

July 24, 1956

E. C. MILLER

2,756,342

ANALYZER

Filed Feb. 25, 1953

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Fig. 1.

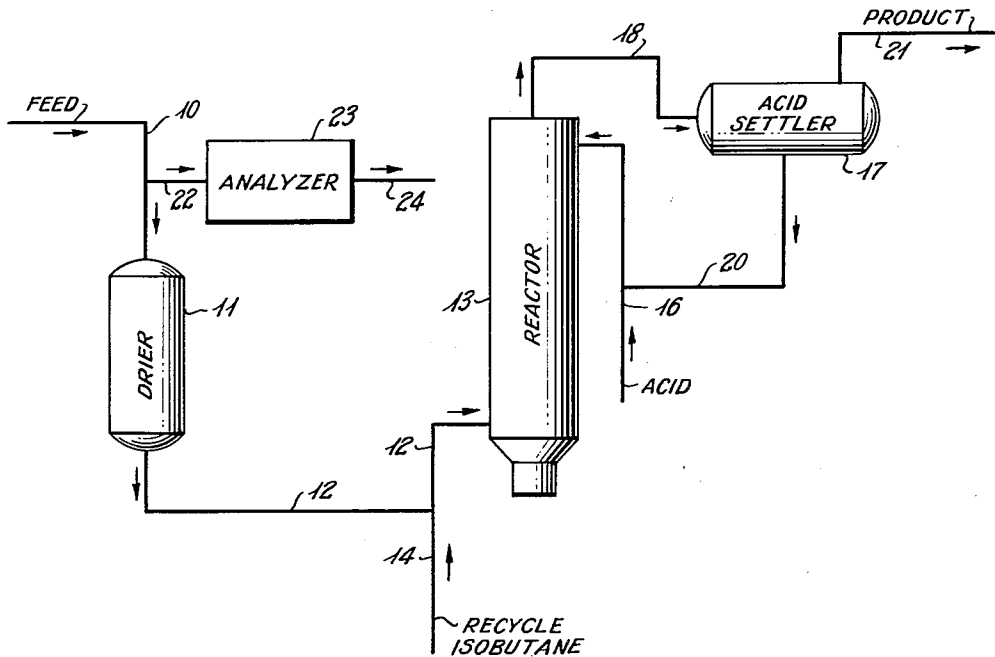
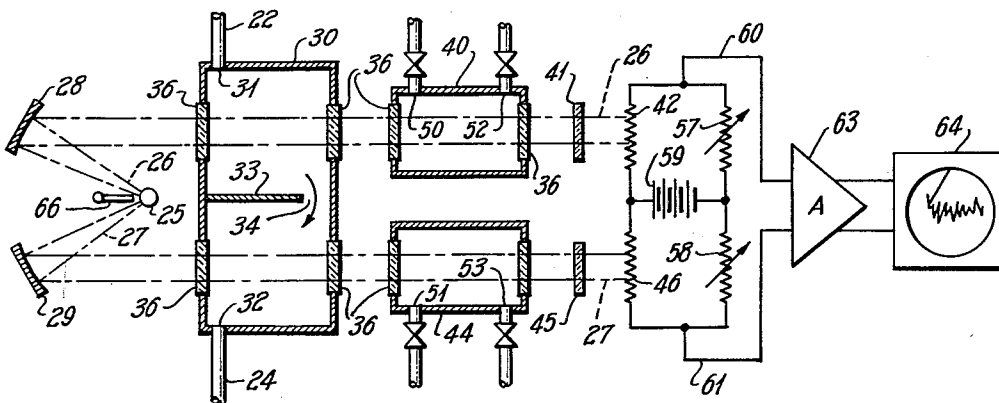


Fig. 2.



INVENTOR.

E. C. Miller

BY

Hudson & Young
ATTORNEYS

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Fig. 3.

