Description

BACKGROUND OF THE INVENTION

This invention relates to a method for the spectroscopic determination of the amount of one constituent of a fluid mixture (e.g. a liquid mixture) in another constituent of the mixture following the separation of the mixture into its constituents. More particularly though not exclusively, the invention relates to the determination of the entrained oil content of wax resulting from the separation, in a dewaxing filter, of a waxy raffinate into dewaxed oil (DWO) and wax. A modification of the invention relates to measuring the amount of one constituent in the fluid mixture. The amount of the one consistituent in the other constituent or in the fluid mixture itself can be expressed as a molar, weight or volume percentage, fraction, or ratio, or an actual weight or volume if the corresponding weight or volume of the other constituent or feed were also known. A particular advantage of the invention is that the method is insensitive to changes in the feed composition or upstream process conditions, as will be explained in more detail hereinbelow.

Petroleum distillates obtained at atmospheric pressure and at temperatures above 370°C, and from further vacuum distillation, can be converted into lubricating oil basestocks. The conversion can be achieved through solvent extraction of a portion of the aromatic species present in the oil, followed by solvent dewaxing, or through other techniques, well-known in the art. Further processing, such as deoiling of the wax, may also be carried out.

In the dewaxing process, the wax is caused to precipitate from the waxy feed at a particular temperature, solvent, and solvent-to-oil ratio, and is separated from the oil by filtration. Oil may be entrained in the wax during this process. Economic credits may be obtained by optimising the entrained oil content of the wax.

Several standard tests can be used to measure the entrained oil content. For example two tests of the American Society of Testing Materials, ASTM D721 and D3235, are currently used to determine the oil content of wax for sale. The ASTM D721 test serves as the American industry definition of the oil content of wax for oil levels below 15 wt %. Neither test, however, gives an accurate measure of the entrained oil content, since the tests report as oil the solvent-extractable portion of the wax at the test conditions. This material is not necessarily the same as the entrained oil in the wax, in quantity or composition, since the solvent and extraction conditions used in the ASTM tests may differ signifantly from those used in the plant dewaxing.

In general, under the ASTM test conditions, not all of the wax is insoluble and not all of the oil is soluble. Consequently, for lower temperature distillation fractions, comprising lower molecular weight species, the ASTM tests are likely to report more oil than is actually entrained, since some of the wax and essentially all of the oil is soluble in the test solvent. Alternatively, for higher temperature distillation fractions, comprising high molecular weight species, the ASTM tests are likely to report less oil than is actually entrained, since some of the oil and essentially all of the wax is insoluble in the test solvents. Thus, in general, the ASTM test methods do not report the correct amount of entrained oil in wax. Finally, the ASTM methods are time-consuming and require considerable operator skill in order to achieve the claimed precision, and are not amenable to online implementation.

Practical needs demand a method preferably for measuring the oil content of the wax, but which has general application to determining the content of a first constituent of a fluid mixture (following separation into that one constituent and at least one further constituent) either in the fluid mixture itself prior to the separation or in one or more further constituents.

Furthermore, the method should be suitable for on-line measurement or batch measurement, as circumstances require. A measurement method in which the need for dilution can be avoided and/or where rapid measurements can be made which can be used to control the separation process, is desirable.

SUMMARY OF THE INVENTION

As used herein, the terms "absorbance" and "absorptivity" will be defined as follows. Absorbance is defined as the logarithm of the ratio of the intensity of light incident on the sample to that transmitted through the sample. According to Beer's law, the absorbance of a medium can in general be expressed in a variety of ways, one of which is the product of the absorption coefficient or absorptivity and the optical pathlength through the medium. The absorptivity therefore, is the absorbance per unit length. The absorptivity, in turn may be expressed as the product of the absorption cross-section of the absorbing species and its concentration.

The present invention provides, in one aspect, a method for the spectroscopic determination of the amount α_{Nn} of the Nth constituent of a fluid mixture 0 in another constituent n of the mixture following the separation of said mixture into M, constituents 1,...,M (where n, N $\leqq$ M) and where, due to imperfect separation, said amount α_{Nn} of constituent N remains present with separated component n, said method comprising the steps

of:-

(i) determining the absorptivity a_N of separated constituent N at a selected wavelength, or at multiple wavelengths across a selected wavelength range, in which constituent N exhibits light absorption;

(ii) determining the absorptivity a_n of said another separated constituent n with said amount α_{Nn} of constituent N present at the same selected wavelength or at the same multiple wavelengths; and

(iii) determining the amount α_{Nn} of said one constituent N present with constituent n from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_n and a_N where the absorptivities are expressed solely as the ratio a_n/a_N.

"Equivalent" as used in the immediately preceding passage refers to the possibility of the mathematical expression used for determining $_{Nn}$ containing terms other than a_n/a_N but which are equivalent. For example, the term a_n/a_N could be replaced by the mathematically equivalent term $1/(a_N/a_n)$. Another example is the mathematical rearrangement of the terms in the mathematical expression, for example by bringing the term a_n outside the remainder of the expression so that the terms within it include $1/a_n$. Another possibility is where the optical pathlength, l, used in the absorbance measurements is variable and set at a different magnitude for each absorbance measurement to yield the same measured absorbance value in both cases, so that α_{Nn} can be determined from an expression containing the ratio of the optical pathlength for constituent N to that for constituent n. This ratio, according to Beer's law, is equivalent to the ratio a_n/a_N for the same optical pathlength used in the determination of both absorptivities a_n and a_N. "Equivalent" is used correspondingly in the case of another ratio a_0/a_N referred to in more detail hereinbelow.

The present invention provides, in another aspect, a method for the spectroscopic determination of the amount α_{N0} of one constituent N of a fluid mixture 0 in that mixture following the separation of said mixture into M constituents 1,...,M, (where $N \leqq M$), said method comprising the steps of:-

(i) determining the absorptivity a_N of separated constituent N at a selected wavelength, or at multiple wavelengths across a selected wavelength range, in which constituent N exhibits light absorption;

(ii) determining the absorptivity a_0 of the fluid mixture prior to the separation, at the same selected wavelength or at the same multiple wavelengths; and

(iii) determining the amount α_{N0} of said one constituent N in the fluid mixture 0 from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_0 and a_N where the absorptivities a_0 and a_N are expressed solely as the ratio a_0/a_N.

In the case that the absorptivities are determined at a single selected wavelength, the mathematical expression may be used to compute the amount of constituent N in constituent n, as indicated above.

However, it is known that intrinsic absorption by constituent n, impurity absorption and/or scattering, instrumental noise, and baseline shifts may result in wavelength-dependent effects that, contribute to the measured, absorbance spectra. Measurement of the absorbance at multiple wavelengths in the selected wavelength range allows least square and other methods to be applied to obtain the value of the ratio of absorptivities which gives rise to the most accurate value of the amount of constituent N present in constituent n.

It will be shown mathematically hereinbelow that the entrained content α_{Nn} (or α_{N0}) of constituent N in constituent n or feed 0 is a function of the quotient a_n/a_N (or a_0 to a_N) or an equivalent expression. It follows that if only constituent N exhibits light absorbance at the selected wavelength or within the selected wavelength range and if the separation process does not alter the fundamental molecular absorption cross-section of constituent N but only its amount, the method is insensitive to changes in feed variability or upstream process conditions since the scale factor which involves the absorption cross-section and which relates the amount of constituent N to the absorptivity of the n, N, or 0 constituents is the same in the numerator and denominator of the ratio a_n/a_N and a_0/a_N. It will be shown hereinbelow that the same is true even where light absorbing molecular contaminants are present and/or scattering is produced by dispersed phase present and/or one or more of the constituents other than constituent N also has absorbing properties at the selected wavelength or in the selected multiple wavelengths, providing the measured absorbances are corrected for the effect of these additional light absorbances or scattering. It follows that a change in the composition of the fluid mixture prior to the separation or (for example in the case of a waxy feed produced from a petroleum distillation column) a change in the upstream processing conditions, will not necessitate any recalibration.

As will be explained below, the invention is based on the assumption that Beer's law applies. Beer's law generally is obeyed by a wide range of absorbing species in dilute solutions, but deviations from linearity typically occur as the concentration increases due, for example, to increasing intermolecular interactions. However, the applicants have determined experimentally that, quite unexpectedly, the absorbance of dewaxed oil does not deviate from the linearity of Beer's law even at high oil concentrations.

Therefore, for the whole range of concentrations of oil in the wax likely to be measured, the measurement of oil content will remain very accurate. For other media for which Beer's law only applies at low concentrations, the spectroscopic methods disclosed herein should only be used for suitably low concentrations. For meas-

urements at higher concentrations, preferably non-absorbing diluent or solvent should be added, to remain within the linear range of the equipment.

Reference has been made above to correcting the measured absorptivities for the effects of contaminating species, light scattering or other absorbing constituents. The correction may be done by modelling the effect, using a mathematical function such as polynomial or exponential functions of wavelength and determining the coefficients of the polynomial by known mathematical procedures such as linear regression analysis.

