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METHOD OF CHARACTERIZING HYDROCARBON MIXTURES

Filed Aug. 10, 1949

2 Sheets-Sheet 1

INFRARED ABSORPTION SPECTRA OF CRUDE OILS

Cell thickness - .27mm.

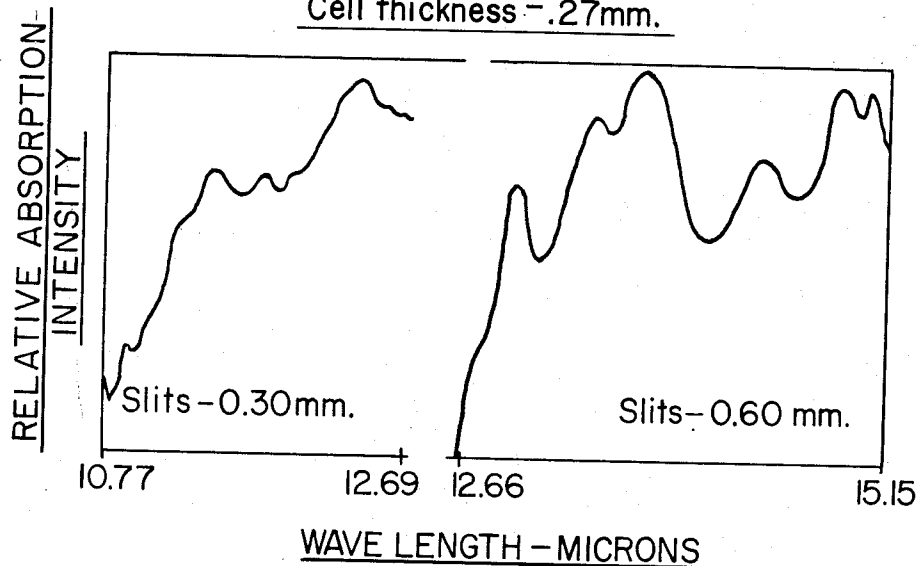


FIG.-3

INFRARED ABSORPTION SPECTRA OF CRUDE OILS

Cell thickness - .27mm.