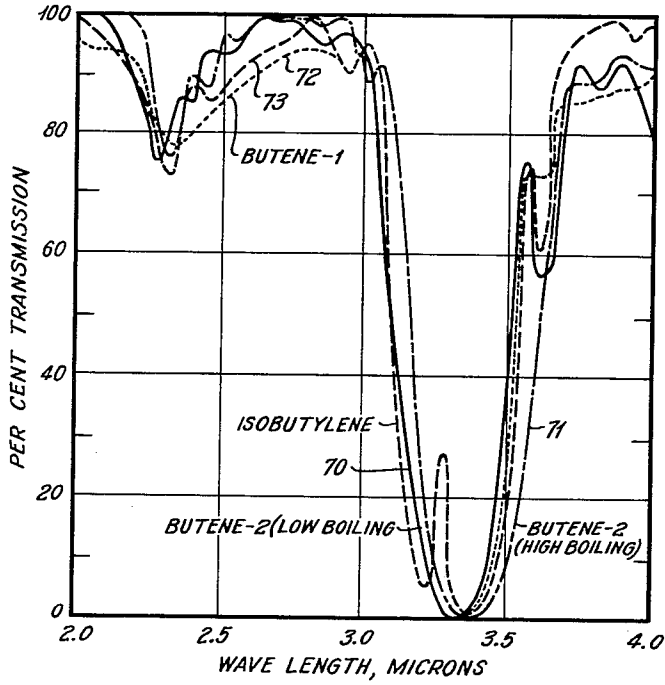
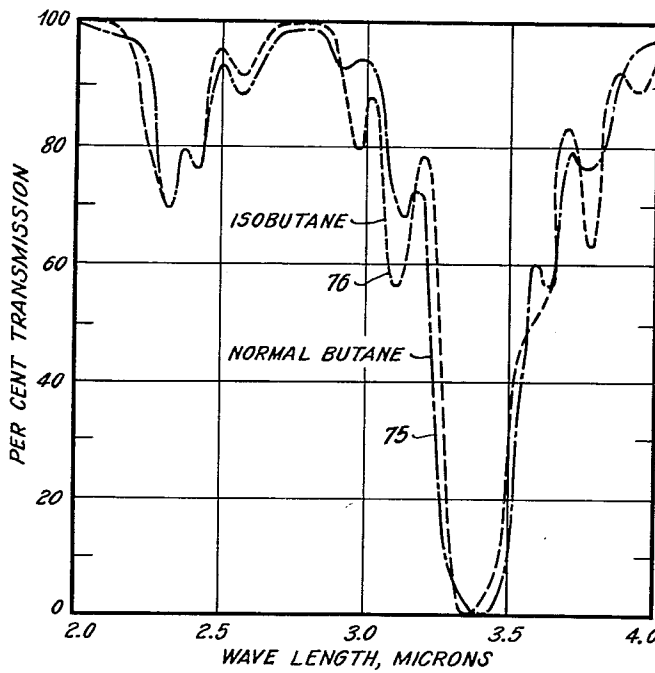


Fig. 4.



INVENTOR.
E.C. Miller
BY
Hudson & Young
ATTORNEYS

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Fig. 5.

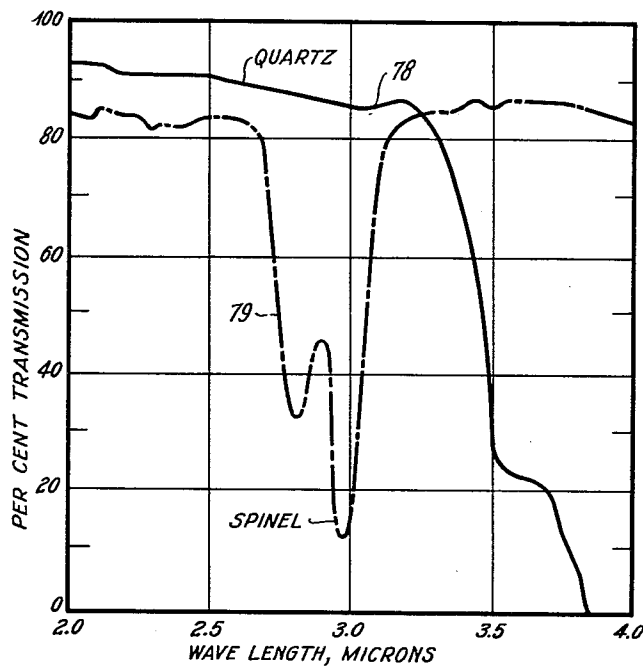


Fig. 6.