For determining the oil content of wax from a dewaxing process, the wavelength range for the absorbance measurement may be 250nm to 650nm, more preferably 316 to 500nm and even more preferably 316 to 450nm. The shortest wavelength of the range over which the absorbance measurements are made may be selected as that for which the measured absorbances are all within the upper limit of linearity of the equipment. Typically, 316nm typically represents the shortest wavelength at which the need for diluting the oil and wax to remain within linear operation does not arise for a pathlength of 2mm. The longest wavelength in this range is chosen to be that for which the measured absorbances are greater than a value representing noise in the equipment and is typically in the range from 400 to 500nm. Because absorbance is a logarithmic function of the ratio of light intensity incident upon the absorbing medium to the light intensity transmitted through the absorbing medium, a very large dynamic range may be required of the detector/amplifiers/electronics in the absorbance-measuring equipment.

In practice, there may be instances where it is desired to limit the range of measured intensities. In order to accommodate measurement over the wavelength range, the pathlength can be varied until the measured absorbances of the one constituent N and other constituent n (containing a quantity of constituent N) are the same, the amount then being determined from the ratio of the respective pathlengths.

The invention relates not only to the novel and inventive method defined hereinabove, but also to apparatus for measuring the amount of constituent N in product constituent n. According then to another aspect of the invention there is provided apparatus for the spectroscopic determination of the amount α_{Nn} of one constituent N of a fluid mixture 0 in another constituent n of the mixture following the separation of said mixture into said constituents 1,...,M (where n, N $\leqq$ M) and where, due to imperfect separation, said amount α_{Nn} of constituent N remains present with separated consituent n, said apparatus comprising:

(i) means arranged to determine the absorptivity a_N of said one separated constituent N at a selected wavelength, or at multiple wavelengths across a selected wavelength range, in which constituent N exhibits light absorption and arranged also to determine the absorptivity a_n of said another constituent n with said amount α_{Nn} of constituent N present at the same selected wavelength or at the same multiple wavelengths; and

(ii) computer means arranged to compute the amount α_{Nn} of said one constituent N present with separated constituent n from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_n and a_N where the absorptivities are expressed solely as the ratio a_n/a_N.

Alternatively the apparatus may be modified so that the absorptivity determining means determines the absorptivity a_0 of the fluid mixture 0 and a_N and the computer means computes the content α_{N0} of constituent N in fluid mixture 0.

In either case the computer means may additionally be arranged to control the separation process in dependence on the computed content α_{Nn} (or α_{N0}), so as to minimise variations between the calculated value of α_{Nn} (or α_{N0}) and a desired value for α_{Nn} (or α_{N0}). Alternatively where α_{N0} is determined, the determined amount may be used to control one or more parameters of the upstream process producing the fluid mixture 0, so as to minimise differences between the determined amount α_{N0} and a desired value for this amount. Another possibility is to use α_{N0} to divert, blend or further process the feed prior to the separation if the determined amount α_{N0} differs from a desired value by more than a predetermined amount. This latter mode of operation would be appropriate, for example in the case where the separation process employs a catalyst which would otherwise quickly become poisoned by constituent N if it were present in the fluid mixture 0 in an excess of a predetermined amount.

In addition, the computer means may be programmed to provide a signal to an operator or process control computer in the event that the determined amount of constituent N in the feed or in a separated constituent n exceeds a predetermined target value, so that the operator or computer may select various processing options. For example, if the separation process involves a feed or a separated constituent n being acted upon by a catalyst or membrane and it has been determined that a critical amount of constituent N can reduce the lifetime or performance of the catalyst or membrane, then the determined value of α_{N0} or α_{Nn} may be used to determine when the amount of constituent N in the feed approaches or exceeds the critical amount so that the feed or separated constituent n can be blended or processed further before contacting the catalyst or membrane, or be diverted from the separation process.

In order to make absorbance measurements on a plurality of the product constituents, it is preferred to

use a single spectrometer and either to repeatedly and sequentially flow the constituents through a spectrometer, for example using appropriate flow control valving operated under computer control, or to use fiber-optic probes to transmit light which has passed through the constituents to the spectrometer in which the light is then repeatedly and sequentially measured. The probes can be located either directly in the main product lines or in slip streams from those lines.

It will be appreciated that the method disclosed herein is suitable where batch separation is effected or for on-line use.

The foregoing and other description and features will now be described in greater detail.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, wherein:

Figure 1 very diagrammatically represents a separation process to which the novel measuring methods to be described hereinbelow can be applied;

Figure 2 illustrates the absorbance spectra of the nth and Nth product constituents from a separation process where an amount of constituent N is present in the nth product constituent and constituent N exhibits absorbance across selected wavelength range but constituent n is such that, in the absence of constituent N, it would not;

Figures 3 and 4 are schematic block diagrams of two forms of equipment in accordance with the invention which are suitable for performing the spectroscopic measurement of the amount of a constituent 2 in another product constituent 1, and optionally the control of the separation process in order that variations from a desired amount are minimised;

Figure 5 illustrates the spectra of a particular dewaxed oil and the corresponding wax, both of which were obtained from dewaxing the same feed, and a model for absorbing impurities, together with the corrected wax spectrum based on the model;

Figure 6 and 7 indicate the accuracy and linearity of the content measurements made by the present spectroscopic method; and

Figure 8 shows the relationship between the entrained oil content of waxes obtained by the present method and that obtained from tests specified by the American Society of Testing Materials, for five different viscosity grades.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 represents, very diagrammatically, a separation process which separates a fluid mixture feed 0 into M separated product constituents 1, 2,...,M. For example, the feed 0 could be a waxy raffinate and the separated constituents 1,2 would then be essentially wax and dewaxed oil (DWO), respectively.

Ideally, each separate output constituent 1,2,...,M from the separation process consists solely of that one constituent. However, in practice, no separation process is perfect and, for example, an amount of one constituent N may be entrained in at least one of the other M-1 constituents. An obvious example is that the wax resulting from a dewaxing process will contain a residual quantity of entrained dewaxed oil. Another example in the petroleum industry is a distillation process where "bottoms" (i.e. material with the highest boiling point) can be entrained in decreasing residual quantities in increasingly higher "sidestreams" (i.e. materials with lower boiling points). However, it is to be understood that the invention finds general application where one constituent is present in amounts in one or more other product constituents. It will now be demonstrated that the amount entrained in each product constituent can be determined solely from absorption measurements on the M product constituents.

Consider an element (mass m_0) of the feed mixture 0 which is separated by the separation process into the M constituents, each having mass $m_1, m_2, \ldots, m_M$. Accordingly

$$m_0 = m_1 + m_2 + \ldots + m_M$$

An element of the nth constituent (the element having mass m_n) of the M product constituents comprises molecules having mass $\hat{m}_n$ and density ρ_n, and also a quantity of constituent N, having mass m_{Nn} and density ρ_n. The quantity α_{Nn} expressed as a weight fraction of constituent N which is entrained in product constituent n is defined as

$$\alpha_{Nn} = m_{Nn}/m_n \quad (1)$$

Thus

$$m_n = \hat{m}_n + \alpha_{Nn}\, m_n \quad (2)$$

The volume V_n of the nth constituent is equal to the sum of the volumes of the molecules of mass m_n and

molecules of mass m_{Nn} of constituent N, so that V_n can be expressed as

$$V_n = \hat{m}_n/\rho_n + \alpha_{Nn}m_n/\rho_N \quad (3)$$

where, as defined above, ρ_n and ρ_N are the densities of the n and N species, respectively.

On substituting for $\hat{m}_n$ in equation (3) using equation (2) and then substituting for m_n using equation (1), it can be shown that

$$\alpha_{Nn}\, m_n/V_n = \alpha_{Nn}/\left[\frac{(1-\alpha_{Nn})}{\rho_n} + (\alpha_{Nn}/\rho_N)\right] \quad (4)$$

The assumption is made in the following analysis that only constituent N is absorbing. In the case of the exemplified dewaxing of waxy feed, it is true to say that across the wavelength range having lower and upper limits approximately equal to 250nm to 650nm, more preferably 316nm to 500nm and even more preferably 316nm to 450nm, any absorbance by the wax itself is negligible, so that the absorption exhibited by the wax is due solely to the entrained oil content. Where one or more of the other constituents does exhibit absorption at the selected wavelength or within the selected wavelength range, it may be possible to correct for this, as described in some detail hereinbelow.

Figure 2 illustrates, diagrammatically, the absorbance spectrum (N) of a medium across a wavelength range (lower and upper limits λ_1 and λ_2) in which that medium exhibits absorption and that (n) of product constituent n which is due solely to the entrained content of constituent N because constituent n itself is non-absorbing. The amount of constituent N in product constituent n is lower than that in product constituent N, so that the magnitude of the absorptivity at any wavelength of constituent n is lower than that of constituent N and the ratio of absorptivity at any wavelength λ between λ_1 and λ_2 is ideally independent of wavelength and is constant.

