Comparison of licanic with  $\beta$ -eleostearic shows differences of 1.3 (Apiezon L) and 1.8 (Resoflex 446) units, ascribable to the 4-keto-constituent. The 9,10cyclopropenoic structure (9) in sterculic  $(C_{19})$  acid is apparently equivalent to the cis, cis-9, 12-dienoic structure in linoleic acid: the difference is exactly 1 unit in both Apiezon L and Resoflex 446. This similarity accounts for our inability to separate the C<sub>18</sub> homolog malvalic acid from linoleic acid when Apiezon L and Resoflex 446 are the liquid phases. The acetylenic position isomers, stearolic and tariric acids, have identical E.C.L.

In the chromatogram of methyl esters of isano oil (Figure 1), the conventional retention time on the abscissa has been replaced by E.C.L. Values are based on the retention times of reference palmitate, stearate, and arachidate peaks. No previous report on the gas chromatographic analysis of isano oil is known, but components a (29%) and b (44%) are believed to be isanolic acid (Apiezon L = 17.1, Resoflex 446 = 24.6), and isanic acid (Apiezon L = 19.8, Resoflex 446 = 25.4), respectively (7).

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Figure 1. Gas chromatogram of isano oil methyl esters (Apiezon L)

of the less common fatty acid methyl esters.

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# Use of a Conventional Mass Spectrometer as a Detector for Gas Chromatography

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Conventional magnetic field mass spectrometers can readily be used as auxiliary gas chromatography detectors in a directly coupled arrangement. Such a system has advantages in the identification of multicomponent chromatographic peaks and of components appearing as shoulders or in the background over trapping procedures. The procedure also gives a good quantitative breakdown of multicomponent peaks. This is illustrated with known mixtu.es and a previously analyzed reformer charge stock.

THE direct connection of a time-of-I flight mass spectrometer to a gas chromatograph for the analysis of complex chemical mixtures was discussed

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recently by Gohlke (2). A small portion of the gas entering the thermal conductivity detector was diverted directly into the mass spectrometer. In a sense, two parallel detectors are being used simultaneously to record separations that occur in the chromatograph column. The advantage of the mass spectrometer is that it identifies the material present in a chromatograph peak and gives a relative measure of how much is present.

The direct combination of the mass spectrometer and gas chromatograph is a very powerful tool for the analysis of volatile organic mixtures. The extent to which a conventional magnetic field mass spectrometer could be used for this purpose is, therefore, of interest. It was soon found that the spectra obtained on such an instrument not only were adequate for identifying unicomponent chromatographic peaks but also several components could be detected simultaneously in chromatographic peaks which contained more than one component. The mass spectra obtained could be used to determine the relative concentrations of these components.

#### INSTRUMENTATION

The method used to connect the mass spectrometer and gas chromatograph is shown schematically in Figure 1.

A portion of the gases exhausted from the thermal conductivity cell is sampled through a capillary tubing which is connected to the mass spectrometer just above the gas leak to ensure a representative sample. The flow rate through the capillary is 2.4 ml. per minute and represents from 3 to 10% of the total effluent. The pressure on the gas leak is adjusted so that the pressure at the vacuum ion gage of the mass spectrometer is about  $5 \times 10^{-5}$  mm. of mercury. The time delay of the sample between the thermal conductivity detector and the mass spectrometer is about 30 seconds.

The gas chromatograph used was temperature-programed with a linear temperature rise of  $0.6^{\circ}$  C. per minute. The initial temperature of the column was  $55^{\circ}$  C.

Temperature programing has the advantage that the chromatogram peak shapes remain approximately constant over a wide boiling range. This is important for two reasons.

1. The conventional mass spectrometers have a relatively slow scan rate. To obtain satisfactory spectra, the composition of sample seen by the mass spectrometer must not vary too rapidly during the scan time; and, therefore, the sharp spikes that are usually obtained at the beginning of a constant temperature chromatogram are avoided. Also, very broad peaks toward the end of such a chromatogram, with corresponding decrease in peak intensity and reduction of apparent mass spectrometer sensitivity, are avoided.