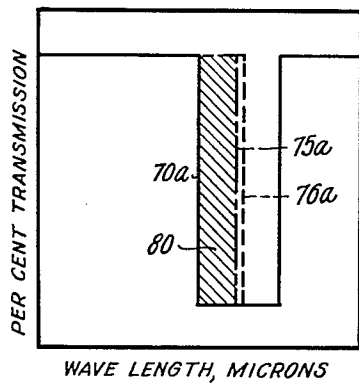
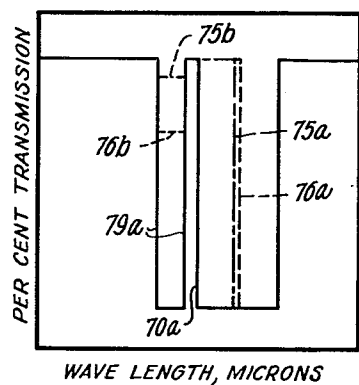


Fig. 7.



INVENTOR.

BY *E. C. Miller*
Hudson & Young
ATTORNEYS

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2,756,342

ANALYZER

Elmer C. Miller, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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18 Claims. (Cl. 250—43.5)

This invention relates to a method of and apparatus for detecting the presence of olefins in a mixture containing olefins and paraffins. In one specific aspect it relates to means for detecting olefins in the presence of paraffins having four carbon atoms per molecule. In another aspect it relates to a filter system for use in a double beam infrared analyzer.

As is well known to those skilled in the art the alkylation process for manufacturing motor fuels is based on a chemical reaction involving the direct union of the traditionally inert paraffins with unsaturated hydrocarbons. A feed stream containing, for example, isoparaffins and olefins can be converted in the presence of the catalyst anhydrous hydrofluoric acid into a stream of isoparaffins having a larger number of carbon atoms per molecule than did the original isoparaffins. This process is hereinafter referred to as HF alkylation. One of the most desirable feed stocks for such a reaction is a mixture of isobutane and butylenes, and such a feed stock can be obtained as a by-product from a catalytic cracking unit employed in petroleum refining operations to break down the heavier hydrocarbon molecules contained in crude oil. However, such a product stream often varies in composition through a rather wide range and as such it is necessary to have an indication of the stream composition in order that the olefin-paraffin ratio supplied to the alkylation reactor can be maintained at a desired value through adjustment of a suitable process variable.

The present invention is directed primarily toward providing an instrument capable of analyzing continuously and automatically a sample stream to determine the presence and total concentration of olefins. This instrument is based upon the property of certain heteratomic molecules to absorb infrared radiation of wave lengths characteristic of the particular molecules. The intensities of radiation of two infrared beams emitted from a common source are compared by means of temperature-sensitive resistance elements forming adjacent arms of an electrical bridge circuit. Both of these beams pass through a common sample cell containing the material under analysis and also through suitable filters to limit the total radiation transmitted to a rather narrow band of selected wave lengths. One of the beams is directed further through a cell containing a paraffin having four carbon atoms per molecule and the other beam is directed through both a cell containing an olefin and a plate of spinel. The purpose of the spinel filter is to compensate for any changes in the relative concentration of the different paraffins which may be present in the sample stream such that a comparison of the intensities of the two resulting beams provides a direct indication of the concentration of olefins present in the sample cell.

Accordingly, it is an object of this invention to provide a method of detecting the presence of olefins in a gaseous stream.

Another object is to provide apparatus for analyzing continuously a gaseous sample stream containing olefins.

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A further object is to provide an optical filter system for an infrared analyzer adapted to detect olefins.

Various other objects, advantages and features of this invention should become apparent from the following detailed description taken in conjunction with the accompanying drawing in which:

Figure 1 is a schematic representation of an HF alkylation unit and the analyzer of this invention associated therewith;

Figure 2 is a schematic view of the analyzer including the optical filter system; and

Figures 3, 4, 5, 6 and 7 illustrate infrared absorption characteristics of selected materials.