From the foregoing, it follows that the absorbances A_n and A_N of the nth and Nth constituents are expressed as

$$A_n = (N_{Nn}/V_n)\varepsilon_N l_n$$
$$A_N = (N_N/V_N)\varepsilon_N l_N$$

where N_{Nn} and N_N are the numbers of absorbing molecules of constituent N in constituents n and N in volume elements V_n and V_N, respectively (so that the concentrations of constituent N in product constituents n and N are (N_{Nn}/V_n) and (N_N/V_N), respectively), ε_N is the absorption cross-section per molecule of constituent N, and l_n and l_N are the optical pathlengths through constituents n and N, respectively.

A_n and A_N can then be expressed as

$$A_n = (m_{Nn}/V_n).\varepsilon_N N_A l_n/MW_N$$

and

$$A_N = \rho_N.\varepsilon_N N_A l_N/MW_N,$$

since $N_{Nn} = m_{Nn}.N_A/MW_N$, where N_A is Avogadro's number and MW_N is the molecular weight of constituent N, $N_N = m_N.N_A/MW_N$, where m_N is the mass of constituent N in product constituent N, and $m_N/V_N = \rho_N$.

From equation (1) $m_{Nn} = \alpha_{Nn}\, m_n$, so that the absorptivities a_n, a_N of the nth and Nth constituents, defined as A_n/l_n and A_N/l_N, respectively can be expressed as

$$a_n = A_n/l_n = (\alpha_{Nn}m_n/V_n)\varepsilon_N N_A/MW_N,$$

and

$$a_N = A_N/l_N = \rho_N\varepsilon_N N_A/MW_N$$

Defining R_{nN} ($= a_n/a_N$) as the ratio of the absorptivity of the nth constituent to the Nth constituent, it follows that

$$\alpha_{Nn}\, m_n/V_n = \rho_N R_{nN} \quad (5)$$

Equating (4) and (5) and solving for α_{Nn} it follows that

$$\alpha_{Nn} = \frac{(\rho_N/\rho_n)\cdot R_{nN}}{1 + R_{nN}\,(\rho_N/\rho_n - 1)}$$

Expressed in words, this equation shows that the amount expressed as a weight fraction α_{Nn} of constituent

N in product constituent n is a function solely of the ratio of the absorptivity of the constituent n to that of the constituent N and the density ratio ρ_N/ρ_n of the constituents N, n, respectively.

It follows that the content of the constituent N can be measured spectroscopically under on-line conditions, using the method disclosed herein. Of course, the method could alternatively be used for batch measurement, where a given quantity of fluid mixture is separated into respective quantities of its product constituents and the spectroscopic measurements then performed, from which the weight fraction α_{Nn} can be calculated. Conveniently, the calculation is performed by a computer into which constituent density data are entered and which receives measured absorbance data, from which the amount of constituent N in one or more of the other M-1 constituents is computed. Conveniently the computer can provide a digital or visual output display of the residual content output data.

A particular advantage of the measuring method disclosed herein is that changes in the composition of the fluid mixture feed or any upstream processing conditions affecting the absorptivity of constituent N will correspondingly change the absorptivity of constituent n because constituent n itself is assumed not to have light absorbing properties at the selected operating wavelength or within the selected wavelength band or can be corrected for any such absorption and because the absorptivity exhibited by constituent n is due solely to the absorbance of the amount of constituent N in product constituent n. It follows that the value of the ratio R_{nN} is unchanged and, importantly, this means that no recalibration is required.

In the particular case of dewaxing in waxy raffinates for example, the product constituents are wax and DWO, M=2, and the wax and DWO could be regarded as product constituents 1 and 2, respectively, with densities ρ_w and ρ_o, respectively, and the ratio of the measured wax absorptivity to measured oil absorptivity R_{wo} (=R_{12}). It would follow that α_{ow}(= α_{21}) would be computed from the formula:

$$\alpha_{ow} = \frac{(\rho_o/\rho_w)R_{wo}}{1 + R_{wo}(\rho_o/\rho_w - 1)} \quad (6)$$

As indicated above a modification involves determining the absorptivity a_{N0} of the feed 0 and computing the content of constituent N in feed 0 from a mathematical formula including the term R_{0N} where $R_{0N} = a_0/a_N$. By applying a mathematical analysis similar to that set out above, it can be shown in a straight forward manner that α_{N0} is given by the formula

$$\alpha_{NO} = (\rho_N/\rho_O) \cdot R_{ON}$$

where ρ_0 is the density of the feed.

The description given above relates to the situation where only the constituent N which is present, due to imperfect separation process, in the other M-1 product constituents, exhibits absorption at the selected wavelength or at multiple wavelengths across the selected wavelength range. These circumstances will apply, at least to a large extent, in a number of practical situations. Indeed, in the case of the dewaxing of waxy raffinate, the wax has negligible absorption in a wavelength range whose lower and upper limits are approximately 250 to 650nm, as mentioned above. However, where one or more other constituents are absorbing and/or contain absorbing contaminants and/or scattering is produced by dispersed phase present, the measured absorbance spectra will be distorted by these effects. In order to overcome inaccuracies in the determined amount due to such effects, the effects can be modelled and the measured absorbance spectra corrected accordingly. The modelling may be based on a polynomial or exponential function of wavelength and the coefficents determined from known mathematical techniques such as linear regression analysis. Other models may be developed and the necessary calculations made. Such techniques do not form part of the invention as such and are well known in the art, and so need to be further described herein. However, by way of example, a specific example of modelling, and correcting for, the contributed spectrum produced by an absorbing contaminant or by scattering due to dispersed phase present, by a quadratic function of wavelength will be described in some detail hereinbelow. Alternatively, if the absorbance spectrum of absorbing constituent n (in the absence of constituent N) or that due to absorbing contaminants and/or scattering is known or may be determined, the measured absorbance of constituent n in the presence of constituent N and any contaminants present may be corrected in accordance with this contributed spectrum.

Referring now to Figure 3, there is shown, schematically, one form of equipment suitable for performing the inventive method online. The fluid mixture feed 0 is separated in separator 10 into two constituents 1, 2,

in product lines 15, 16, respectively. Successive quantities of product constituents 1, 2 from sidestreams 17, 18 of product lines 15, 16 respectively, are fed, though appropriate valving 11 under operation by a computer system 12, alternatively and sequentially through a spectral analyser 13 which includes a spectrometer which performs the required absorption measurements and supplies its output data to system 12. The constituent leaving the spectral analyser 13 is then discharged to waste or (if the constituent has sufficient value) returned, by further valving (not shown), also under control by the computer system 12, to line 15 (constituent 1) or line 16 (constituent 2). The computer system 12 calculates the amount α_{21} of constituent 2 from the output data received from the spectral analyser 13, compares the result with a desired value for the amount α_{21}, and controls one or more parameters of the separation performed in separator 10, so as to minimise any difference between the calculated content and the desired value. If the equipment is used solely for providing on-line monitoring of the content of the constituent 2, then computer control of the separation process is not required and the computer system merely generates an output indication (e.g. an alarm, a visual display or a printout) of the calculated amount α_{21}.

A modification is shown in Figure 4 where fiber-optic probes 17, 18 which as shown, are inserted in the product lines of constituents 1, 2, respectively (or in slipstreams, derived from these product lines), receive the light intensity which has passed through constituents 1, 2 and direct the light, through fiber-optic cables 19, 20, to spectrometer 13 which alternately samples the intensity of light from the fiber-optic cables. The computerised management system 12 responds to the output data from spectral analyser 13 in exactly the same way as in the Figure 3 embodiment, whether to provide an output indication of the amount α_{21} or to control the operation of the separation process.

The Figures 3 and 4 embodiments are used where the separator provides only two product constituents 1, 2 and the absorptivity measurements are performed on those two constituents. It will be readily apparent to the skilled reader, however, how to adapt the equipment where the feed 0 is separated into more than two product constituents and further description of this, therefore, will not be given. Where α_{NO} is to be determined, either a slipstream is taken from feed 0 to the spectrometer (rather than from product line 15) or a fiber-optic link is used between a fiber-optic probe, through which the feed 0 passes or which is positioned in a slipstream from the feed 0, and the spectral analyser.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

A preferred way of performing the invention will now be described. The wax absorbance should be measured at elevated temperature, typically at 60°-120°C, more preferably 70°-110°C, where the wax and entrained oil comprise a single, miscible phase. The temperature value is not critical but should be chosen to be greater than the temperature at which the wax melts and less than the temperature which causes degradation of the wax or other operational difficulties. Operation at these conditions minimizes fluctuations in the measurements due to absorption inhomogeneities and to scattering by immiscible components. Hot filtration of the wax may be required if scale or other particulates are present which can cause significant scattering of the light.