2. By maintaining the peak shape of the chromatogram uniform, the relative amount of materials can be determined by computation from the mass spectra without measuring areas under the derived spectral change vs. time curves.

Ten- and 30-foot columns were used with G.E. silicone SF 96 on firebrick as the packing. The mesh size was 42/60 and the weight ratio of fluid to brick was 29 to 100. The helium flow



Figure 1. Schematic diagram of gas chromatograph coupled to cycloidal mass spectrometer

rates were between 20 and 50 ml. per minute.

Two magnetic field analyzer-type mass spectrometers were tried. The first was a Consolidated Electrodynamics Corp. (CEC) Model 21-620 cycloidal path mass spectrometer, designed for monitoring purposes. It was modified by replacing the a.c. amplifier with an Applied Physics Corp. Model 30 vibrating reed electrometer and increasing the gas leak rate a factor of 10 times to 250 micron ml. per second at 1-mm. pressure. The scan rate was increased four times, so that it covered masses 55 through 120 in 40 seconds. Pressure in the ion source was  $10^{-4}$  mm. as measured with a VG-1. Resolution is about 1 part in 120.

Figure 2 is a reproduction of eight scans obtained with this instrument at the time that methylcyclohexane, trimethylcyclopentane, dimethylhexanes, and, finally, toluene, in that order, were eluted from the gas chromatograph. The spectra obtained are very useful for identification purposes, and the instrument continues to be used for this purpose.

Success with the small mass spectrometer led to experiments with the larger analytical CEC Model 21-103B. This is a 180-degree mass spectrometer with resolution of 1 part in 600.

Simple modifications consisted of adapting the inlet for the capillary tubing to introduce the sample between the gold leak and inlet vacuum pump and increasing the scan rate so that the mass range 40 to 160 could be swept in 30 seconds. The instrument was equipped with an Applied Physics Corp. Model 36 vibrating reed amplifier. The pressure in the ion source was regulated by one of the valves to the inlet vacuum pump and maintained at a pressure of about  $4 \times 10^{-6}$  mm. An ionizing current of 100  $\mu$ a. and 70e.v. ionizing voltage were used.

Two typical mass spectra, reproduced in Figure 3, show the presence of  $C_9$  and  $C_{10}$  cycloparaffins and xylenes in the chromatograph peak. An additional desirable feature of this instrument is the use of a five-galvanometer recording system, so that a wide range of sensitivities can be recorded without the necessity of switching from one range to another to accommodate the ion currents measured.

The spectra obtained under these conditions are reproducible and the same as obtained under normal operating conditions. Therefore, all the reference data previously obtained on the instrument can be used, as well as the existing compilations of mass spectral data.

All the results discussed below were obtained with the CEC Model 21-103B mass spectrometer. The sensitivity of equipment on low range is such that with a  $40-\mu$ l. charge to the gas chromatograph, the mass spectrum of components present to about 0.5% is satisfactory for identification purposes.

#### QUANTITATIVE BREAKDOWN

Often, in the analysis of hydrocarbon mixtures by gas chromatography, sev-



Figure 2. Mass spectra from Model 21-620

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Figure 3. Sample mass spectra from Model 21-103B

Table I. Mass Spectra of 3-Methylheptane and 4-Methylheptane Relative Intensity 3-Methyl-Peak 4-Methylm/eheptane heptane  $2.9 \\ 0.8 \\ 49.0$ 114 3.1 $99 \\ 85 \\ 84 \\ 71 \\ 70 \\ 43$  $0.9 \\ 4.4$ 3.052.727.3 $\frac{3.0}{2.5}$ 46.1100  $10\overline{0}$ 

eral components have retention times so similar that they come out in a single peak. When the mass spectra of these components are different, qualitative determination of the components present is not difficult. However, it has not yet been shown that the many mass spectra obtained by close connection of the spectrometer and chromatograph might also be used to determine the relative amounts of the materials in the gas chromatographic peak with any degree of accuracy. This problem has now been evaluated and good quantita-



Figure 4. Plot of masses 71 and 85 from chromatograph peak of  $4-\text{MeC}_7$  and  $3-\text{MeC}_7$ 

1, cis-t-DHCH n-Octane 1,cis-2,tr-4-THCP 3,3-0HI 3,3-0HI 3,3-0HI 3,3-0HI 3,3-0HI 1,cis-2,tr-4-THCP 1,cis-2,tr-4-THCP 3,3-0HI 1,cis-2,tr-4-THCP 1,

TIME, MINUTES

80

90

100

tive agreement with known mixtures found.