Referring now to the drawing in detail and to Figure 1 in particular there is shown a simplified flow diagram of an HF alkylation unit. The feed stream to the process, which can be obtained from a catalytic cracking unit, not shown, is passed through a line 10 to a drier unit 11 wherein it is dehydrated by a suitable drying agent such as bauxite or alumina. The feed stream then passes through a line 12 into a reactor 13. A line 14 communicates with line 12 to add thereto a quantity of isobutane which is obtained as a recycle product from the purification system, not shown, connected to the output of the reactor unit. Hydrofluoric acid also is passed into reactor 13 through a line 16. From the reactor 13 the alkylate-acid stream is transferred to an acid settling tank 17 through a line 18. The acid contained in the stream passing through line 18 settles to the bottom of tank 17 wherefrom it is recycled through a line 20 back into reactor 13. The remaining alkylate is removed from settler 17 through a product line 21 for further treating.

As previously mentioned it is important that the ratio of the paraffins to olefins in the feed stream entering reactor 13 be maintained at a preselected value. This ratio normally can be maintained at the desired value by regulating the addition of isobutane through line 14. However, this requires a knowledge of the composition of the feed stream entering the system through line 10. To this end it has been proposed to analyze continuously the concentration of olefins present in line 10. This is accomplished by removing a sample stream from line 10 through a conduit 22 and passing the same to an analyzer 23. This sample stream subsequently is vented from analyzer 23 through a line 24.

As illustrated in greater detail in Figure 2 analyzer 23 includes a source of infrared radiation 25 which can be a heated Nichrome wire from which two beams of radiation 26 and 27 are directed against a pair of respective front surface concave reflectors 28 and 29. The two radiation beams are directed by these reflectors through a common sample cell 30 having an inlet opening 31 connected to line 22 and having an outlet opening 32 which is connected to vent line 24. Cell 30 preferably is divided by a partition 33 having an opening 34 positioned at the opposite end of the cell from the inlet and outlet openings. This assures continuous circulation of the sample stream throughout both sides of the cell. Cell 30 is provided with thin quartz windows 36 which are transparent to infrared radiation at wave lengths corresponding to the absorption bands of interest of the olefins under analysis.

Radiation beam 26 further is directed through a filter cell 40, through a solid filter 41 and then impinges upon a first temperature-sensitive electrical resistance element 42. Radiation beam 27, on the other hand, passes through a filter cell 44, a solid filter 45 and then impinges upon a second temperature-sensitive electrical resistance element 46. Cells 40 and 44, which are of like construction, are adapted to be filled with reference fluids. These two cells are provided with respective inlet openings 50 and 51 and with respective outlet openings 52 and 53 and

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with quartz window 36. Solid filter 41 is formed of spinel ($\text{MgO} \cdot 3.5\text{Al}_2\text{O}_3$) and solid filter 45 is formed either of quartz (SiO_2) or white sapphire (Al_2O_3). Elements 42 and 46 are thermistors, such as bolometers, for example, having a high temperature coefficient of thermal resistivity whereby radiation impinging thereon produces changes in the electrical resistivities thereof. With the apparatus arranged as described differences in the resistance of the two elements are representative of the concentration of olefins present in the sample stream circulated through cell 30.

Elements 42 and 46 are connected in a Wheatstone bridge circuit with balancing variable resistors 57 and 58. A source of voltage 59 is connected across first opposite terminals of the bridge circuit and output leads 60 and 61 are connected to the second pair of opposite terminals of the bridge circuit. Leads 60 and 61 are connected to the input terminals of an amplifier 63, the output signal of which is applied to a recorder 64. In operation, the bridge circuit is balanced initially with a known concentration of olefins present in the sample stream. This balance is obtained by adjustment of resistors 57 and 58 and/or by rotation of a trimmer 66 which comprises a small opaque vane rotatable into either of the radiation beams 26 or 27 to reduce the total intensity thereof. As will be more fully explained hereinafter, any change in concentration of olefins in the same stream results in unbalance of the bridge circuit due to the change in total radiation absorbed by these olefins. The potential difference between leads 60 and 61 representing this unbalance is amplified and recorded.

As an example of a preferred embodiment of this invention satisfactory results were obtained with an instrument in which: cells 30, 40 and 44 each were approximately 2 inches in length; quartz windows 36 each were approximately 2.0 millimeters thick; spinel filter 41 was approximately .16 inch thick; and quartz filter 45 was approximately .193 inch thick. Cell 40 was filled with butene-2 (low boiling) and cell 44 was filled with normal butane. A typical sample stream under analysis had the following composition:

Component:	Liquid volume per cent
Propylene -----	15.7
Propane -----	13.8
Total olefins having four carbon atoms per molecule -----	23.5
Isobutane -----	29.2
Normal butane -----	17.8
	100.0

The analyzer provided a measurement of the total concentration of olefins, that is, the sum of the propylene and the olefins having four carbon atoms per molecule.

