cell which is placed in another detector, by means of a heatable capillary line. With a two-pen recorder and operating both detectors in the dual-wavelength mode, four analytical channels can be provided for multiwavelength chromatographic analysis of single injections.

Fig. 13 illustrates what type of recordings can be obtained in this manner. It must be pointed out that the traces shown do not represent what is obtainable under ideal conditions. The second detector available for this demonstration was an older prototype with only one-tenth the sensitivity or signal-to-noise ratio of the more recent system used for the upper two channels. The connecting line was 20 ft. long, because of space problems, and was not heated. Therefore, some loss of separation and poorer peak shapes can be observed, resulting from some adsorption on the line walls and additional volumes. Also, the experimental filters were far from ideal providing one or two orders of magnitude less sensitivity than if properly selected for this application. For example, the carbonyl filter was more than 0.5 μm wide and centered at 5.6 μm whereas 5.8 μm is the proper carbonyl wavelength. One-fifth of this band width would be desirable for general carbonyl work, and one-tenth or less for differentiating between esters, ketones and aldehydes. The hydroxyl filter, although somewhat narrower, was centered at 9.8 μm instead of 9.5 μm where generally most primary alcohols have their peak absorption. This proves, however, that satisfactory results can still be obtained in many cases even if the filters on hand are not perfect and that high spectroscopic resolution is not necessary for most GC functional group analyses.

The upper traces in Fig. 13 produced by one of the detectors have hydrocarbon response upward and halogen response downward. The lower trace, produced by the other detector, has carbonyl response upward and hydroxyl response downward. As expected, trimethylpentane, although present in a concentration of 20%,

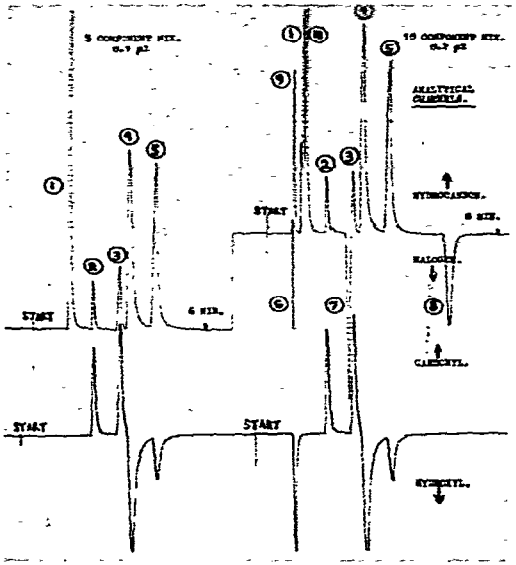

Fig. 13. Analysis of two multicomponent mixtures. Column: 50 ft. × 0.50 mm I.D. SCOT prepared with Carbowax 1540 liquid phase; column temperature: 70°, isothermal; IR detector sensitivity: 0.2 a.u.f.s.; two double-wavelength IR detectors with 3.4 and 12 μm (detector No. 1) and 5.6 and 9.8 μm (detector No. 2) filters. Peaks: 1, 2,2,4-trimethylpentane, 2, acetone, 3, ethyl acetate, 4, methanol, 5, ethanol, 6, Freon, 7, carbon tetrachloride, 8, chloroform, 9, *n*-hexane, 10, *n*-heptane.

does not show in the hydroxyl and carbonyl channels. It has, however, off-scale response in the upper channel obtained with the C–H filter.

The two traces on the right were obtained when analyzing a ten-component mixture, each component present in a concentration of 10%. Freon also absorbs at 9.8 μm and therefore, shows in the hydroxyl channel. This possibility, that a component may have an absorption band at a functional group frequency for which it in itself does not have the functional group, always exists, but is fairly unlikely. Even in such cases, the retention times and the chromatograms obtained at other wavelengths usually will clear up the confusion and provide clear identification. In the present case it would be obvious that peak No. 6 could not possible be an alcohol.

With additional narrow-band filters it is possible to provide more specific sensitization in order to distinguish for the carbonyl channel whether the peaks correspond to esters, aldehydes or ketones. The same can also be done for hydroxyl group-containing components, in order to determine whether they are primary, secondary or tertiary alcohols. The procedure merely is to use relatively wide band filters to determine group functionality and then to repeat the chromatograms with narrower band filters to determine functional group type. This approach should be of considerable value in the essential oil, food, flavor and alcoholic beverage industries.