The problem can be illustrated by the case of 3-methylheptane and 4-methylheptane. The mass spectra of these two components are given in Table I. The 3-methylheptane is characterized by mass 85, while 4-methylheptane is characterized by mass 71. These ion intensities have been plotted in Figure 4 from the mass spectra obtained on a gas chromatographic peak containing these two components. A partial separation of the two components has taken place, and, in practice, with a better chromatographic column, the two can be completely resolved without the aid of the mass spectrometer. Any necessary correction due to the contribution of each mass spectrum to the other is made, and maximum value for each of the two characteristic masses is determined. These are corrected for the relative sensitivities and give the ratio of the two components in the peak directly. This can be related to the whole sample by determining the percentage of this chromatograph peak in the whole sample in the normal manner from area measurements. The key for quantitative work with this combination of equipment is



60

70



110

to get sufficient mass spectral data to plot reliably the appearance and disappearance of characteristic m/e values as the composition changes throughout the separation.

To test the usefulness of the procedure, a known blend of 20 C7 and C8 saturated hydrocarbons was made. The gas chromatogram of the mixture is given in Figure 5, using the 10-foot silicone column and a helium flow rate of 20 ml. per minute. The resolution of the chromatograph is nowhere near that which is currently obtainable, but our primary interest at the time was the principle involved in the mass spectrometer breakdown of a complex gas chromatographic peak. The results are compared with the known composition in Table II. The average deviation is 0.3 absolute, which is good for a mixture of this complexity. The results are even more remarkable because they were obtained without the use of chromatogram areas but rather with simple maxima from the plotted mass spectra. Since no trends in the deviations are noted over the entire range of the sample, it is reasonable to conclude that this method for calculations is justifiable, especially for chromatograph peaks which do not extend over so long a time as this mixture.

Of more practical interest is the analysis of a C5-C8 California naphtha whose composition (3) was determined cooperatively by 12 laboratories under the sponsorship of the American Petroleum Institute's Committee on Analytical Research. The samples were distilled into a number of cuts, and these were analyzed by infrared and mass spectrometers to obtain detailed information on C<sub>6</sub> and C<sub>7</sub> components. Recently, a gas chromatography method (1) involving three columns with different column packings gave essentially the same results for the saturate fraction of the sample. The analysis was repeated with the mass spectrometer-gas chromatography equipment to gain further confidence in the accuracy of the method and to demonstrate the usefulness of the technique for the determination of C<sub>8</sub> hydrocarbons. However, time and instrumentation involved would not make this an attractive analysis for the determination of the C6 and C7 components by themselves.

Figure 6 shows the gas chromatogram of the sample obtained with the 10foot column. The resolution of the gas chromatograph is again much inferior to what is possible. Along the zero line is listed the position of each component identified. A number of peaks contained more than one component, and the details of the mass spectrometer analyses are given in Figures 7 through 12. In each figure, the shape of the chromatogram peak is outlined heavily; and the corrected ion currents which



Figure 6. Gas chromatogram of  $C_5$  to  $C_8$  hydrocarbons in a California naphtha

are characteristic of each component are plotted also. The legend identifies each component by its characteristic mass number and gives the calculation and composition for each chromatography peak. The first three chromatography peaks were single components, and the mass spectrometer was used only to make identification.

