Infrared Identification of Fumarates and Maleates

W. LEWIS WALTON and RAYMOND B. HUGHES

Alkyd Products Section, General Electric Co., Schenectady, N. Y.

Seven absorptions in the region of 7.7 to 15 microns are shown to be relatively constant in wave length and intensity for the fumarates. By contrast, the maleic esters have only four peaks at constant wave lengths in the same region. One of these is at about 8.2 microns; it proves to be generally useful in the measurement of maleates in the presence of fumarates.

QUALITATIVE recognition of maleic and fumaric esters has been accomplished by many "wet chemical" procedures, all of them less convenient than the spectroscopic method presented here. A convenient quantitative method, developed first by Kistiakowsky and Smith (*3*), depended upon miscibility of the esters with paraffin oil, the fumarates being miscible at lower temperature than the corresponding maleates. It is applicable only where the esterifying alcohol is known and the pure esters have been prepared and their mixtures studied. Spectroscopic methods have been applied by Gauthier in the study of maleoid-fumaroid isomerization of simple esters (*2*). Here isomeric structures were recognized directly on the esters, but only the methyl and ethyl esters (and inconveniently in the gas phase).

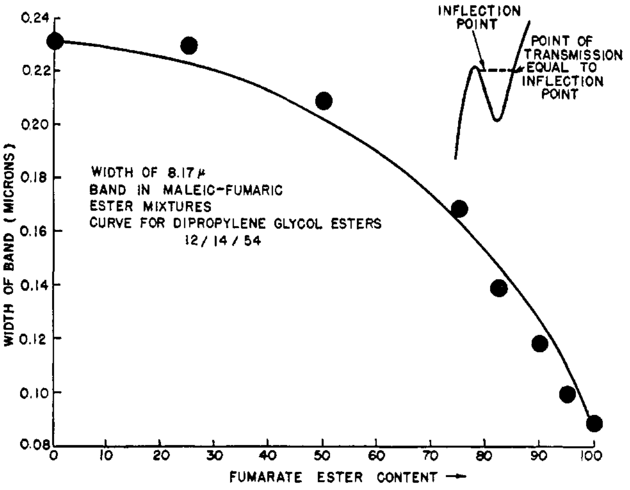

Figure 1

That Gauthier's work does not constitute a satisfactory, direct, spectroscopic method is further indicated by the reports of more recent workers (*4*, *5*), who apparently abandoned direct methods in favor of converting the ester to the ethyl ester (by way of the acid), or to a potassium salt, or to an *N*-benzylamide, followed by spectroscopic examination of these derivatives. These methods suffer from the fact that an organic reaction yield is introduced before the identification step, as well as the possibility that some of the material may be isomerized.

RESULTS

It was found that a series of absorptions at 7.7, 7.9, 8.5, 8.6, 10.2, 12.9, and 15.0 microns is highly constant in wave length in the fumarate esters. (The combination of all these absorptions in an unknown constitutes adequate identification of fumarate.) A less prominent peak is also found at 8.17 microns; this is always weak by comparison to the strong absorption of maleates at about 8.2 microns. The possibility of this can be read from the Colthup (*1*) chart. What is offered here goes farther, in that there have been no exceptions to the generalizations that a strong maleate absorption is always observed in the part of one maleate range which is not overlapped by a range given for fumarates in the Colthup (*1*) chart.

The maleates have a strong absorption in the 11- to 12.5-micron range, which will be useful in measurement of maleate structure where the alcohol or polyol is known and working curves have been plotted. This peak (or group of peaks) is too variable in position to afford much value in qualitative identification of maleates. The peaks which are of value from this standpoint are found at 7.75, 8.00, 8.20, and 8.60 microns. The one at 8.2 to 8.3 microns is first or second strongest of the reliable ones. Because of this strength this peak can be used for measuring the cis structure, even in low concentrations in the presence of much of the fumarate. By measuring the width of the 8.17-micron peak of such mixtures a rough (about ±5%) measure of maleate fumarate percentage can be made. This is a case of measuring the apparent "broadening" of the 8.17-micron absorption of the fumarate by superposition of the unresolved 8.2 to 8.3-micron absorption due to the smaller amount of maleate ester.

This quick and facile measurement is of particular value, as many commercial polyesters prepared from maleic anhydride are actually largely isomerized to the fumarate structure. It has the further practical advantage that in the commercially important mixtures other materials used do not particularly interfere with this measurement. Styrene and vinyl toluene are transparent at this wave length, whereas phthalates (though more highly absorbing because of their ester linkage) do not interfere too severely.