Absorbance measurements on the dewaxed oil are made at the same, or nearly the same temperature as for the wax. This minimizes errors in the density ratio of the oil and wax which is used in the equation relating the absorbance ratio to the wt % of entrained oil. It also ensures that the absorbance of the oil, which may be temperature sensitive, is the same in both constituents by keeping the temperature substantially the same.

Both the wax and dewaxed oil samples may need to be diluted in order to measure their absorbances in optical cells of convenient pathlength. White oils such as Isopar H (a high purity isoparaffinic solvent with a narrow boiling range and low aromatics level made by the Exxon Company U.S.A.) are ideal diluents, since they exhibit low absorption in the measurement wavelength range, are non-volatile at the measurement temperature, are chemically inert and are miscible with both the molten wax and the dewaxed oil.

The same white oil should also be used as a reference. Reference measurements should be made in the same pathlengths as used for the wax and dewaxed oil measurements. Dilution and optical pathlengths may be chosen to adjust the measured absorbances to be significantly above the noise level yet remain within the range of linear response of the instrument.

The wt % of oil in the wax sample, α_{ow} may be calculated from the measured absorbance of the wax and dewaxed oil by

$$\alpha_{ow} = R_{wo} K_1/\{K_2 - R_{wo} K_3\} \quad (7)$$

where

R_{wo} = a_w/a_o

a_w = absorptivity of the wax (= A_w/l_w, where A_w is the measured absorbance of the wax and l_w is the optical pathlength through the wax)

a_o = absorptivity of the oil ($=A_o/l_o$, where A_o is the measured absorbance of the wax and l_o is the optical pathlength through the oil).

K_1 = $\{Z_{ow}+(W_{sw}/W_w)Z_{os}\}$

K_2 = $\{1+(W_{so}/W_o)Z_{os}\}$

K_3 = $\{1-Z_{ow}\}$

and where

Z_{ow} = ratio of oil density to wax density

Z_{os} = ratio of oil density to solvent density

W_{sw} = weight of solvent added to dilute wax sample

W_w = weight of wax sample

W_{so} = weight of solvent added to dilute dewaxed oil sample

W_o = weight of oil sample

The wax absorbance which is used in the above formula is preferably corrected for the absorption and scattering by components of the wax other than the dewaxed oil. The corrected wax spectrum is obtained by the following method.

The measured wax absorbance is considered to be due to the sum of two effects. The first is the absorption by the entrained dewaxed oil. This spectrum is identical to that measured for the dewaxed oil except for a scale factor, K (where K<1). Consequently, the entrained oil contributes the absorbance spectrum, KA_o to the measured wax spectrum.

The second effect, absorption by molecular contaminants, such as asphaltenes, and/or scattering by an unwanted dispersed phase, contributes the spectrum, B, to the measured wax spectrum. We have found that this spectrum may be approximated by a quadratic function of the wavelength, λ, as

$$B = B_0 + B_1\lambda + B_2\lambda^2$$

over the selected wavelength range.

Thus, the measured wax absorbance A_w can be expressed as

$$A_w = KA_o + B_0 + B_1\lambda + B_2\lambda^2$$

The coefficients, K, B_0, B_1, and B_2, are obtained by a least squares regression of the measured wax spectrum, A_w to A_o, the measured dewaxed oil spectrum, A_o, λ and λ^2. The corrected wax spectrum is the product of the regression coefficient, K, and the dewaxed oil spectrum, A_o. Consequently, the ratio (A_w/A_o) reduces simply to the regression coefficient, K, and equation (7) becomes

$$\alpha_{ow} = R_{wo}K_1/(K_2 - R_{wo}K_3)$$

where

$$R_{wo} = K(l_o/l_w)$$

A preferred wavelength range for the method is 316-450mm. The pathlength and dilutions are chosen to give absorbance levels between 3.0 and 0.002 AU (AU = absorbance units), more preferably 2.2 and 0.02 AU and even more preferably 2 and 0.05 AU.

The spectra of a dewaxed oil (coded BR 150N, and obtained from Exxon Company, U.S.A., Baton Rouge refinery, having ISO viscosity grade of 150) and the wax derived from the same feed as that oil, containing 0.4% oil and which is contaminated by absorbing impurities are shown as curves 1 and 2 in Fig 5. Curve 3 is the function, B, which is quadratic in wavelength and best approximates the contaminant absorbance and where coefficients B_0, B_1 and B_2 (together with coefficient K) are obtained from a least squares linear regression analysis. The corrected spectrum of the wax, which is obtained by multiplying the measured oil spectrum A_o by the determined value of coefficient K, is shown as curve 4. This spectrum differs from the dewaxed oil spectrum only by the scale factor K which, in this case, represents an entrained oil content of 0.4 wt.%.

The accuracy of the method for measuring entrained oil content is shown in Figs 6 and 7. Oil (coded BR 100N and BT 600N) obtained from Exxon Company, U.S.A., Baton Rouge and Baytown refineries, respectively, and having respective ISO viscosity grades of 100 and 600) was added back to plant wax samples derived from those oils, respectively. It was assumed that the optical method gave the correct oil content for the "as received" wax. Known additions of dewaxed oil resulted in values for the actual wt % oil which is plotted on the ordinate of each graph. It can be seen that the method is accurate over the range of 0.2% to 50% entrained oil.

The precision of the method was demonstrated by repeat measurements made by different operators in different laboratories. The measured standard deviation for the optical method compares favourably with, and is usually superior to, the claimed standard deviation for the ASTM tests. The measurement time for the optical method is less than 10 minutes, while the ASTM tests take approximately an hour to perform.

With reference to Fig. 8, entrained oil content of waxes, obtained by the optical method, is related to the solvent extractable wax content, obtained by the ASTM test D 3235. This relationship differs with viscosity grade but is independent of feed or process changes. The ASTM wt.% oil versus that predicted from the last

described optical method is shown in Fig. 10 for five viscosity grades, MCT-5, 10, 20, 30, and 60, (lubricating oils designated by MCT-5, MCT-10, MCT-20, MCT-30, MCT-60: "Medium cold test" lubricating oil basestocks having ISO viscosity grades of approximately 100, 150, 500, 600, and 850, respectively obtained from Imperial Oil Ltd) with standard errors of estimates of 0.41%, 0.12%, 3.13%, 1.36%, and 0.85%, respectively.

The present method provides a simple and fast laboratory procedure, and should result in a reliable optical oil-in-wax analyser for on-line applications.

A preferred way of operating the equipment will now be described, in which the following steps are carried out.

- Measure separately, the absorbance spectra of the oil, A_o, and wax, A_w, without dilution in a 2 mm pathlength cell, over the wavelength range 316 to 500 nm.
- Determine a wavelength, λ_1, as the minimum wavelength in this range for which both the oil and wax absorbances are < 2.2 AU (absorbance units), where this value of 2.2 AU is selected as defining the approximate upper limit of the linear range of the instrument.
- Determine a wavelength λ_2 as the maximum wavelength in this range for which both the oil and wax absorbances are > 0.01 AU, where this value is chosen as exceeding the approximate maximum level of noise in the equipment by at least a factor of 5.
- Over the wavelength range $\{\lambda_1, \lambda_2\}$, fit the wax absorbance spectrum to the function $KA_o + B_0 + B_1\lambda + B_2\lambda^2$; where λ is the wavelength, and K, B_0, B_1 and B_2 are coefficients to be determined by a least-squares criterion.
- As in the original method, the wt% oil in wax is calculated from K and the oil and wax pathlengths and densities, as in equation (7).

The spectrometer used for measuring the absorbances may be operated under microcomputer control, in which the microcomputer can be programmed to determine λ_1 and λ_2 for each oil/wax pair once their spectra are measured. Thus, the regression range $\{\lambda_1, \lambda_2\}$ is optimally and automatically determined for each sample. This method of dynamic wavelength selection ensures that accurate absorbances for both the oil and wax are used in the determination of oil content.

Both the oil and wax may be measured undiluted, thereby eliminating the need for sample preparation (i.e. dilution) steps. This simplification has been found to reduce the total measurement time to approximately 5 minutes and minimizes errors due to inaccurate sample and/or diluent weighings.

Exactly the same method as originally demonstrated in the laboratory was incorporated into an on-line analyser version using a process diode array spectrometer made by the Dupont company. Since the present method uses longer wavelengths, dynamically determined by the analyser, the corresponding weaker specific absorbances permit the use of a longer path flow cell (say 2mm) for both the oil and wax. This use of longer path flow cells minimizes the chances of plugging and the effects of film formation, resulting in a more reliable and accurate analyser.