The operation of the filter system of this invention which enables the analyzer to detect olefins in the presence of paraffins having four carbon atoms per molecule can best be explained in conjunction with the graphs of Figures 3, 4, 5, 6 and 7. The curves 70, 71, 72 and 73 of Figure 3 represent the percent transmission of infrared radiation of various wave lengths passed through a sample cell containing butene-2 (low boiling), butene-2 (high boiling), butene-1 and isobutylene, respectively. The curves 75 and 76 of Figure 4 represent the per cent transmission of infrared radiation of various wavelengths passed through a sample cell containing normal butane and isobutane, respectively. The curves 78 and 79 of Figure 5 represent the percent transmission of infrared radiation of various wave lengths passed through a plate of quartz 8.0 millimeters thick and through a plate of spinel .193 inch thick, respectively. From an inspection of these curves it can be seen that the four olefins, namely butene-2 (low boiling), butene-2 (high boiling), butene-1 and isobutylene have approximately the same absorption characteristics, particularly in the region between approxi-

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mately 3.0 and 3.5 microns. The paraffins, namely normal butane and isobutane, have absorption characteristics which approximate one another to a certain extent, and each has an absorption band in the region between approximately 3.2 and 3.5 microns. The 8.0 millimeter thick plate of quartz absorbs practically all radiation of wave lengths longer than approximately 3.5 microns. Spinel has a distinct absorption band at approximately 2.9 microns.

As previously mentioned cell 40 is filled with butene-2 (low boiling) and cell 44 is filled with normal butane. Thus, with sample cell 30 empty and with filters 41 and 45 removed, the quantity of radiation impinging upon element 42 is represented by the area under curve 70 in Figure 3 (this curve being extended to zero wave length). In order to simplify the explanation of the invention this area is represented in a schematic manner in Figure 6 as the area under curve 70a. The quantity of radiation impinging upon element 46 is represented by the area under curve 75 of Figure 4 (also extended to zero wave length). This latter area is represented schematically in Figure 6 as the area under curve 75a (curve 75a is superimposed on curve 70a except in the region between approximately 3.0 to 3.2 microns). Thus, the difference in intensity of the two beams impinging upon respective elements 42 and 46 is represented by the shaded area 80 illustrated in Figure 6. If the sample stream passing through cell 30 contains any of the four olefins herein mentioned the radiation impinging upon element 46 is reduced in intensity in accordance with the concentration of the olefins present. This is evident because a portion of the radiation of beam 27 as represented by area 80 in Figure 6 is reduced by the amount of radiation absorbed by the olefins at these wave lengths. Beam 26, however, is unaffected because the radiation represented by area 80 already is absorbed therefrom by the butene-2 (low boiling) contained in sample cell 40. Thus, the variance in intensity of the two beams impinging upon elements 42 and 46 is representative of the quantity of olefins circulated through sample cell 30. It should readily be apparent that sample cell 40 can be filled with any one of the described olefins or by a mixture of one or more of these olefins in place of butene-2 (low boiling). It should likewise be apparent that cell 44 can be filled with isobutane or a mixture of isobutane and normal butane.

The filter system thus far described provides accurate results in the detection of olefins in a sample stream containing paraffins having four carbon atoms per molecule as long as the relative concentrations of normal butane and isobutylene individually to the total concentration of the paraffins does not vary. However, these relative concentrations often do vary. From an inspection of Figure 4 it can be seen that the absorption band of normal butane in the region of approximately 3.2 to 3.3 microns occurs at a slightly lower wave length than does the corresponding absorption band of isobutane. Thus, should the sample stream circulated through cell 30 tend to increase in concentration of isobutane and decrease in concentration of normal butane, even though the total paraffin concentration does not vary, the total radiation transmitted by beam 27 to element 46 tends to increase somewhat. This is true because the isobutane absorbs less radiation of wave lengths in the region of approximately 3.2 to 3.3 microns than does normal butane. It should be noted that the total radiation absorbed from beam 27 is determined by the combined absorption in cells 30 and 44, and that cell 44 is not of sufficient length to absorb all possible radiation of wave lengths corresponding to the absorption bands of normal butane. In the schematic representation of Figure 6 curve 75a thus represents the total absorption with cell 30 containing no isobutane whereas curve 76a represents the absorption with cell 30 containing no normal butane. Accordingly, with the apparatus thus far described it is impossible to determine if small changes in the total resulting radiation of beams 26 and 27 is