Peak 4, which contains five components, could have been treated as three separate peaks; but the results in Table III show it can be treated as five and, therefore, further demonstrate the validity of the calculation procedure. The gas chromatographic peak at 45 minutes contains the cyclopentane, 2-methylpentane, and 2,3-dimethylbutane. The similarity of pattern between the two paraffins and the low concentration of the 2,3-dimethylbutane made a quantitative breakdown impossible. Therefore, the total concentration for 2,3-dimethylbutane and 2-methylpentane is given. M/e 70, which is used to determine cyclopentane, is plotted on an expanded scale. The peak with a retention time of 49 minutes is 3-methylpentane, which is characterized by m/e 57. Some overlap due to the *n*hexane in the peak at 53 minutes is noted; but the interference at the peak is negligible, and no corrections were made.

Peak 5, shown in Figure 8, is mostly methylcyclopentane, as is evidenced by the large m/e 84. The presence of the C<sub>7</sub> paraffins was determined from m/e 100 and 85. The data for m/e 85 and 100 are again plotted on an expanded scale. The scatter in data is due to the low intensity of the ion cur-



Figure 7. Plot of ion intensities characteristic of compounds in peak 4

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Figure 8. Plot of ion intensities characteristic of compounds in peak 5 rent for m/e 100. The paraffins assigned were 2,2-dimethylpentane, 2,4dimethylpentane, and 2,2,3-trimethylbutane. 2,2,3-Trimethylbutane has not been detected previously and may, by the nature of the data, not be real.

Peak 6, shown in Figure 9, is complicated with a total of nine components determined. This is an excellent example of the potential of the mass spectrometer-gas chromatograph to obtain additional information from a gas chromatograph. In addition to the determination of the major components, one finds relatively minor components which might be overlooked as a shoulder or zero shift on the gas chromatograph.



Figure 9. Plot of intensities characteristic of compounds in peak 6

 
 Table II.
 Quantitative Analysis of a Known Mixture Using Chromatograph and Mass Spectrometer (CEC 103B)

	Per Cent by Weight		
	Measured	Known	Deviation
Peak 1			
3,3-Dimethylpentane Cyclohexane 2,3-Dimethylpentane 3-Methylhexane 3-Ethylpentane 1-cis-3-Dimethylcyclopentane 1-trans-2-Dimethylcyclopentane	$8.1 \\ 2.8 \\ 6.1 \\ 13.2 \\ 5.4 \\ 2.2 \\ 1.9$	$8.3 \\ 2.8 \\ 6.1 \\ 12.4 \\ 5.0 \\ 2.8 \\ 1.7$	$\begin{array}{c} 0.2 \\ 0.0 \\ 0.0 \\ 0.8 \\ 0.4 \\ 0.6 \\ 0.2 \end{array}$
Peak 2			
1-cis-2-Dimethylcyclopentane 1,1,3-Trimethylcyclopentane Methylcyclohexane 2,5-Dimethylhexane Ethylcyclopentane 2,2,3-Trimethylpentane 3,3-Dimethylhexane 1-trans-2-cis-3-Trimethylcyclopentane	3.5 5.1 4.2 4.9 12.2 1.8 8.3 3.0	$3.3 \\ 5.0 \\ 4.1 \\ 12.8 \\ 2.8 \\ 8.3 \\ 2.8 \\ 2.8 \end{cases}$	$\begin{array}{c} 0.2 \\ 0.1 \\ 0.8 \\ 0.6 \\ 1.0 \\ 0.2 \end{array}$
Peak 3			
3-Methyl-3-ethylpentane 1-cis-2-trans-4-Trimethylcyclopentane 1-cis-3-Dimethylcyclohexane n-Octane 1-cis-4-Dimethylcyclohexane	$2.8 \\ 6.6 \\ 3.0 \\ 2.6 \\ 2.8$	2.8 6.6 2.8 2.8 2.8	$\begin{array}{c} 0.0 \\ 0.0 \\ 0.2 \\ 0.2 \\ 0.0 \end{array}$

A number of the components, such as benzene, cyclohexane, 3-methylhexane, 2-methylhexane, and *n*-heptane are determined readily from the mass spectra because of little or no interference to their mass spectra from other components. Considerable difficulty arose in determining *trans*-1,2-dimethylcyclopentane and the combined *cis*- and *trans*-1,3-dimethylcyclopentane. This was accomplished by the use of simultaneous equations using m/e 112 and 97.