The detectors/amplifiers/electronics used in the spectroscopic equipment for making the absorptivity measurements may need to have a very large dynamic range. In practice though, cost, accuracy and the like may dictate that the operating range of the spectrometer be limited to, say, one decade, or similar. In order to maintain spectroscopic measurements over the same range of light intensities, the absorbance measuring apparatus may be equipped with some suitable arrangement for varying the optical pathlength and the absorptivity determinations made according to the following steps:-

- Choose a value for the minimum optical path length, l_{min}, for the oil which is practical for an on-line measurement, i.e. to avoid or minimise clogging up of the flow gap by particulate material. Typically, $l_{min} \geqq 0.5$ mm.
- Specify a maximum absorbance, A_{max}, which the instrument can determine quantitatively. A_{max} must be a value which is below the maximum for which the instrumentation is within its linear operating range. Typically, $A_{max} \leqq 3$.
- For the dewaxed oil (DWO) of interest, determine the wavelength, λ, for which the absorbance, A_{DWO}, in a pathlength l_{min}, is equal to A_{max}.
- Determine the optical pathlength l in the wax for which the absorbance at wavelength λ in the oily wax is A_{max}. The oil content of the wax is then given by equation (7), where $R_{wo} = l_{min}/l$.

It could happen that for a wax whose oil content is very small, the foregoing steps would need to be performed with the instrument operating in a domain where the noise level in the instrument becomes significant or dominant. In order to be able to measure such a low oil content accurately, for a wax with the minimum oil content of interest, O_{min}, the optical pathlength, l_{max}, should be determined, for which the absorbance A_{min} at wavelength λ is equal to a threshold absorbance, A_t. The threshold absorbance, A_t, is determined such that effects other than bulk intrinsic absorbance (e.g. scattering, refraction, etc.) are negligible. A typical value of A_t is 0.02 AU. The maximum oil content which can be measured will then be $O_{min}.(A_{max}/A_{min})$; or typically 150

$x O_{min}$. The equipment is then suitable for measuring oil contents between these maximum and minimum values only.

It is implicit in the description above that the intrinsic absorption properties of the absorbing species (i.e. constituent N) present at the time the absorbance measurements are made are preferably the same or, expressed another way, the absorbing species were mixed together in a common element of the feed 0 prior to the separation. The operation of the equipment preferably takes account of this consideration, which is more important when, for example, the flowrate of product constituent N is significantly different from that of product constituent n (or 0) whose absorbance is also being measured and/or when the composition of the feed is likely to change significantly with time.

Claims

1. A method for the spectroscopic determination of the amount α_{Nn} of the Nth constituent of a fluid mixture 0 in another constituent n of the mixture following the separation of said mixture into M constituents 1,...,M (where n, $N \leqq M$) and where, due to imperfect separation, said amount α_{Nn} of constituent N remains present with separated constituent n, said method comprising the steps of:-
   (i) determining the absorptivity a_N of separated constituent N at a selected wavelength, or at multiple wavelengths, across a selected wavelength range, in which constituent N exhibits light absorption;
   (ii) determining the absorptivity a_n of said another separated constituent n with said amount α_{Nn} of constituent N present at the same selected wavelength or at the same multiple wavelengths; and
   (iii) determining the amount α_{Nn} of said one constituent N present with constituent n from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_n and a_N where the absorptivities are expressed solely as the ratio a_n/a_N.

2. A method for the spectroscopic determination of the amount α_{N0} of one constituent N of a fluid mixture 0 in that mixture following the separation of said mixture into M constituents 1,...,M (where $N \leqq M$), said method comprising the steps of:-
   (i) determining the absorptivity a_N of separated constituent N at a selected wavelength, or at multiple wavelengths across a selected wavelength range, in which constituent N exhibits light absorption;
   (ii) determining the absorptivity a_0 of the fluid mixture prior to the separation, at the same selected wavelength or at the same multiple wavelengths; and
   (iii) determining the amount α_{N0} of said one constituent N in the fluid mixture 0, from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_0 and a_N where the absorptivities a_0 and a_N are expressed solely as the ratio a_0/a_N.

3. A method as claimed in claim 1 for the spectroscopic determination of the oil content of wax produced from a dewaxing process of a waxy hydrocarbon oil boiling in the lubricating oil range, when the oil amount, α_{ow}, is determined in step (iii) as a weight fraction of the wax from the formula

$$\alpha_{ow} = \frac{(\rho_o/\rho_w)\, R_{wo}}{1 + R_{wo}\,(\rho_o/\rho_w - 1)}$$

where ρ_o and ρ_w are the densities of the oil and wax respectively and R_{wo} ($=a_w/a_o$) is the ratio of the absorptivities (a_w, a_o respectively) of the wax and oil determined in steps (i) and (ii).

4. A method as claimed in claim 3, wherein the absorbance A_w of the oil-bearing wax (where $A_w = a_w.l_w$, l_w being the optical pathlength in the oil-bearing wax for the absorbance measurement of the oil-bearing wax) and the absorbance A_o of the dewaxed oil (where $A_o = a_o.l_o$, l_o being the optical pathlength in the dewaxed oil for the absorbance measurement of the dewaxed oil) are measured and the absorbance A_w of the oil-bearing wax is corrected to absorbance spectrum KA_o, (where $K(<1)$ is a proportionality constant) for the absorbance spectrum contributed by absorption by molecular contaminants in the oil-bearing wax and/or by scattering by dispersed phase present in the oil-bearing wax, said correction being made by determining the coefficients K, B_o, B_1 and B_2 of the formula $A_w = KA_o + B_o + B_1\lambda + B_2\lambda^2$ where $B_o + B_1\lambda + B_2\lambda^2$ approximate said contributed absorbance spectrum, by a least squares regression of the measured wax absorbance to A_o, λ and λ^2 and by using the corrected absorbance (KA_o) to determine the oil amount, α_{ow}, of the wax from said formula for α_{ow} where

$$R_{wo} = \frac{A_w.l_o}{A_o.l_w}$$

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$x O_{min}$. The equipment is then suitable for measuring oil contents between these maximum and minimum values only.

It is implicit in the description above that the intrinsic absorption properties of the absorbing species (i.e. constituent N) present at the time the absorbance measurements are made are preferably the same or, expressed another way, the absorbing species were mixed together in a common element of the feed 0 prior to the separation. The operation of the equipment preferably takes account of this consideration, which is more important when, for example, the flowrate of product constituent N is significantly different from that of product constituent n (or 0) whose absorbance is also being measured and/or when the composition of the feed is likely to change significantly with time.

Claims

1. A method for the spectroscopic determination of the amount α_{Nn} of the Nth constituent of a fluid mixture 0 in another constituent n of the mixture following the separation of said mixture into M constituents 1,...,M (where n, N ≦ M) and where, due to imperfect separation, said amount α_{Nn} of constituent N remains present with separated constituent n, said method comprising the steps of:-
   (i) determining the absorptivity a_N of separated constituent N at a selected wavelength, or at multiple wavelengths, across a selected wavelength range, in which constituent N exhibits light absorption;
   (ii) determining the absorptivity a_n of said another separated constituent n with said amount α_{Nn} of constituent N present at the same selected wavelength or at the same multiple wavelengths; and
   (iii) determining the amount α_{Nn} of said one constituent N present with constituent n from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_n and a_N where the absorptivities are expressed solely as the ratio a_n/a_N.

2. A method for the spectroscopic determination of the amount α_{N0} of one constituent N of a fluid mixture 0 in that mixture following the separation of said mixture into M constituents 1,...,M (where N ≦ M), said method comprising the steps of:-
   (i) determining the absorptivity a_N of separated constituent N at a selected wavelength, or at multiple wavelengths across a selected wavelength range, in which constituent N exhibits light absorption;
   (ii) determining the absorptivity a_0 of the fluid mixture prior to the separation, at the same selected wavelength or at the same multiple wavelengths; and
   (iii) determining the amount α_{N0} of said one constituent N in the fluid mixture 0, from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_0 and a_N where the absorptivities a_0 and a_N are expressed solely as the ratio a_0/a_N.

3. A method as claimed in claim 1 for the spectroscopic determination of the oil content of wax produced from a dewaxing process of a waxy hydrocarbon oil boiling in the lubricating oil range, when the oil amount, α_{ow}, is determined in step (iii) as a weight fraction of the wax from the formula

$$\alpha_{ow} = \frac{(\rho_o/\rho_w)\, R_{wo}}{1 + R_{wo}\,(\rho_o/\rho_w - 1)}$$

where ρ_o and ρ_w are the densities of the oil and wax respectively and R_{wo} ($=a_w/a_o$) is the ratio of the absorptivities (a_w, a_o respectively) of the wax and oil determined in steps (i) and (ii).