There is one problem with the dual-wavelength mode when components of different functionality respond with opposite signal polarity. Many components have more than one functional group in their molecules. If two of these groups respond to the two analytical wavelengths chosen for one detector, the two signals generated

will counteract each other. The stronger of the two will dominate but the net result is a loss in sensitivity. This is the reason for the loss of sensitivity for some aromatics as mentioned earlier in connection with the analysis of a gasoline sample. All alkyl-aromatics have absorptions at both the aromatic and alkane wavelengths. Thus, the sensitivity in the dual-wavelength mode is not as good as in the single-wavelength mode. In a few rare cases, the two opposing signals may actually cancel out and no peak will be recorded. However, by selecting which filter should be used against the other one, this difficulty can be avoided by tandem and sequential operation.

For this reason the carbonyl filter was selected together with the hydroxyl filter in the example in Fig. 13 since none of the components had carbonyl and hydroxyl groups at the same time. Another drawback is when two peaks are poorly separated and correspond to two components with opposing functional detector responses. Their shapes will be peculiar and exhibit quick transition from one polarity to the other as can be seen in Fig. 13 for Freon in the upper trace and in Figs. 11 and 12 for the dual-wavelength recording of gasoline components. In spite of these shortcomings, however, the dual-wavelength mode offers many qualitative advantages as long as good care is given to proper column and filter selection.

Simultaneous multiwavelength mode (multichannel IR chromatography)

The disadvantage of the dual-wavelength mode, which was mentioned above, led to the design of a novel multiwavelength photometer[9] that is capable of providing simultaneous chromatograms generated by detector signals at more than two wavelengths and without counteracting filter response. In this instrument several analytical wavelengths and one reference (for better stability) are alternated on the detector. A special optical arrangement makes it possible to have the filters in a static position for ease of interchangeability which is necessary for application flexibility. The signals are separated into corresponding output channels of single polarity by a special electronics system. The channels are connected to a multi-pen recorder and have separate adjustable sensitivity controls.

Fig. 14 illustrates the results obtainable with such a system. The chromatogram on the left is from one channel only, full recorder scale. A wide-band hydrocarbon linkage filter constitutes an ideal monitor (somewhat similar to the FID) since most molecules have CH groups in their molecule. The chromatograms on the right were obtained for one single injection, from the outputs of the different wavelength channels of the detector. In this case, four channels are shown, from top to bottom: halogen, carbonyl, hydroxyl and hydrocarbon (alkane and cycloalkane, olefin and aromatic) functional groups. A 15-component mixture, in which each substance is present in about equal proportions, was used to demonstrate how this detector is capable of breaking down a mixture into different component categories. There is some minor response from carbonyl components in the hydroxy channel and from others in the halogen channel. This again is due to the wide-band filter situation mentioned previously.

It is interesting to note that, in addition to the convenient presentation aspect for chromatograms obtained with the multichannel detector, new qualitative information is also generated. The three alcohols have simultaneous response in both the CH and OH channels. The CH/OH ratio for each alcohol, however, varies significantly and increases with the chain-length, as is to be expected. This chromatogram,

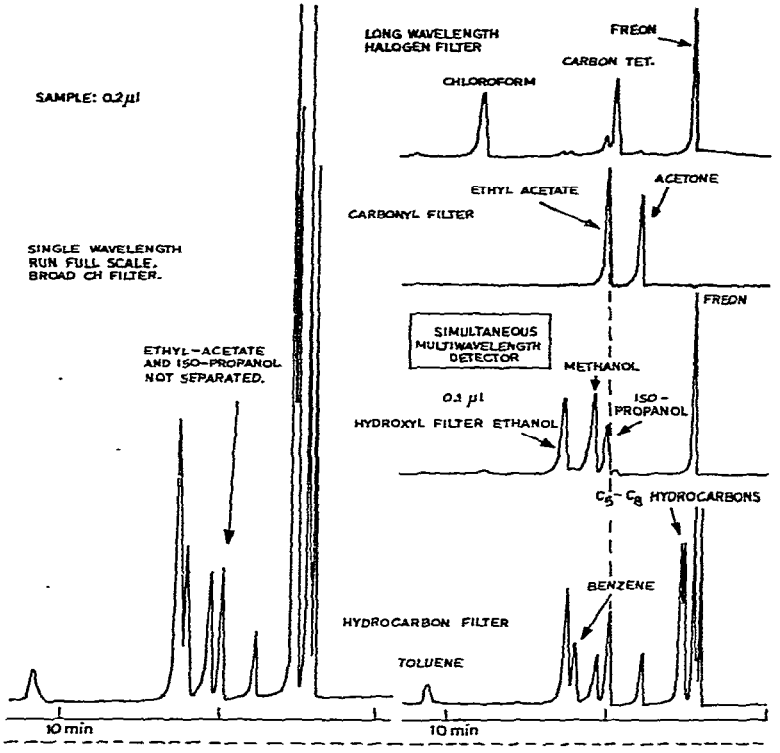

Fig. 14. Analysis of a 15-component mixture. Column: as in Fig. 5; column temperature: 80°, isothermal; sample volume: 0.2 µl, no inlet split; simultaneous multiwavelength detector; sensitivity in all channels: 0.2 a.u.f.s.; left side: 3.4 µm (wide) filter. Other filters and sample volumes identified in the figure.