Peak 7 (Figure 10) is a mixture of  $C_7$ and  $C_8$  hydrocarbons, the major component being methylcyclohexane. The determination of 1,1,3-trimethylcyclopentane is an example of a practical analysis which is difficult even with the use of more elaborate gas chromatography such as that used by Eggertsen and Groennings (1). To determine 1,1,3-trimethylcyclopentane, they found it necessary to trap a sample for mass spectrometer analysis.

Peaks 8 and 9, shown in Figures 11 and 12, respectively, are primarily  $C_8$  paraffins and cycloparaffins. The exceptions are toluene and 1,1,3,3-tetramethylcyclopentane. Although considerable detailed information on com-



Figure 10. Plot of ion intensities characteristic of compounds in peak 7



Figure 11. Plot of ion intensities characteristic of compounds in peak 8

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C₹ 2n - C

 $\mathbf{C}_{\mathbf{6}}$ 2, 2, 2-

Figure 12. Plot of ion intensities characteristic of compounds in peak 9

position is obtained, it is necessary to lump certain isomers, such as the dimethylcyclohexanes, ethyl methylcyclopentanes, and some of the trimethylcyclopentanes. Further chances for determining all of these isomers individually are not known. However, much improvement is still possible in the instrumentation, which should greatly aid in attaining such a goal.

The percentage of each component in the whole sample was obtained by combining the data obtained above on the individual peak with the areas from the gas chromatograph. The results are given in Table III. It was assumed that the area was proportional to the weight per cent of the sample. The C5-C7 concentrations are in very good agreement with those obtained by the other two methods. It is unfortunate that there are no results for comparison in the C<sub>8</sub> range. There is, however, no reason to believe that they are any less reliable than those obtained for the lighter materials.

The use of gas chromatography columns with higher resolution would result in a far greater number of resolved components than was illustrated in Figure 6. Under such conditions, the mass spectrometer is used mainly for qualitative identification. The rapid progress being made in gas chromatography will open the door to the detailed analysis of even heavier materials than is now possible.

To show the results of a step in this direction, the 10-foot column was replaced with a 30-foot column and used with the mass spectrometer to analyze qualitatively a sample of California straight-run naphtha with 227° C. end point. The resulting chromatogram is given in Figure 13, with the mass spectrometer identification made along the bottom. The compositions of this sample and that discussed earlier are similar, so that a reasonable idea of the improvement in resolution can be obtained from examination of the C7 and C8 components. Beyond the  $C_6$ - $C_8$  portion which has been discussed, it is interesting to

,		Per Cent by Weight				
	Pe					
	MS-gas chromatography <sup>a</sup>	API-COAR <sup>b</sup>	Gas chromatography			
Methylbutane Pentane vclopentane	$0.04 \\ 0.2 \\ 0.3$	$\begin{array}{c} 0.2\\ 0.3 \end{array}$	$\begin{array}{c} 0.2 \\ 0.4 \end{array}$			
2-Dimethylbutane 3-Dimethylbutane { Methylpentane } Methylpentane Hexane ethyloydopentane	0.1 5.3 3.8 7.6 10.8	$0.1 \\ 0.6 \\ 4.4 \\ 3.8 \\ 7.8 \\ 10.4$	$\begin{array}{c} 0.1 \\ 0.7 \\ 4.2 \\ 3.7 \\ 7.5 \\ 10.6 \end{array}$			
-1-1	10.0	10.4	10.0			