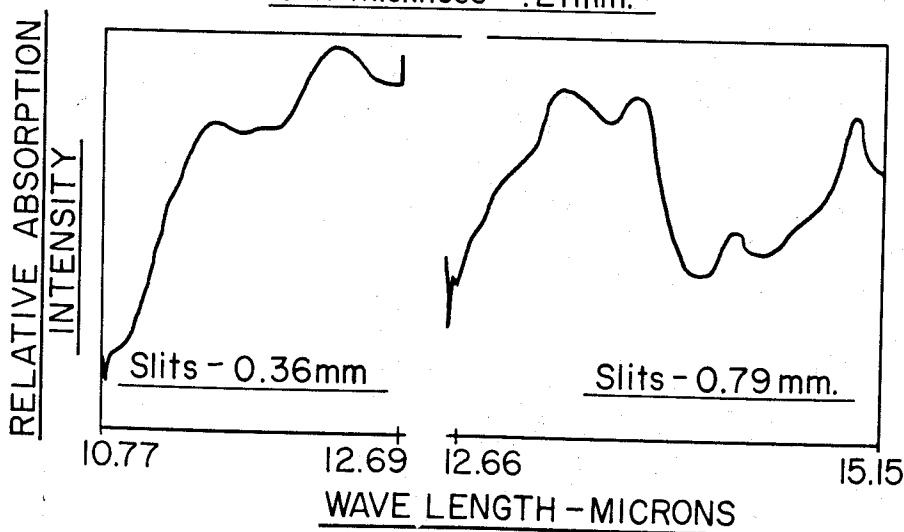


FIG.-4

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2 Sheets-Sheet 2

NATURALLY OCCURRING TAR

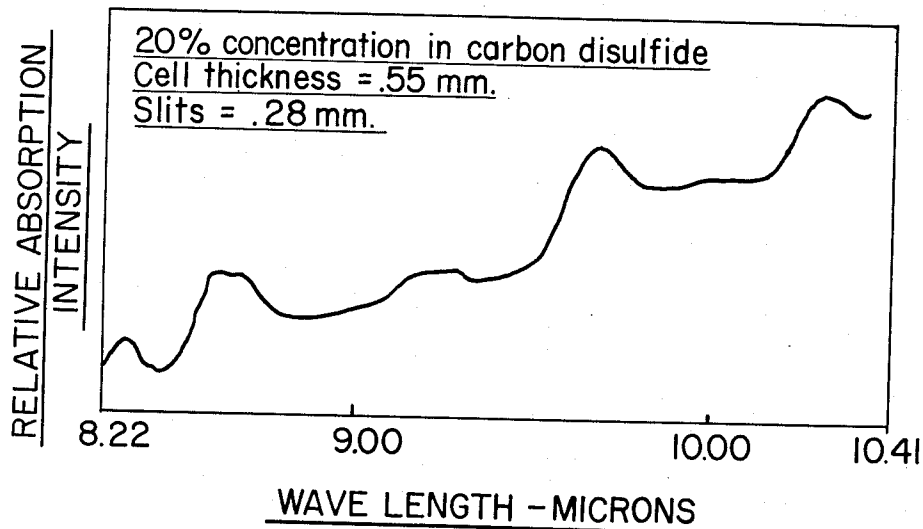


FIG. - 2

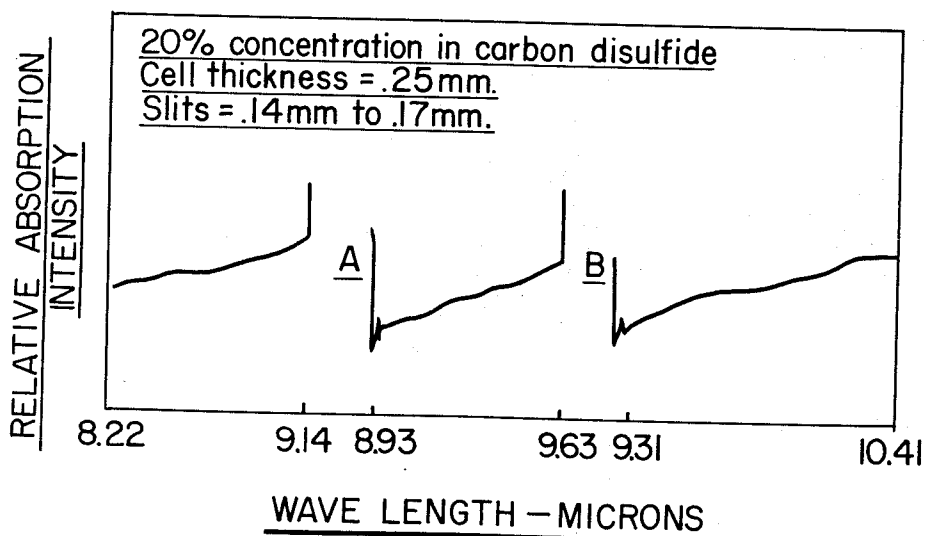


FIG. - 1

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METHOD OF CHARACTERIZING
HYDROCARBON MIXTURES

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3 Claims. (Cl. 250—43.5)

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This invention relates to an improved method of infrared spectrometry by which samples are analyzed according to their infrared absorption characteristics. The invention is directed to a new method of infrared spectrometry generally advantageous in providing analytical results of improved sensitivity. The invention is of particular application in the characterization of hydrocarbon mixtures of a similar nature. For example, the invention is of particular application in distinguishing between crude oils of approximately the same composition.

While the general application of the present invention is relatively broad, the objectives and advantages of this invention may be well understood by referring to a particular application such as the characterization of hydrocarbon mixtures. As an example of this particular application reference may be made to the problem of distinguishing crude oils of similar characteristics. Thus in the production of crude oils from oil wells, it is frequently desirable to have some means of readily characterizing the oil produced from a given well. This is of application for instance in order to establish from what oil pool a particular well may be producing. By obtaining this information, it is often possible to plan strategically the location of other wells which should be drilled to tap the same oil pool. Again, by having a means of characterizing crude oils, it is possible to determine which producing stratum should be utilized in order to obtain a crude oil of desired characteristics. As a further example, in the refining of crude oils, by having a means of readily checking the similarity or dissimilarity of two crude oils, it is frequently possible to conduct more advantageously the refining operations. Similarly, the invention has application to the characterization of lubricating oils or asphalts, providing a convenient means to establish the chemical similarity between closely related lubricating oils or asphalts. It is, therefore, to be understood that this invention is of broad application to the characterization of any hydrocarbon mixture. Consequently, it may be stated that the principal objective of this invention is to provide a means for readily and effectively characterizing a hydrocarbon mixture.