4. A method as claimed in claim 3, wherein the absorbance A_w of the oil-bearing wax (where $A_w = a_w.l_w$, l_w being the optical pathlength in the oil-bearing wax for the absorbance measurement of the oil-bearing wax) and the absorbance A_o of the dewaxed oil (where $A_o = a_o.l_o$, l_o being the optical pathlength in the dewaxed oil for the absorbance measurement of the dewaxed oil) are measured and the absorbance A_w of the oil-bearing wax is corrected to absorbance spectrum KA_o, (where K(<1) is a proportionality constant) for the absorbance spectrum contributed by absorption by molecular contaminants in the oil-bearing wax and/or by scattering by dispersed phase present in the oil-bearing wax, said correction being made by determining the coefficients K, B_o, B_1 and B_2 of the formula $A_w = KA_o + B_o + B_1\lambda + B_2\lambda^2$ where $B_o + B_1\lambda + B_2\lambda^2$ approximate said contributed absorbance spectrum, by a least squares regression of the measured wax absorbance to A_o, λ and λ^2 and by using the corrected absorbance (KA_o) to determine the oil amount, α_{ow}, of the wax from said formula for α_{ow} where

$$R_{wo} = \frac{A_w.l_o}{A_o.l_w}$$

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5. A method as claimed in claim 4, wherein step (i) is performed over the wavelength range 316 nm to 500 nm, a first wavelength, λ_1, is determined as the shortest wavelength in this range for which both A_w and A_o are less than a value representing the upper limit of the linear range of the equipment used for measuring A_w and A_o, a second wavelength, λ_2, is determined as the longest wavelength in this range for which both A_w and A_o are greater than a value representing the noise in said equipment, and said correction of the measured absorbance is performed by said least squares regression of the measured wax absorbance to A_o, λ and λ^2 over the wavelength range from λ_1 to λ_2, said value representing the upper limit of the linear range of the equipment used for measuring A_w and A_o is 3.0 AU and said value representing the noise in said equipment is 0.002 AU.

6. A method as claimed in claim 3, wherein the optical pathlengths, l_w and l_o, in the oil-bearing wax and the dewaxed oil, respectively, are variable, at least one of these pathlengths being varied until the measured absorbances A_w and A_o are the same and the oil amount, α_{ow}, of the wax then being determined from said formula for α_{ow} where $R_{wo} = l_o/l_w$.

7. A method as claimed in claim 3, wherein l_o is selected as equal to a minimum optical pathlength, $l_{min} \geqq 0.5$ mm, and a wavelength λ is selected for which the absorbance of the dewaxed oil over the pathlength l_{min} is equal to a specified maximum value $A_{max} \leqq 3$, for the absorbance of the dewaxed oil at a wavelength, λ, said maximum value not exceeding the upper limit of linearity of the equipment used for measuring A_o, and wherein the optical pathlength is varied to determine an optical pathlength l for which the absorbance of the dewaxed oil is equal to A_{max}, and the oil amount, α_{ow}, of the wax is determined from said formula for α_{ow} where $R_{wo} = l_{min}/l$.

8. A method as claimed in claim 3, wherein solvent is added to samples of the oil-bearing wax and the dewaxed oil before step (i) is performed and wherein the oil amount, α_{ow}, expressed as a weight fraction of the wax is determined from the formula :-

$$\alpha_{ow} = R_{wo}K_1/\{K_2 - R_{wo}K_3\}$$

where

R_{wo} $= a_w/a_o$

K_1 $= \{Z_{ow}+(W_{sw}/W_w)Z_{os}\}$

K_2 $= \{1+(W_{so}/W_o)Z_{os}\}$

K_3 $= (1-Z_{ow})$

and where

Z_{ow} = ratio of oil density to wax density

Z_{os} = ratio of oil density to solvent density

W_{sw} = weight of solvent added to dilute wax sample,

W_w = weight of wax sample

W_{so} = weight of solvent added to dilute dewaxed oil sample

W_o = weight of oil sample, and

wherein the measured absorbance A_w of the oil-bearing wax is corrected to absorbance spectrum KA_o, (where K(<1) is a proportionality constant) for the absorbance spectrum contributed by absorption by molecular contaminants in the oil-bearing wax and/or by scattering by dispersed phase present in the oil-bearing wax, said correction being made by determining the coefficients K, B_o, B_1 and B_2 of the formula $A_W = KA_o + B_o + B_1\lambda + B_2\lambda^2$ where $B_o + B_1\lambda + B_2\lambda^2$ approximates said contributed absorbance spectrum, by a least squares regression of the measured wax absorbance to A_o, λ and λ^2 and by using the determined value of coefficient K to determine the oil amount, α_{ow}, of the wax from said formula for α_{ow}, where $R_{wo} = Kl_o/l_w$, l_o and l_w being, respectively, the optical pathlengths through the dewaxed oil and wax.

9. Apparatus for the spectroscopic determination of the amount α_{Nn} of one constituent N of a fluid mixture 0 in another constituent n of the mixture following the separation of said mixture into said constituents 1,...,M (where n, N $\leqq$ M) and where, due to imperfect separation, said amount α_{Nn} of constituent N remains present with separated constituent n, said apparatus comprising:

(i) means arranged to determine the absorptivity a_N of said one separated constituent N at a selected wavelength, or at multiple wavelengths across a selected wavelength range, in which constituent N exhibits light absorption and arranged also to determine the absorptivity a_n of said another separated constituent n with said amount α_{Nn} of constituent N present at the same selected wavelength or across the same selected wavelength range; and

(ii) computer means arranged to compute the amount α_{Nn} of said one constituent N present with sepa-

rated constituent n from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_n and a_N where the absorptivities are expressed solely as the ratio a_n/a_N.

10. Apparatus for separating a fluid mixture 0 into a plurality of constituents 1,...,M (M≧2), comprising:
(i) a separator for effecting the separation; and
(ii) spectroscopic apparatus according to claim 9, wherein said computer means is further arranged to control the separator so as to minimise variations between the computed amount α_{Nn} and a desired value for this amount.

11. Apparatus for the spectroscopic determination of the amount α_{N0} of one constituent N of a fluid mixture 0 in the fluid mixture itself following the separation if said mixture into said constituents 1,...,M (where N ≦ M), said apparatus comprising:
(i) means arranged to determine the absorptivity a_N of said one separated constituent N at a selected wavelength, or at multiple wavelengths across a selected wavelength range in which constituent N exhibits light absorptivity and arranged also to determine the absorptivity a_0 of said fluid mixture 0 at the same selected wavelength or across the same selected wavelength range; and
(ii) computer means arranged to compute the amount α_{N0} of said one constituent N from a mathematical expression which contains, or is equivalent to an expression which contains, the absorptivities a_n and a_N where the absorptivities are expressed solely as the ratio a_0/a_N.

12. Apparatus as claimed in claim 9, 10 or 11, wherein the absorptivity measuring means is provided with sampling means operable under the control of the computer means to repeatedly and sequentially feed portions of constituents n and N from the separation through the absorptivity measuring means, for enabling the absoptivities a_n and a_N of constituents n and N to be determined.

13. Apparatus as claimed in claim 9, 10 and 11, wherein the absorptivity measuring means is provided with fiber optic probes each arranged to detect the intensity of light which has passed through a respective one, n, of the M constituents resulting from the separation and to guide the detected light to the absorbance measuring means which is arranged to measure the absorptivity of the light received from the fiber optic probes sequentially under the control of the computer means.

Patentansprüche

1. Verfahren zur spektroskopischen Bestimmung der Menge α_{Nn} des N. Bestandteils einer Fluidmischung O in einem weiteren Bestandteil n der Mischung nach der Trennung der Mischung in M Bestandteile 1,...,M (wobei n, N ≦ M) und wobei aufgrund von unvollkommener Trennung die Menge α_{Nn} von Bestandteil N in dem abgetrennten Bestandteil n vorhanden bleibt, bei dem
(i) der Absorptionskoeffizient a_N des abgetrennten Bestandteils N bei einer ausgewählten Wellenlänge oder mehreren Wellenlängen über einen ausgewählten Wellenlängenbereich, in welchem der Bestandteil N eine Lichtabsorption zeigt, bestimmt wird,
(ii) der Absorptionskoeffizient a_n des weiteren abgetrennten Bestandteils n bei der gleichen ausgewählten Wellenlänge oder den gleichen mehreren Wellenlängen bestimmt wird, wobei die Menge α_{Nn} des Bestandteils N anwesend ist, und
(iii) die Menge α_{Nn} des einen Bestandteils N, der in Bestandteil n vorhanden ist, aus einem mathematischen Ausdruck, der die Absorptionskoeffizienten a_n und a_N enthält, oder einem Ausdruck äquivalent ist, der die Absorptionskoeffizienten a_n und a_N enthält, bestimmt wird, wobei die Absorptionskoeffizienten nur als das Verhältnis a_n/a_N ausgedrückt werden.