3-Methylpentane n-Hexane Methylcyclopentane Cyclohexane Benzene	$3.8 \\ 7.6 \\ 10.8 \\ 5.6 \\ 2.0$	$3.8 \\ 7.8 \\ 10.4 \\ 6.7 \\ 2.6$	3.7 7.5 10.6 6.6
C7 paraffins			
2,2-Dimethylpentane 2,4-Dimethylpentane 3,3-Dimethylpentane 2,3-Trimethylputane 2,3-Dimethylpentane 2-Methylhexane 3-Methylhexane 3-Ethylpentane <i>n</i> -Heptane	0.3 0.3 0.1 0.9 3.7 4.8 7.6	$\begin{array}{c} 0.3 \\ 0.6 \\ 0.2 \\ \cdots \\ 1.6 \\ 2.9 \\ 4.0 \\ 0.4 \\ 7.6 \end{array}$	$\begin{array}{c} 0.3 \\ 0.6 \\ 0.0 \\ \dots \\ 1.3 \\ 2.8 \\ 3.7 \\ \dots \\ 7.0 \end{array}$
$C_7$ cycloparaffins			
1,1-Dimethylcyclopentane 1-cis-3-Dimethylcyclopentane 1-trans-3-Dimethylcyclopentane 1-trans-2-Dimethylcyclopentane 1-cis-2-Dimethylcyclopentane Ethylcyclopentane Methylcyclohexane Toluene	$1.4 \\ 8.0 \\ 5.2 \\ 1.8 \\ 1.1 \\ 12.1 \\ 4.9$	$1.7 \\ 3.2 \\ 2.5 \\ 5.9 \\ 1.3 \\ 0.9 \\ 12.2 \\ 5.6$	$1.2 \\ 3.8 \\ 3.6 \\ 5.8 \\ 0.7 \\ 1.3 \\ 13.4^d$
$C_s$ paraffins			
2,5-Dimethylhexane 2,4-Dimethylhexane 2-Methylheptane 3-Methylheptane 4-Methylheptane <i>n</i> -Octane	$\begin{array}{c} 0.3\\ 0.4\\ 1.5\\ 0.8\\ 0.4 \end{array} \right) '3.8$	4.1	
$C_8$ cycloparaffins			
1,1,3-Trimethylcyclopentane 1-trans-2-cis-4-trimethylcyclo- pentane 1-trans-2-cis-3-trimethylcyclo- pentane 1,1,2-Trimethylcyclopentane Trimethylcyclopentane 1-cis-3-Dimethylcyclohexane and 1,trans-4-dimethylcyclo- hexane 1-trans-2, 1-trans-3- and 1-cis- 4-dimethylcyclohexane Ethylmethylcyclopentane Ethylmethylcyclopentane	$ \begin{array}{c} 1.8\\ 1.4\\ 1.4\\ 0.3\\ 0.3\\ 2.1\\ 0.7\\ 0.2\\ 0.1 \end{array} $ 8.3	7.8	1.1
Total $C_8$ paraffins and cycloparaffins Xylene	$\begin{array}{r}12.1\\0.3\\\overline{99.94}\end{array}$	$\begin{array}{r}11.9\\0.2\\-98.3\end{array}$	$     \begin{array}{r}       11.8 \\       12.9^{a} \\       \overline{91.3^{e}}     \end{array} $
<sup>a</sup> This work.			

• See (1).

<sup>d</sup> To include 1.1% 1,1,3-trimethylcyclopentane.

<sup>e</sup> Saturate portion only.

see the number of peaks that can be identified. Some of the more interesting are bicyclo (3.3.0)-octane octahydropentaline), the large number of resolved  $C_{10}$  bicycloparaffins, the occurrence of a number of C<sub>2</sub> cycloparaffins as individual peaks, indan, methylindan, Tetralin (1,2,3,4-tetrahydronaphthalene), naphthalene, and methylnaphthalenes.

The ability to watch the rise and fall of the individual species in the chromatographic peaks gives a more positive

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# Table III. Analysis of C<sub>5</sub> to C<sub>8</sub> Hydrocarbons in a California Naphtha



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identification of components than is possible by taking the spectrum of a trapped peak of unknown composition.

The foregoing examples also demonstrate the quantitative aspects of the powerful analytical combination of a gas chromatograph closely coupled to a Model 21-103 mass spectrometer. The time involved in collecting the mass spectrometer data is the same as that involved in running a temperatureprogramed chromatograph. The wealth of data obtained currently takes about a week of calculating time to get the most out of them. As this work continues, faster data reduction techniques will undoubtedly be developed.