To understand the method of this invention, it is desirable to review the basic method involved in infrared spectrometry. The basic principle upon which infrared spectrometry depends is that different chemical compositions generally possess varying degrees of opacity to

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infrared radiation. Furthermore, different substances will adsorb different bands of energy within the infrared spectrum. Consequently, it is possible to identify such substances by determining their characteristic infrared absorption characteristics. To carry this method out, suitable apparatus is commercially available to determine the infrared absorption characteristics of substances to be tested. Such apparatus comprises a suitable source of infrared light energy arranged to irradiate a sample cell having infrared transparent faces within which the sample may be contained. Infrared light energy emitted by the source is conducted through the sample cell towards a suitable energy detecting device which may consist, for example, of a bolometer or a thermocouple. This infrared detector is electrically connected so as to impress its output on a suitable amplifying and recording system so that the integral apparatus will produce a record of the energy picked up by the detector. The apparatus generally incorporates a monochromator which is effective to disperse the infrared energy into an infrared spectrum. Entrance and exit slits of the monochromator are generally arranged to provide for the continuous scanning of a particular portion of the infrared spectrum.

In using the general type of infrared absorption apparatus described, it is the general practice in conducting an analysis to adjust critically two variables. First, it is necessary to adjust critically the thickness of the sample cell, and, secondly, it is necessary to adjust critically the total amount of radiation falling on the entrance slit of the monochromator. It is necessary that the sample cell have a particular thickness in order that sufficient radiation can be transmitted through the sample, and in order to secure detectable infrared absorption characteristics. This is a particular limitation in the case of hydrocarbon mixtures since all constituents of a hydrocarbon mixture are somewhat opaque to infrared energy. Consequently, if the sample to be analyzed is contained in a sample cell which is too thick, substantially all infrared energy will be absorbed by the sample with the result that no appreciable infrared energy will pass through the sample. Similarly if the sample cell is too thin, due largely to the complexity of a hydrocarbon mixture, sufficient infrared absorption will not occur to characterize the mixture properly.

Similarly, it is necessary to adjust critically the total amount of infrared energy emitted by the

monochromator so as to obtain optimum resolution while utilizing sufficient light energy for practical detection. In order to control the amount of energy, the monochromator is generally provided with what are called entrance and exit slits operative to control the amount and band width of energy entering and leaving the monochromator. By adjusting these slits, it is consequently possible to control the total amount of energy which will impinge on the detector so as to secure optimum analytical results. If the monochromator slits are opened too widely, the result will be that the apparatus will be incapable of proper resolution due to the passage of a relatively broad band of infrared energy through the monochromator. Alternatively, if the slits of the monochromator are too narrowly adjusted, sufficient light energy will not reach the detector to produce a usable output.