Figure 1 gives a plot of "width of the 8.17-micron peak" *vs.* composition in known mixtures of polyesters of dipropylene glycol maleate and fumarate. Figures 2 and 3 give evidence that such a plot could be developed for mixtures of the esters in general.

The characteristic absorption of fumarates have intensities which are constant to within a factor of about 5. Table I shows the absorbances based on estimated background interpretations for the three absorptions of longest wave length for some of the esters. Widths at half density and product of absorbance and half density widths (relative integrated intensities) are also given. All values are relative to the arbitrarily chosen standard, the 12.9-micron absorption.

From Table I it is clear that intensities can be used as approximate confirmation of the identity of the absorptions for qualitative analytical purposes.

EXPERIMENTAL

Figures 2 and 3 show the spectra of the maleate and fumarate esters, recorded by means of a Perkin-Elmer 21 spectrophotometer. In general, a cell of 0.0268-mm. thickness was used and both a dilution in carbon disulfide (at stated concentration) and the pure ester were run. The exceptions were: The dimethyl fumarate curve was run in a cell of about 0.165-mm. thickness with carbon disulfide in a cell of 0.175-mm. thickness in reference beam (this introduces a small error of negative absorption at about 11.7 microns). The curves of isobutyl, cyclohexyl, and *sec*-butyl

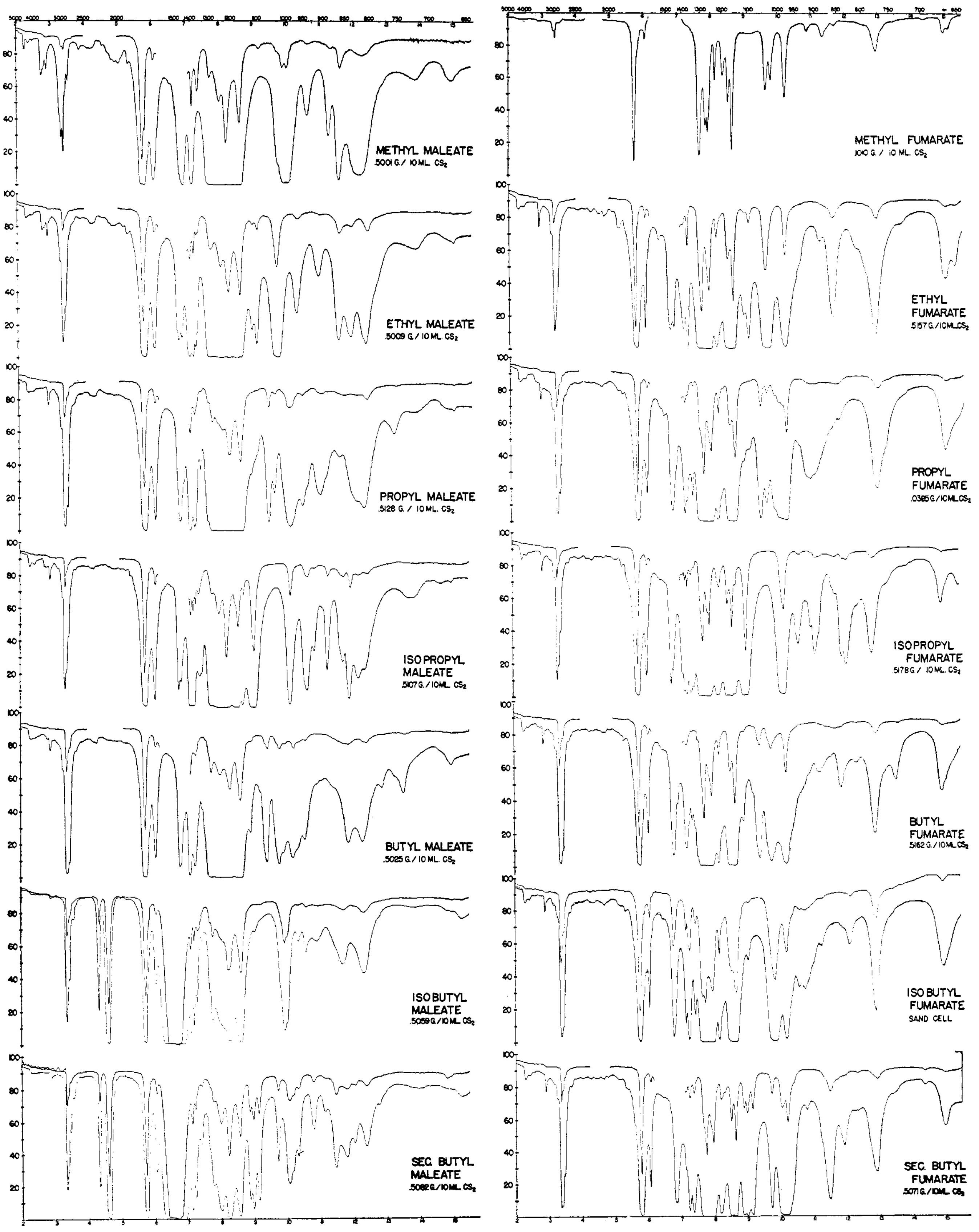
METHYL MALEATE
.5001 G./ 10 ML. CS_2
METHYL FUMARATE
.100 G. / 10 ML. CS_2
ETHYL MALEATE
.5009 G./ 10 ML. CS_2
ETHYL FUMARATE
.5157 G./10ML.CS_2
PROPYL MALEATE
.5128 G. / 10 ML. CS_2
PROPYL FUMARATE
.0385G./10ML.CS_2
ISOPROPYL MALEATE
.5107G./10ML. CS_2
ISOPROPYL FUMARATE
.5178G./ 10ML. CS_2
BUTYL MALEATE
.5025 G./10 ML. CS_2
BUTYL FUMARATE
.5162 G./10ML.CS_2
ISOBUTYL MALEATE
.5059G./10ML. CS_2
ISOBUTYL FUMARATE
SAND CELL
SEC. BUTYL MALEATE
.5082G./10ML. CS_2
SEC. BUTYL FUMARATE
.5071G./10ML. CS_2
100
80
60
40
20
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 950 900 850 800 750 700 650
2 3 4 5 6 7 8 9 10 11 12 13 14 15