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# Reduction of Noise in Thermal Conductivity Detectors for Gas Chromatography

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▶ The signal from conventional thermistor thermal conductivity detectors in gas chromatographs frequently shows a noise level on the order of 10 to 20  $\mu$ v., while the electrical noise level inherent in the (8000-ohm) thermistors is usually about 0.3  $\mu$ v. peakto-peak. The higher observed noise results from convective heat transfer from the thermistor, from ambienttemperature changes, and from bridge power-supply variations. Techniques for the elimination of noise from these sources are described. Application of these techniques results in a detector whose noise level (0.3  $\mu$ v.) corresponds to about  $2 \times 10^{-8}$  mole of organic vapor per mole of helium  $(pQ_0 =$ 8.7). A brief description of the electrical measurement circuit is given.

THE YIELD OF product quality of chemical manufacturing processes is frequently critically dependent upon the concentration of trace levels of impurities in the process streams. Because of the broad applicability of gas chromatography to process stream analysis, the development of a high-sensitivity process chromatograph was undertaken. To achieve high sensitivity, it was necessary to identify and eliminate the various sources of noise which commonly exist in thermal conductivity detectors. Much of the noise evident in most gas chromatographs using thermistor detectors can be eliminated by proper instrument design. Application of the techniques described produces an approximate 50-fold improvement in signal-to-noise ratio over thermistor detectors of conventional design. While the major effort in this work was devoted to thermistor detectors, theory and preliminary experiments indicate that the observations made apply at least qualitatively to hot-wire detectors.

The observed sources of noise in a



#### Figure 1. Noise level

Left, measuring circuit Right, thermistor detector

thermistor thermal conductivity detector are: flow variations, shock or vibration, ambient-temperature variations, bridge-current variations, and electrical noise generated within the thermistor.

These subjects are treated in detail below.

# EXPERIMENTAL EQUIPMENT

All experiments were made with a stainless steel detector block 1.5  $\times$  2.5  $\times$  3 inches in which the 0.25-inch diameter bores containing the thermistors were parallel and approximately 0.06 inch apart. The block was 0.06 inch apart. The block was mounted on 0.1-inch diameter stainless steel posts 1 inch long, in an aluminum-walled oven. All walls of the oven were uniformly heated electrically, wall tem-perature being controlled with an electronic proportioning temperature controller. Except where noted otherwise, temperature was controlled at about 40° C. Helium was used as a carrier gas.

All work reported was performed with Fenwal G-112 (8000-ohm) thermistors. [According to the manufacturer, the material used in the fabrication of the 8000-ohm bead thermistor is the most stable of the several formulations available for different thermistor characteristics. Experiments with 2000-, 8000-, and 100,000-ohm beads (all of the same nominal dimensions) showed that both noise level and response to gas composition change were proportional to the square root of thermistor resistance, so that none offered a specific advantage in signal-to-noise ratio.]

The detector output signal was measured with a self-balancing potentiomured with a self-balancing potentiom-eter having a full-scale response time of 0.5 second. The noise level of the measuring equipment, as shown in Figure 1, was about 0.1  $\mu$ v. peak-to-peak. The circuit is described in more data it before detail below.

#### FLOW SENSITIVITY

One of the major sources of noise in a thermal-conductivity detector of the type ordinarily employed in gas chromatography is flow noise. Diffusion and convection-diffusion type cell designs have been employed (3) to minimize this noise, at the expense of 10- to 20fold reduction in speed of response. It was reasoned that the advantage of the diffusion cell might be retained without the limitation of its slow response if the length of the diffusion path could be made very short. To achieve this end, a mounted thermistor was fitted with a surrounding open-ended cylindrical baffle made of per-forated nickel sheet (Pyramid Screen Co. Type 125-T, 0.0035 inch). The clearance between thermistor and screen was about 0.025 inch.

The screened thermistor was mounted in a 0.25-inch diameter cell, the thermistor being centered and the cylindrical screen being parallel to the axis of the cell. Gas flowed at right angles to the

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