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due to changes in olefin concentration or difference in the relative concentration of normal butane and isobutane.

To overcome this difficulty spinel filter 41 is disposed in beam 26. As illustrated in Figure 5 spinel absorbs radiation in the region of approximately 2.7 to 3.1 microns, particularly at approximately 2.9 microns. This filter reduces the total transmitted radiation of beam 26 by the amount absorbed by filter 40, which condition is represented schematically in Figure 7 by the absorption region of curve 79a. From a closer inspection of curves 75 and 76 in Figure 4 it can be seen that in the region of approximately 2.9 microns isobutane has a considerably stronger absorption band than does normal butane. Thus, as the concentration of isobutane increases and the concentration of normal butane decreases in cell 30 the total transmitted radiation in beam 27 tends to decrease. This is exactly opposite the effect in the region of approximately 3.2 to 3.3 microns, and the two effects cancel one another whereby variance in the relative concentration of isobutane and butane in the total paraffin concentration does not affect the calibration of the analyzer with respect to the detection of olefins having four carbon atoms per molecule. This change in concentration in the region of approximately 2.9 microns is represented by curves 75b and 76b, which curves balance the change between curves 75a and 76a, respectively. That is, as the relative concentration of isobutane in sample cell 30 increases the radiation in beam 26 at wave lengths between approximately 3.2 and 3.3 microns is increased, and the radiation of wave lengths at approximately 2.9 microns is decreased. The two effects are of approximately equal magnitude and tend to balance one another. Exactly the converse is true if the relative concentration of normal butane increases in cell 30. The purpose of quartz or white sapphire filter 45 is to reduce the total radiation of beam 27 in order to aid in securing an initial balance, and such filter obviously is not essential to satisfactory operation. Filter 45 can be a plate of quartz approximately .193 inch thick or a plate of white sapphire .060 inch thick, for example, when employed with the apparatus previously described.

As employed herein, the term "olefin" refers to any open-chain hydrocarbon containing one or more double bonds. The analysis system of this invention provides an indication of such total olefin concentration in the presence of paraffins having four carbon atoms per molecule. However, the olefin concentration can be detected even though the sample stream contains paraffins having more or less than four carbon atoms per molecule. The sample cell and filter cells are filled with components in the gaseous state under the conditions of analysis. Butene-2 (low boiling) refers to the cis isomer of butene-2 and butene-2 (high boiling) refers to the trans isomer.

From the foregoing description of a preferred embodiment of this invention it should be apparent that there has been provided a filter arrangement for use with a double beam infrared analyzer whereby olefins having four carbon atoms per molecule can be detected in the presence of paraffins having four carbon atoms per molecule. While this analyzer has been described in conjunction with a simple Wheatstone bridge detecting circuit, it should be apparent that various other detecting systems can be employed to compare the intensities of radiation of two beams. One such system comprising a self-balancing bridge circuit with automatic standardization is disclosed in U. S. Patent 2,579,825. A second alternative is to employ a pair of sensitive thermocouples as the detecting elements. It further should be apparent that the output electrical signal can be employed to control any desired process variable so as to effect automatic control. Thus, while the invention has been disclosed in conjunction with present preferred embodiments thereof, it should be apparent that the invention obviously is not limited thereto.

What is claimed is:

1. The method of detecting olefins in the presence of

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paraffins having four carbon atoms per molecule which comprises establishing two beams of infrared radiation of predetermined intensity, directing both of said beams through a gaseous sample of material under analysis, further directing one of said beams through a predetermined quantity of a gaseous paraffin, further directing the other of said beams through a gaseous olefin and through a filter adapted to absorb radiation at wave lengths of approximately 2.9 microns, and measuring the resulting intensities of the two beams whereby changes in the ratio of intensities are indicative of changes in concentration of the olefins present in the material under analysis.