Figure 2

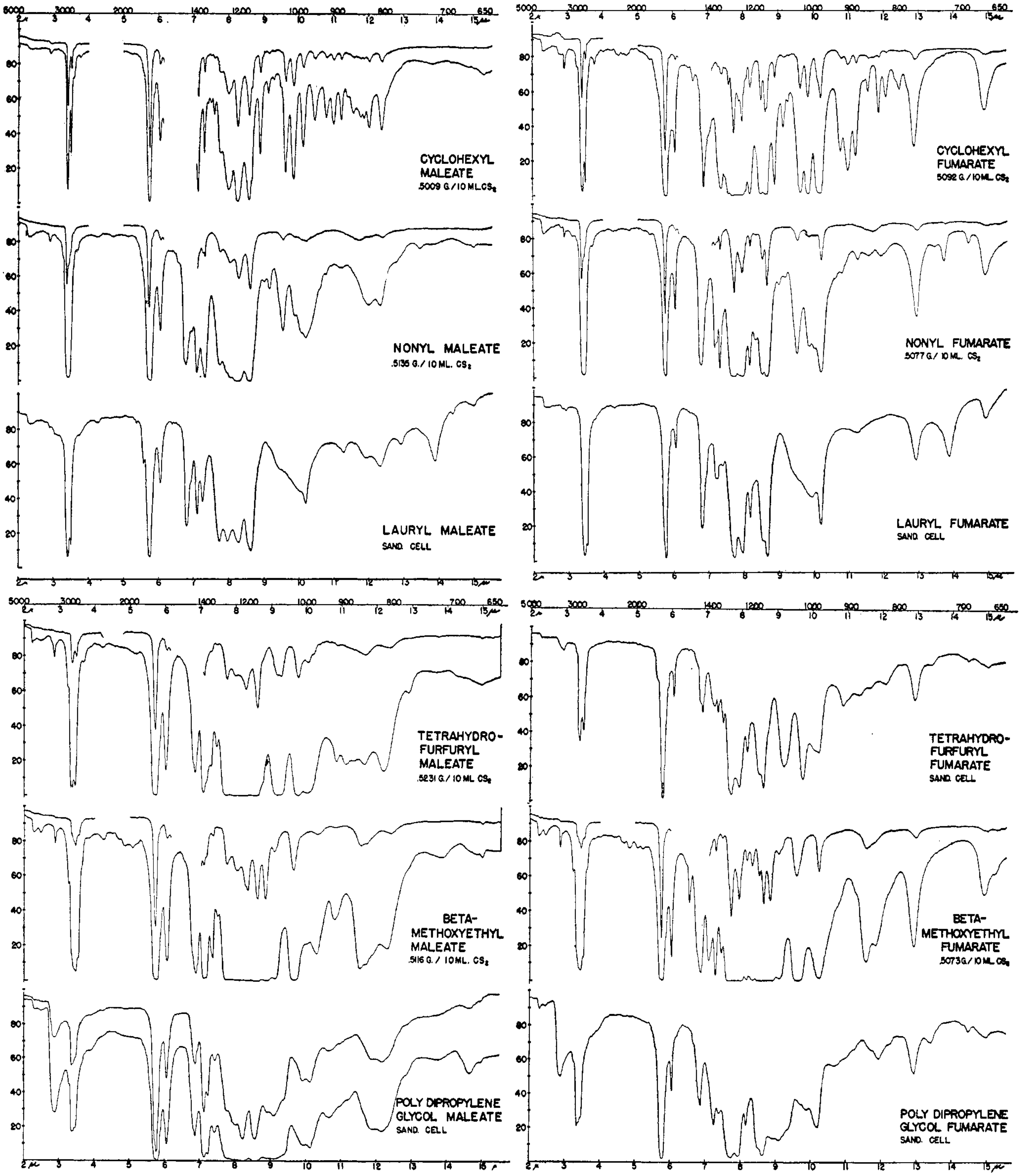
5000
3000
2000
1400
1200
1000
900
800
700
650
2μ
3
4
5
6
7
8
9
10
11
12
13
14
15μ
80
60
40
20
CYCLOHEXYL MALEATE
.5009 G./10 ML. CS₂
CYCLOHEXYL FUMARATE
.5092 G./10 ML. CS₂
NONYL MALEATE
.5135 G./10 ML. CS₂
NONYL FUMARATE
.5077 G./10 ML. CS₂
LAURYL MALEATE
SAND. CELL
LAURYL FUMARATE
SAND. CELL
TETRAHYDRO-FURFURYL MALEATE
.5231 G./10 ML. CS₂
TETRAHYDRO-FURFURYL FUMARATE
SAND. CELL
BETA-METHOXYETHYL MALEATE
.5116 G./10 ML. CS₂
BETA-METHOXYETHYL FUMARATE
.5073 G./10 ML. CS₂
POLY DIPROPYLENE GLYCOL MALEATE
SAND. CELL
POLY DIPROPYLENE GLYCOL FUMARATE
SAND. CELL