2. Verfahren zur spektroskopischen Bestimmung der Menge α_{N0} eines Bestandteils N einer Fluidmischung O in der Mischung nach der Trennung der Mischung in M Bestandteile 1,...,M (wobei N ≦ M), bei dem in Stufen
(i) der Absorptionskoeffizient a_N des abgetrennten Bestandteils N bei einer ausgewählten Wellenlänge oder mehreren Wellenlängen über einen ausgewählten Wellenlängenbereich, in welchem der Bestandteil N eine Lichtabsorption zeigt, bestimmt wird,
(ii) der Absorptionskoeffizient a_0 der Fluidmischung vor der Trennung bei der gleichen ausgewählten Wellenlänge oder den gleichen mehreren Wellenlängen bestimmt wird, und

(iii) die Menge a_{NO} des einen Bestandteils N in der Fluidmischung O aus einem mathematischen Ausdruck, der die Absorptionskoeffizienten a_0 und a_N enthält, oder einem Ausdruck äquivalent ist, der die Absorptionskoeffizienten a_0 und a_N enthält, bestimmt wird, wobei die Absorptionskoeffizienten nur als das Verhältnis a_0/a_N ausgedrückt werden.

3. Verfahren nach Anspruch 1 zur spektroskopischen Bestimmung des Ölgehaltes von Paraffin, das aus einem Entparaffinierungsverfahren eines paraffinhaltigen, im Schmierölbereich siedenden Kohlenwasserstofföls hergestellt worden ist, wobei die Ölmenge α_{OW} in Stufe (iii) als Gewichtsfraktion des Paraffins aus der Formel

$$\alpha_{ow} = \frac{(\rho_o/\rho_w)\, R_{wo}}{1 + R_{wo}\,(\rho_o/\rho_w - 1)}$$

bestimmt wird, in der ρ_o und ρ_w die Dichten des Öls beziehungsweise des Paraffins sind und R_{wo} ($=a_w/a_o$) das Verhältnis der in den Stufen (i) und (ii) bestimmten Absorptionskoeffizienten (a_w beziehungsweise a_o) des Paraffins und des Öls ist.

4. Verfahren nach Anspruch 3, bei dem die Absorption A_W des öltragenden Paraffins (wobei $A_w = a_w \bullet l_w$, wobei l_w die op tische Weglänge in dem öltragenden Paraffin für die Absorptionsmessung des öltragenden Paraffins ist) und die Absorption A_o des entparaffinierten Öls (wobei $A_o = a_o \bullet l_o$, wobei l_o die optische Weglänge in dem entparaffinierten Öl für die Absorptionsmessung des entparaffinierten Öls ist) gemessen werden und die Absorption A_w des öltragenden Paraffins um das Absorptionsspektrum, zu dem durch Absorption von molekularen Verunreinigungen in dem öltragenden Paraf fin und/oder durch Streuung infolge dispergierter Phase, die in dem öltragenden Paraffin vorhanden ist, beigetragen wird, auf das Absorptionsspektrum KA_o korrigiert wird (wobei K(<1) eine Proportionalitätskonstante ist), wobei die Korrektur durch Bestimmung der Koeffizienten K, B_o, B_1 und B_2 aus der Formel $A_w = KA_o + B_o + B_1\lambda + B_2\lambda^2$ erfolgt, wobei $B_o + B_1\lambda + B_2\lambda^2$ sich dem Absorptionsspektrum durch eine Regression der kleinsten Quadrate der gemessenen Paraffinab sorption an A_o, λ und λ^2 und durch Verwendung der korrigierten Absorption (KA_o) zur Bestimmung der Ölmenge α_{ow} in dem Paraffins aus der Formel für α_{ow} annähern, wobei

$$R_{wo} = \frac{A_w \bullet l_o}{A_o \bullet l_w}$$

5. Verfahren nach Anspruch 4, bei dem Stufe (i) über den Wel lenlängenbereich von 316 nm bis 500 nm durchgeführt wird, eine erste Wellenlänge λ_1 als die kürzeste Wellenlänge die ses Bereichs bestimmt wird, für die sowohl A_w als auch A_o geringer als ein Wert sind, der den oberen Grenzwert des linearen Bereichs des zur Messung von A_w und A_o verwendeten Geräts angibt, eine zweite Wellenlänge λ_2 als die längste Wellenlänge dieses Bereichs bestimmt wird, für die sowohl A_w als auch A_o größer als ein Wert sind, der das Rauschen in dem Gerät wiedergibt, und die Korrektur der gemessenen Absorption durch die Regression der kleinsten Quadrate der gemessenen Paraffinabsorption an A_o, λ und λ^2 über den Wellenlängenbereich von λ_1 bis λ_2 durchgeführt wird, wobei der Wert, der den oberen Grenzwert des linearen Bereichs des zur Messung von A_w und A_o verwendeten Geräts wiedergibt, 3,0 AU ist und der Wert, der das Rauschen in dem Gerät wiedergibt, 0,002 AU ist.

6. Verfahren nach Anspruch 3, bei dem die optischen Weglängen l_w und l_o in dem öltragenden Paraffin beziehungsweise dem entparaffinierten Öl veränderbar sind und mindestens eine dieser Weglängen verändert wird, bis die gemessenen Absorptionen A_w und A_o gleich sind und die Ölmenge α_{ow} des Paraffins dann aus der Formel für α_{ow} bestimmt wird, wobei $R_{wo} = l_o/l_w$ ist.

7. Verfahren nach Anspruch 3, bei dem l_o gleich einer minimalen optischen Weglänge $l_{min} \geqq 0{,}5$ mm gewählt ist, und eine Wellenlänge λ gewählt ist, für die die Absorption des ent paraffinierten Öls über die Weglänge l_{min} gleich einem angegebenen Maximalwert $A_{max} \leqq 3$ für die Absorption des entparaffinierten Öls bei einer Wellenlänge λ ist, wobei der Maximalwert den oberen Grenzwert der Linearität des zur Messung von A_o verwendeten Geräts nicht überschreitet, und wobei die optische Weglänge verändert wird, um eine optische Weglänge 1 zu bestimmen, für die die Absorption des entparaffinierten Öls gleich A_{max} ist, und die Ölmenge α_{ow} des Paraffins aus der Formel für α_{ow} bestimmt wird, wobei $R_{wo} = l_{min}/l$ ist.

8. Verfahren nach Anspruch 3, bei dem Lösungsmittel zu den Proben des öltragenden Paraffins und des entparaffinierten Öls gegeben wird, bevor Stufe (i) durchgeführt wird, und wobei die Ölmenge α_{ow}, ausgedrückt als Gewichtsfraktion des Paraffins, aus der Formel

$$\alpha_{ow} = R_{wo}K_1/\{K_2 - R_{wo}K_3\}$$

bestimmt wird, in der

R_{wo} = a_w/a_o
K_1 = $\{Z_{ow} + (W_{sw}/W_w)Z_{os}\}$
K_2 = $\{1 + (W_{so}/W_o)Z_{os}\}$
K_3 = $(1 - Z_{ow})$

und

Z_{ow} = Verhältnis von Öldichte zu Paraffindichte
Z_{os} = Verhältnis der Öldichte zu Lösungsmitteldichte
W_{sw} = Gewicht des zugesetzten Lösungsmittel zu der verdünnten Paraffinprobe
W_w = Gewicht der Paraffinprobe
W_{so} = Gewicht des der verdünnten entparaffinierten Ölprobe zugesetzten Lösungsmittels
W_o = Gewicht der Ölprobe

ist, und die gemessene Absorption A_w des öltragenden Paraf fins A_w um das Absorptionsspektrum, zu dem die Absorption durch molekulare Verunreinigungen in dem öltragenden Paraffin und/oder Streuung infolge dispergierter Phase, die in dem öltragenden Paraffin vorhanden ist, beitragen, auf das Absorptionsspektrum KA_o korrigiert wird, (wobei K(<1) eine Proportionalitätskonstante ist) wobei die Korrektur durch Bestimmung der Koeffizienten K, B_o, B_1 und B_2 aus der Formel $A_w = KA_o + B_o + B_1\lambda + B_2\lambda^2$ erfolgt, wobei $B_o + B_1\lambda + B_2\lambda^2$ sich dem Absorptionsspektrum, zu dem beigetragen wird, durch eine Regression der kleinsten Quadrate der gemessenen Paraffinabsorption an A_o, λ und λ^2 und durch Verwendung des bestimmten Werts des Koeffizienten K annähern, um die Ölmenge α_{ow} des Paraffins aus der Formel für α_{ow} zu bestimmen, wobei $R_{wo} = Kl_o/l_w$, wobei l_o und l_w die optischen Weglängen durch das entparaffinierte Öl beziehungsweise das Paraffin sind.