2. The method in accordance with claim 1 wherein said predetermined quantity of paraffin is a paraffin having four carbon atoms per molecule and said predetermined quantity of olefin is an olefin having four carbon atoms per molecule.

3. The method in accordance with claim 1 wherein said second beam of radiation is directed through a plate of spinel.

4. The method in accordance with claim 3 wherein said predetermined quantity of paraffin is normal butane and wherein said predetermined quantity of olefin is butene-2 (low boiling).

5. The method in accordance with claim 3 which further comprises directing both of said beams through filter means adapted to absorb radiation of wave lengths longer than approximately 3.5 microns.

6. The method in accordance with claim 5 wherein said filter means is formed of quartz.

7. The method of detecting olefins in the presence of paraffins which comprises establishing two beams of infrared radiation of predetermined intensity, directing both of said beams through a gaseous sample of material under analysis, further directing one of said beams through a predetermined quantity of a gaseous paraffin, further directing the other of said beams through a gaseous olefin, and measuring the resulting intensities of the two beams whereby changes in the ratio of intensities are indicative of changes in concentration of the olefins present in the material under analysis.

8. An analyzer adapted to detect olefins in the presence of paraffins having four carbon atoms per molecule comprising a sample cell adapted to contain a gaseous sample of material under analysis, a source of infrared radiation, means to direct two beams of radiation from said source through said sample cell, a first filter cell containing a gaseous paraffin having four carbon atoms per molecule disposed in one of said beams, a second filter cell containing a gaseous olefin disposed in the other of said beams, a spinel filter disposed in said other beam, and radiation detecting means to measure the resulting intensities of said beams whereby changes in the ratio of intensities are indicative of changes in concentration of olefins present in the sample cell.

9. The combination in accordance with claim 8 wherein said first filter cell contains a paraffin having four carbon atoms per molecule and wherein said second filter cell contains an olefin having four carbon atoms per molecule.

10. The combination in accordance with claim 8 wherein said first filter cell contains normal butane and wherein said second filter cell contains butene-2 (low boiling).

11. The combination in accordance with claim 8 wherein each of said three mentioned cells is provided with quartz windows through which the respective radiation beams are directed.

12. The combination in accordance with claim 8 further comprising a white sapphire filter disposed in the first of said beams of radiation.

13. An analyzer adapted to detect olefins in the presence of paraffins having four carbon atoms per molecule comprising a sample cell adapted to contain a gaseous sample of material under analysis, a source of infrared radiation, means to direct two beams of radiation from

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said source through said sample cell, a filter cell containing a gaseous paraffin having four carbon atoms per molecule disposed in one of said beams, a filter cell containing an olefin disposed in the other of said beams, a spinel filter disposed in the other of said beams, a first temperature sensitive resistance element disposed in the path of the first of said beams of radiation, a second temperature sensitive resistance element disposed in the path of the second of said beams of radiation, and a bridge circuit including said first and second resistance elements to measure the relative intensities of the two beams of radiation impinging upon said resistance elements.

14. The combination in accordance with claim 13 further comprising a filter of a material selected from the group consisting of quartz and white sapphire disposed in the first of said beams.

15. The combination in accordance with claim 13 wherein each of said three cells is approximately two inches long, wherein each of said cells is provided with quartz windows each approximately two millimeters thick, and wherein said spinel filter is approximately .193 inch thick.

16. The combination in accordance with claim 15 further comprising a plate of quartz approximately two millimeters thick disposed in the first of said beams.

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17. The combination in accordance with claim 15 further comprising a plate of white sapphire approximately .060 inch thick disposed in the first of said beams.

18. An analyzer adapted to detect olefins in the presence of paraffins comprising a sample cell adapted to contain a gaseous sample of material under analysis, a source of infrared radiation, means to direct two beams of radiation from said source through said sample cell, a first filter cell containing a gaseous paraffin disposed in one of said beams, a second filter cell containing a gaseous olefin disposed in the other of said beams, and radiation detecting means to measure the resulting intensities of said beams whereby changes in the ratio of intensities are indicative of changes in concentration of olefins present in the sample cell.

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