Figure 3

Table I. Characteristic Fumarate Absorptions

Ester	Absorbances 10.2	Absorbances 12.9	Absorbances 15.0	Half Density Widths, μ 10.2	Half Density Widths, μ 12.9	Half Density Widths, μ 15.0	Relative Integrated Intensities 10.2	Relative Integrated Intensities 12.9	Relative Integrated Intensities 15.0
Methyl	3.10	1.00	0.51	0.10	0.17	0.13	1.83	1.00	0.39
Ethyl	3.56	1.00	0.28	0.10	0.23	0.33	1.55	1.00	0.40
n-Propyl	5.35	1.00	0.21	0.11	0.32	0.30	1.85	1.00	0.26
Isopropyl	8.15	1.00	0.36	0.16	0.23	0.21	5.66	1.00	0.33
n-Butyl	4.67	1.00	0.55	0.09	0.18	0.41	2.33	1.00	0.125
sec-Butyl	7.4	1.00	0.36	0.12	0.30	0.25	2.96	1.00	0.30
Isobutyl	1.57	1.00	0.45	0.14	0.19	0.43	1.16	1.00	1.02
Cyclohexyl	5.7	1.00	0.54	0.13	0.18	0.30	4.12	1.00	0.90
Nonyl	4.7	1.00	0.40	0.08	0.20	0.30	1.88	1.00	0.60
Lauryl	2.8	1.00	0.45	0.12	0.22	0.30	1.53	1.00	0.61