So far as is known, it has been impossible to adapt the type of apparatus described to the analysis of complex hydrocarbon mixtures. This has principally been because of the difficulty of successfully choosing a sample cell thickness and monochromator slit adjustments to get suitable analytical results. Thus, in the case of crude oil sample, such a sample contains a great many isomeric hydrocarbons of similar infrared absorption characteristics. Consequently, if such a sample is contained in a reasonably thick sample cell, sufficient infrared absorption will occur so that it is difficult to transmit detectable amounts of radiation through the sample. For this reason it has generally been the practice in attempting to analyze complex hydrocarbon mixtures to employ a relatively thin sample cell to contain these mixtures. Insofar as it has been the practice to employ what may be called a thin sample cell it has also been the practice to utilize relatively narrow monochromator slit openings so as to maintain the resolution of the analytical apparatus. However, when using a system of this type it has been discovered that it is impossible to distinguish between similar complex hydrocarbon mixtures. In other words when using an infrared analysis apparatus to analyze a complex hydrocarbon mixture, if a relatively thin sample cell is employed in conjunction with relatively narrow monochromator slit adjustments adapted to provide high resolution, it is generally impossible to characterize the hydrocarbon mixture. Examining a record produced by an apparatus of this type, it will be found that few if any discrete absorption maxima characteristic of a particular hydrocarbon mixture are indicated. In accordance with this invention, it has been discovered that the general method and apparatus of infrared spectrometry heretofore described may be adapted to the successful identification of complex hydrocarbon mixtures. One principle on which this invention is based is that contrary to conventional practice a relatively thick sample cell is an essential requisite. It has been found that in order to obtain significant discrete maxima in the infrared analysis of crude oils, it is necessary that the infrared energy be passed through a relatively thick sample. This is probably due to the fact that the production of characteristic maxima depend upon the concentration of particular components in the mixture. Insofar as a hydrocarbon mixture, such as crude oil, is a fairly complex mixture, many of the individual components present occur in extremely small percentages. This factor coupled with the factor that the absorption bands of a single com-

ponent of a mixture are weak, combine to dictate the necessity for utilizing a relatively thick sample cell.

It has also been discovered that in order suitably to characterize a complex hydrocarbon mixture by infrared absorption techniques, it is necessary to employ relatively wide settings of the monochromator slits. While theoretically the use of wide monochromator slit openings would simply result in a loss of resolution, contrary to what has hitherto been supposed, the loss of resolution appears to be advantageous rather than disadvantageous. This is probably due to the fact that maxima produced by reducing resolution are the accumulated result of the absorption characteristics of many individual components having similar infrared absorption characteristics. In any case, it has been discovered that successful characterization of complex mixtures such as crude oils may be achieved by employing unconventionally broad monochromator slit openings.

As indicated, therefore, the method of this invention depends upon utilizing a sample cell which is relatively thick and on utilizing monochromator slit openings which are relatively broad.

The nature and objectives of this invention will be better understood from a consideration of the accompanying drawing in which:

Figure I represents the infrared absorption spectrum of a naturally occurring hydrocarbon tar as obtained by conventional absorption methods, and

Figure II represents an infrared absorption spectrum of the same tar as obtained by the method and apparatus of this invention;

Figure III represents the infrared absorption spectrum obtained for two crude oils obtained from the two wells of the Leduc field determined in accordance with this invention; and finally,

Figure IV represents the infrared spectrum of a Lloydminster crude oil determined in accordance with this invention.

Figure I, as stated, represents the absorption spectrum of a tar obtained by conventional infrared absorption technique. The tar employed was a naturally occurring seep and the sample was dissolved in 20% concentration in carbon disulfide. The analytical apparatus employed was that produced by the Perkin-Elmer Corporation identified as model 12A. The sample cell thickness employed in preparing the data of Figure I was 0.25 millimeter. The slit widths of the monochromator were .14 millimeter to .17 millimeter, corresponding to a spectral slit width of .036 to .042 micron at 10 microns. The curve illustrated in Figure I, is an essentially continuous curve except that the curve is broken at the points A and B due to the necessity for broadening the slit openings of the monochromator in order to compensate for the gradual drop of energy with increased wave length due to the principles of black body radiation. Referring to Figure I it will be noted that the curve plotted as the spectrum of the tar contained relatively no significant peaks. Based on the most careful examination of the three curves illustrated in Figure I, only one or two points on the curve could be singled out as apparently indicating a characteristic absorption spectrum.

Referring to Figure II, the spectrum represented was obtained by employing the same type of apparatus identified above. In this case, however, the cell thickness was more than doubled and the width of the monochromator slits were also

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approximately doubled. The cell thickness employed was actually 0.55 millimeter while the slit width was 0.28 millimeter corresponding to a spectral band width of .072 micron at 10 microns. It will be noted that the spectrum plotted in Figure II covers the same wave length region indicated in Figure I but that contrary to the plot of Figure I, a curve was obtained containing at least five distinctive discrete maxima. It will, therefore, be seen that the method of this invention is operative to produce a spectrum from a complex hydrocarbon mixture which is clearly characteristic of the particular mixture.