for example, tells the analyst that isopropanol elutes first, which is the case with polar columns since isopropanol has the lowest polarity. With some columns the relative polarity–boiling point relationship affecting the order of component elution is not always too well predictable and varies with temperature. Thus, it is quite helpful to be able to obtain chain-length information to ascertain in which order components belonging to a given functionality elute. If a printing integrator is used with this detector, simple ratio-recording circuitry between selected channels will directly provide numerical data that can be calibrated to arrive at chain-length or molecular configurations. IR spectroscopists know that precise measurement of extinction coefficients also represents useful qualitative information in addition to specific wavelength absorption.

Another qualitative bonus derived from simultaneous multiwavelength recording is evident from the fact that ethyl acetate and isopropanol are not separated in the hydrocarbon channel, which would also be the case for other chromatography detectors, under these column and temperature conditions. However, examination of the hydroxyl and carbonyl channels in this case tells the analyst that two components are actually present and also gives information on their functional groups. This means that more components can be spotted or separated with a given column which

would not show up in a normal chromatogram. As a result, less efficient columns might be needed for the analysis of complex mixtures, or components which are difficult to separate on a given column may still be detected in this fashion.

For IR detectors the number of channels is limited by the relatively slow thermocouple response, and to four or five channels for 0.3–1.0-sec time constants. Pyroelectric detectors are faster and could accommodate more simultaneous wavelengths within the desirable time constants; however, their signal-to-noise characteristics at present are one order of magnitude inferior. Cooled photoconductors are fast and also provide much higher sensitivities. Unfortunately, however, they would add to the cost and complexity of the GC detector system. On the other hand, special analytical requirements could justify this degree of sophistication.

The filters in the multichannel detector are also readily interchangeable. Thus, without much additional expense, additional channels can be obtained by making repeat runs with different filter combinations, which will provide more information for a relatively small effort and with a small increase in the time of analysis.

The principles of instrumentation and techniques described above can be readily extended to UV and fluorescence detectors and for LC. UV detectors could also be useful in GC, particularly for the determination of aromatics and some double-bond configurations. The cells which are commonly used with LC–UV systems can be readily used for gas chromatographs since their path length and diameter is identical to the cells which were used in the present investigations. However, provisions would have to be made for heating the cell and the connecting lines.

IR detectors can also be attached to any liquid chromatograph since the cell requirements are identical. However, in LC, the applications are more limited in scope because of strong opacity of many solvents in the infrared. Thus water or a number of other polar substances would be impractical as solvents. However, good results have been obtained for hydrocarbons which represent a problem with UV detectors— and other samples that can be analyzed using carbon tetrachloride, Freon or other solvents having reasonable transmittance at the wavelengths of interest.

CONCLUSIONS

The examples shown indicate that IR detectors can be made available for GC with sufficient sensitivity to provide a whealth of qualitative information relative to peaks in simple and complex chromatograms. Selective sensitization and desensitization represent valuable tools to the GC user either for identification purposes or as new variables for improving existing column performance. Detector cost and complexity is not significantly different from other widely used detectors such as flame ionization, electron capture and flame emission detectors.

IR detectors have a promising future because of their many advantages. A few are listed below: (i) They permit component identification by functional group. Additional structure information through peak ratios at two wavelengths can also be obtained; (ii) They permit the separation of unresolved peaks in chromatograms obtained with non-selective detectors; (iii) Solutions can be injected without recording the large solvent peaks, and components otherwise hidden under the solvent peak will be recorded; (iv) They are insensitive to flow, pressure and temperature changes; (v) A large number of gases and vapors can be chosen as the mobile phase, thus making

improvement of column performance possible. This might even lead to gradient elution or reversed-phase techniques in GC; (vi) Component identification and data interpretation is much less complex and costly than in mass spectrometry.

The equipment and hardware used in this work can certainly be significantly improved through future development efforts. Many new areas of interesting and useful applications lie ahead for both GC and LC by using IR detectors and multiwavelength detectors in all spectroscopic modes and spectral regions.

GC and LC represent the most widely used and universal analytical tools in research and industry. Their dominating advantage is the ability to separate components to be analyzed. Their weakness is, however, often the difficulty in identifying unknown sample components. The use of absorption spectroscopy and fluorescence for qualitative analysis of complex mixtures has been severely limited in the past although they are ideal techniques for qualitative identification of single components. It therefore makes good sense to combine the best techniques representing component separation with relatively simple spectroscopic methods of identification, arriving in this way to a method expressed in the true sense by the word "chromatography".

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