Table II. Physical Properties of Experimental Materials

Alcohol or Glycol Group	M.P., ° C.	B.P., ° C.	n_D
	Maleates		
Methyl	...	...	1.4390/27
Ethyl	...	...	1.4374/27
Propyl	...	102–3/3	1.4404/26
Isopropyl	...	...	1.4342/27
Butyl	...	...	...
sec-Butyl	...	90/1	1.4391/26
Isobutyl	...	103/2	1.4393/27
Cyclohexyl	86	...	...
Nonyl[a]	...	190/2	1.4518/27
Lauryl	...	...	1.4434/27
Tetrahydrofurfury	...	...	...
β-Methoxyethyl	...	...	...
Dipropylene[b]	...	...	1.4815/27
	Fumarates		
Methyl	103	...	...
Ethyl	1.6	...	1.4380/27
Propyl	...	...	1.4380/27
Isopropyl	2.1	208/760	...
Butyl	−13.5	...	1.4450/27
sec-Butyl	...	...	1.4396/27
Isobutyl	...	...	1.4408/27
Cyclohexyl	35–36	...	1.4891/27[c]
Nonyl[a]	...	...	1.4540/27
Lauryl	32–33	...	1.4508/27[c]
Tetrahydrofurfuryl	...	...	...
β-Methoxyethyl	...	...	1.4541/27
Dipropylene	...	...	1.4842/27

[a] 3,5,5-Trimethylhexyl.
[b] From commercial dipropylene glycol.
[c] On supercooled melt.

maleate were run on the same solution, the less intense in the usual 0.0268-mm. cell and the more intense in the cell of about 0.165 mm. The spectra of lauryl maleate, poly(dipropylene glycol maleate), lauryl fumarate, tetrahydrofurfuryl fumarate, and poly(dipropylene glycol fumarate) were run by the "sandwich" technique (film of unknown thickness between optical salt blocks).

Some of the compounds studied were obtained as commercial materials; others were prepared from maleic anhydride and the appropriate alcohol by azeotropically removing the water liberated when 50% excess of alcohol (over theory) and anhydride were heated with toluenesulfonic acid and benzene. Isomerization of maleates to fumarates was found to be essentially quantitative on heating at 200° C. for 1 hour in the presence of a trace of iodine. Sealed tubes were used. After the tube was opened, the mixture was heated to about 180° C. with sparging with nitrogen to remove the iodine and yield colorless fumarate product in essentially quantitative yield. In general, purification procedures applied to these products resulted in negligible changes in their infrared spectra.

In Table II are given data on the materials used for the spectra in Figures 2 and 3.

The presence of some minor impurities is evident from the spectra of lauryl maleate (in which traces of maleic anhydride and lauryl fumarate are evident) and tetrahydrofurfuryl maleate (in which a trace of tetrahydrofurfuryl fumarate is evident).

In the preparation of poly(dipropylene glycol maleate), toluene was employed as azeotroping agent and the temperature in the esterifying mixture was maintained below 125° C. (Thiophene-containing benzene has been avoided in these experiments because of the known catalytic effect of sulfur compounds on the isomerization of maleates.)

LITERATURE CITED

(1) Colthup, N. B., *J. Opt. Soc. Amer.* 40, 397 (1950).
(2) Gauthier, G., *Compt. rend.* 233, 617–19 (1951); *Bull. soc. chim. France* 1951, 919–25.
(3) Kistiakowsky, G. B., Smith, W. R., *J. Am. Chem. Soc.* 56, 638 (1934).
(4) Shay, J. F., Skilling, S., Stafford, R. W., ANAL. CHEM. 26, 656 (1954).
(5) Stafford, R. W., Francel, R. J., Shay, J. F., *Ibid.*, 21, 1454–7 (1949).

RECEIVED for review December 12, 1955. Accepted May 3, 1956.

Systematic Approaches to Continuous Infrared Analyzer Sensitization

W. J. BAKER
Monsanto Chemical Co., Texas City, Tex.

Several years' experience with sensitization of negative, nondispersive-type infrared analyzers for the continuous analysis of field sample streams has led to the formulation of a system by which a satisfactorily compensated cell filling may be readily determined. The basis of the system lies in the logarithmic relationship between the concentration of a gas in a compensator cell and the analyzer response to that gas in the sample cell. The problem is complicated by component inconsistencies of the analyzers and by pressure-broadening effects. Pressure-broadening effects appear to be a severe limitation to the application of infrared analyzers to many sample streams.

In recent years there has been an increased demand by industry for instruments that can continuously determine a specific component of a sample stream at the point of operation. The infrared analyzers are at present the major analytical instrument for process analysis. This is principally because they are more versatile than analyzers based on such techniques as thermal conductivity, density, and pressure. There is, however, the problem of sensitizing the infrared analyzer in such manner that it is sensitive only to a specific gas in a background of other similar infrared-absorbing gases. Several methods of obtaining such a sensitization have been developed for the negative, nondispersive (*2*) and the selective detector types of analyzers (*5*). A method which has proved successful for sensitizing the negative, non-