Referring now to the remaining figures of the drawings the infrared absorption spectrum of different crude oils are reproduced as obtained according to the principles of this invention. Thus in each case a relatively thick sample cell was employed having a cell thickness of .27 millimeter. Again, wide monochromator slit openings were maintained, as will be specifically pointed out with reference to the different figures.

Referring first to Figure III, this figure represents the spectrum of an oil obtained from the Leduc oil field at depths of 5,029 feet to 5,066 feet, in a particular well. Monochromator slit widths of .300 millimeter were maintained while determining the portion of the spectrum from 10.77 to 12.66 microns. Monochromator slit widths of .600 millimeter were maintained over the portion of the spectrum from 12.66 to 15.15 microns. It will be observed that the spectrum obtained for this crude oil had numerous and clearly identifiable peaks, clearly characterizing this particular crude oil.

Using the identical sample cell and slit widths as were employed in obtaining Figure III, the infrared spectrum was obtained for a different crude oil from the Leduc field. The crude oil was obtained from a different well in the field, from a depth of 5,297 feet to 5,313 feet. It was found that a spectrum was obtained which precisely corresponded with that formerly obtained for the different crude oil as represented in Figure III. At the time the crude samples were taken there was reason to believe that the crude oils, while obtained from different wells, were flowing from the same oil pool. From a comparison of the spectrum obtained according to the method of this invention, it appeared conclusive that in fact these oils were of substantially identical characteristics, and must have been derived from the same oil pool.

As contrasted to this, as shown by Figure IV, a clear distinction between different types of oils may be made by the method of this invention. Thus in Figure IV, the absorption spectrum of a Lloydminster crude oil is shown. This absorption spectrum was obtained using a sample cell thickness of .27 millimeter. The monochromator slit widths were .360 millimeter in the region from 10.77 to 12.66 millimeters, and the monochromator slit width were .790 millimeter in the region from 12.66 microns to 15.15 microns. Again, it will be observed that Figure IV is characterized by numerous characteristic peaks. In comparing Figure IV, with Figure III, while a similarity of the two crude oils is indicated, nevertheless a clear distinction between the oils is shown. Particularly in considering the portion of the spectrum above 12.66 microns, it is apparent that the oils could not have been obtained from the same oil pool, and could not be of the same nature. As brought out by this consideration of Figures III, and IV, therefore, the utility of this invention, in

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identifying similar crude oils, or in distinguishing different crude oils is convincingly demonstrated.

In order more fully to appreciate the nature of this invention, it is necessary to understand the manner in which characteristic absorption spectra are produced by the method of this invention. In this connection, it is apparent that the results secured are distinctly different from those obtainable by conventional analysis procedures. Thus, the characteristic maxima notable in Figure II could not be ascertained by even a microscopic examination of the type of plot illustrated in Figure I. As formerly brought out, the maxima discernible in Figure II are apparently due both to increasing the cell thickness utilized and to increasing the spectral band width of the monochromator slits. This relationship may be expressed by the following formula:

$$\Delta H \propto \frac{S_f^2}{S_i^2} \times \frac{t_f}{t_i}$$

Where ΔH represents the increase in the height of discernible peaks; t_i represents a sample cell of arbitrarily chosen initial thickness; t_f represents a final sample cell of a greater thickness; S_i represents the initial slit openings of the monochromator in millimeters; S_f represents the final slit openings in millimeters.

It should be noted from the formula that increase in peak height is obtainable in the case where both the cell thickness t_i and the slit width S_i are increased over the values t_i and S_i . The total increase in peak height is proportional to the product of the square of the ratio of the slit openings times the ratio of the cell thickness. The formula indicated is of utility in a particular situation wherein it is desired to secure a peak magnification of a given value. Thus, if it is desired arbitrarily to increase the height of peaks by a factor of 4, the slit widths required to achieve this are twice the initial slit openings. By evaluating the formula, it is possible then to determine what cell thickness should be employed in order to obtain the desired increase in peak height.

While in employing this formula, extremely wide slit widths appear most desirable, it must be recalled, that the resolution obtainable is dependent on the slit widths. Consequently, it is not practical to employ unreasonably large slit widths in the practice of this invention. It is apparent that the particular size of suitable monochromator slit widths will depend on the particular sample examined and will, in turn, depend upon the amount of resolution required to secure a distinctive spectrum. The practical limitation on the width of the slits is that the spectral width provided by the slit openings be no greater than the band in which the peak occurs.

While a practical method of adopting the principles of this invention has been described above, other methods may be employed in determining the critical cell thickness and slit widths to be used. A convenient method which may be used is essentially a trial and error method in which the cell thickness and the slit widths are experimentally increased until the desired results are obtained. As an example of this method, let it be assumed that a hydrocarbon sample is to be analyzed for which the conventional cell thickness and slit widths give no characteristic absorption spectrum. A first step in the procedure to be used consists of increasing the cell thickness until the apparatus "blacks out" or in other words, until the amount of

infrared energy passing through the sample and reaching the detector is substantially undetectable. The second step in the procedure is to then increase the width of the monochromator slits until a detectable amount of energy is picked up by the energy detectors. When these two steps have been completed, it may be found that a characteristic absorption spectrum for the sample will be obtained. Alternately, it may be found necessary to repeat the steps of this procedure by further increasing the thickness of the sample cell and the width of the monochromator slits.

As an indication of the particular application of this invention to an analysis of hydrocarbon mixtures, it may be noted that in general when analyzing a hydrocarbon mixture, the cell thickness which is employed is conventionally about .04 to .1 millimeter in thickness. Cells having a thickness of greater magnitude have been and are being used in the analysis of relatively simple hydrocarbon mixtures such as a 2 component mixture of paraffins. So far as is known, the greatest cell thickness conventionally employed in any hydrocarbon analyses is about 0.25 millimeter. As contrasted to this, in the practice of this invention, cell thicknesses are employed having a value of about .3 to .6 millimeter. Similarly, in conventional infrared absorption spectrometry, the slit widths which have been used for hydrocarbon identification are about .048 micron at 7.5 microns to .057 micron at 12.6 microns spectral band widths. In accordance with this invention, the spectral band widths which are utilized are about .087 micron at 7.5 microns to .136 micron at 12.6 microns. More particularly, the distinction between conventional slit widths and slit widths employed in this invention are indicated in the following table. It will be noted from this table that the particular slit width employed is a function of the wave length of the particular portion of the energy spectrum examined. The slit widths employed according to this invention are several times the conventional slit widths.

Wavelength (microns)	Conventional Slit Widths, mm.	Slit widths in accordance with this invention, mm.
7.5.....	.126	.260
10.8.....	.216	.360
12.6.....	.342	.900

What is claimed is:

1. In a process for characterizing complex liquid mixtures of hydrocarbons by infrared absorption characteristics in which the mixture to

be characterized is first placed in a relatively thin sample cell, and for which no characteristic absorption spectrum can be obtained utilizing substantially monochromatic infrared energy, the improvement which comprises a first step of increasing the sample cell thickness until the amount of infrared energy passed through the sample is substantially undetectable, and thereafter increasing the band width of the infrared energy passed through the cell until a detectable amount of energy is passed through the sample, and thereafter continuing these steps until a characteristic absorption spectrum is obtained.

2. An improved method for characterizing complex liquid mixtures of hydrocarbons selected from the class consisting of crude oils, lubricating oils and asphalts, comprising the steps of placing the said hydrocarbon mixture in a sample cell having a thickness of about 0.3 to 0.6 millimeter, dispersing infra-red energy to obtain an infra-red spectrum, and thereafter passing successive portions of the said spectral energy through the said sample employing a band width of infra-red energy somewhat greater than about 0.07 micron.

3. In infra-red absorption apparatus adapted for characterizing complex mixtures of liquid hydrocarbons the improvement which comprises an infra-red energy source, a monochromator positioned in the range of radiation from said source adapted to disperse the infra-red energy to provide an infra-red spectrum, means associated with said monochromator to provide a portion of the said spectrum somewhat greater than about 0.07 micron in band width, and a sample cell having a thickness of about 0.3 to 0.6 millimeter positioned adjacent said monochromator in the range of radiation of the said band width from the monochromator.

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Number	Name	Date
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