9. Gerät zur spektroskopischen Bestimmung der Menge α_{Nn} eines Bestandteils N einer Fluidmischung O in einem weiteren Be standteil n der Mischung nach der Trennung der Mischung in die Bestandteile 1,...,M (wobei n, N ≦ M), wobei aufgrund von unvollständiger Trennung die Menge α_{Nn} des Bestandteils N in dem abgetrennten Bestandteil n vorhanden bleibt, das

(i) Einrichtungen, die zur Bestimmung des Absorptionsko effizienten a_N des einen abgetrennten Bestandteils N bei einer gewählten Wellenlänge oder mehreren Wellenlängen über einen gewählten Wellenlängenbereich, in dem Bestandteil N Lichtabsorption zeigt, eingerichtet sind und außerdem zur Bestimmung des Absorp tionskoeffizienten eines weiteren abgetrennten Bestandteils n bei der gleichen gewählten Wellenlänge oder über den gleichen gewählten Wellenlängenbereich eingerichtet sind, wobei die Menge α_{Nn} des Bestandteils N anwesend ist, und

(ii) Rechnereinrichtungen umfaßt, die zur Berechnung der Menge α_{Nn} des einen Bestandteils N, der in dem abgetrennten Bestandteil n vorhanden ist, aus einem mathematischen Ausdruck, der die Absorptionskoeffizienten a_n und a_N enthält oder einem Ausdruck äquivalent ist, der die Absorptionskoeffizienten a_n und a_N enthält, eingerichtet sind, wobei die Absorptionskoeffizienten nur als das Verhältnis a_n/a_N ausgedrückt sind.

10. Gerät zum Trennen einer Fluidmischung O in mehrere Bestandteile 1,...,M (M ≧ 2), das

(i) eine Trennvorrichtung zum Bewirken der Trennung und

(ii) ein spektroskopisches Gerät nach Anspruch 9 umfaßt, wobei die Rechnereinrichtung außerdem so eingerichtet ist, daß sie die Trennvorrichtung steuert, um so Veränderungen zwischen der berechneten Menge α_{Nn} und einem gewünschten Wert für diese Menge zu minimieren.

11. Gerät zur spektroskopischen Bestimmung der Menge α_{N0} eines Bestandteils N einer Fluidmischung O in der Fluidmischung selbst nach der Trennung der Mischung in die Bestandteile 1,...,M (wobei (N ≦ M), das

(i) Einrichtungen, die zur Bestimmung der Absorption a_N des einen abgetrennten Bestandteils N bei einer gewählten Wellenlänge oder mehreren Wellenlängen über einen gewählten Wellenlängenbereich, in dem Bestand teil N Lichtabsorption zeigt, eingerichtet sind und außerdem zur Bestimmung des Absorptionskoeffizienten a_0 der Fluidmischung O bei der gleichen gewählten Wellenlänge oder über den gleichen gewählten Wellenlängenbereich eingerichtet sind, und

(ii) Rechnereinrichtungen umfaßt, die zur Berechnung der Menge α_{N0} des einen Bestandteils N aus einem mathematischen Ausdruck, der die Absorptionskoeffizienten a_0 und a_N enthält, oder einem Ausdruck äquivalent ist, der die Absorptionskoeffizienten a_0 und a_N enthält, vorgesehen ist, wobei die Absorptionskoeffizienten nur als das Verhältnis a_0/a_N ausgedrückt sind.

12. Gerät nach Anspruch 9, 10 oder 11, bei dem die Einrichtung zum Messen des Absorptionskoeffizienten

* C L M S *

mit Einrichtungen zur Probengewinnung versehen ist, deren Betrieb durch die Rechnereinrichtung steuerbar ist, um wiederholt und sequentiell Portionen der Bestandteile n und N aus der Trennung durch die Einrichtungen zum Messen des Absorptionskoeffizienten hindurch einzuleiten, um eine Bestimmung der Absorptionskoeffizienten a_n und a_N der Bestandteile n und N zu ermöglichen.

13. Gerät nach einem der Ansprüche 9, 10 und 11, bei dem die Einrichtung zur Messung des Absorptionskoeffizienten mit Faseroptiksonden versehen sind, die jeweils so eingerichtet sind, daß sie die Intensität des Lichts wahrnehmen, das durch jeweils einen, n, der M Bestandteile, die aus der Trennung resultieren, hindurchgedrungen ist, und das wahr genommene Licht zu den Einrichtungen zum Messen der Absorption führen, die so eingerichtet sind, daß sie die Absorptionskoeffizienten aus dem Licht messen, das sie aus den Faseroptiksonden erhalten, die sequentiell von den Rechnereinrichtungen gesteuert werden.

Revendications

1. Procédé de détermination spectroscopique de la quantité α_{Nn} du Nième constituant d'un mélange de fluides O dans un autre constituant n du mélange après la séparation dudit mélange en M constituants 1, ..., M (où n, N ≦ M) et où, en raison d'une séparation imparfaite, ladite quantité α_{Nn} du constituant N reste présente avec le constituant séparé n, ledit procédé comprenant les stades suivants :
   (i) on détermine la capacité d'absorption a_N du constituant séparé N à une longueur d'onde sélectionnée ou à de multiples longueurs d'onde, sur une plage de longueurs d'onde sélectionnée dans laquelle le constituant N présente une absorption de lumière,
   (ii) on détermine la capacité d'absorption a_n dudit autre constituant séparé n avec ladite quantité α_{Nn} de constituant N présente à la même longueur d'onde sélectionnée ou aux mêmes multiples de longueurs d'ondes, et
   (iii) on détermine la quantité α_{Nn} dudit premier constituant N présent avec le constituant n à partir d'une expression mathématique qui contient, ou qui équivaut à une expression, qui contient les capacités d'absorption a_n et a_N, expression dans laquelle les capacités d'absorption sont exprimées uniquement sous la forme du rapport a_n/a_N.

2. Procédé de détermination spectroscopique de la quantité α_{NO} d'un constituant.N d'un mélange de fluides O dans ce mélange après la séparation dudit mélange en M constituants 1, ..., M (où N ≦ M), ledit procédé comprenant les stades suivants :
   (i) on détermine la capacité d'absorption a_N du constituant séparé N à une longueur d'onde sélectionnée ou à de multiples longueurs d'onde, sur une plage de longueurs d'onde sélectionnée dans laquelle le constituant N présente une absorption de lumière,
   (ii) on détermine la capacité d'absorption a_O du mélange de fluides avant la séparation à la même longueur d'onde sélectionnée ou aux mêmes multiples de longueurs d'onde, et
   (iii) on détermine la quantité α_{NO} dudit premier constituant N dans le mélange de fluides O à partir d'une expression mathématique qui contient, ou qui équivaut à une expression, qui contient les capacités d'absorption a_O et a_N, où les capacités d'absorption a_o et a_N sont exprimées uniquement sous la forme du rapport a_O/a_N.

3. Procédé selon la revendication 1 pour la détermination spectroscopique de la teneur en huile d'une paraffine produite par un procédé de déparaffinage d'une huile hydrocarbonée paraffinée bouillant dans la plage des huiles de lubrification, lorsque la quantité d'huile α_{ow} est déterminée dans le stade (iii) sous la forme d'une fraction pondérale de la paraffine à partir de la formule :

$$\alpha_{ow} = \frac{(\rho_o/\rho_w)\, R_{wo}}{1 + R_{wo}\,(\rho_o/\rho_w - 1)}$$

   où ρ_o et ρ_w sont les densités de l'huile et de la paraffine, respectivement, et R_{wo} ($=a_w/a_o$) est le rapport des capacités d'absorption (a_w, a_o, respectivement) de la paraffine et de l'huile déterminées dans les stades (i) et (ii).

4. Procédé selon la revendication 3, dans lequel la capacité d'absorption A_w de la paraffine contenant l'huile (où $A_w = a_w.l_w$, l_w étant la longueur de la trajectoire optique dans la paraffine contenant l'huile pour la mesure de la capacité d'absorption de la paraffine contenant l'huile) et la capacité d'absorption A_o de l'huile déparaffinée (où $A_o = a_o.l_o$, l_o étant la longueur de la trajectoire optique dans l'huile déparaffinée pour la mesure de la capacité d'absorption de l'huile déparaffinée) sont mesurées et la capacité d'absorption A_w

de la paraffine contenant l'huile est corrigée au spectre d'absorption KA_o (où K(<1) est une constante de proportionnalité) pour le spectre d'absorption auquel contribue l'absorption par des contaminants moléculaires dans la paraffine contenant l'huile et/ou la diffusion par la phase dispersée présente dans la paraffine contenant l'huile, ladite correction étant faite en déterminant les coefficients K, B_o, B_1 et B_2 de la formule $A_w = KA_o + B_o + B_1\lambda + B_2\lambda^2$ où l'expression $B_o + B_1\lambda + B_2\lambda^2$ représente approximativement ledit spectre d'absorption de contribution, par une régression des moindres carrés de la capacité d'absorption de la paraffine mesurée à A_o, λ et λ^2 et en utilisant la capacité d'absorption corrigée (KA_o) pour déterminer la quantité d'huile α_{OW} de la paraffine à partir de ladite formule pour α_{OW} où :

$$R_{wo} = \frac{A_w.l_o}{A_o.l_w}$$

5. Procédé selon la revendication 4, dans lequel le stade (i) est effectué sur la plage de longueurs d'onde de 316 nm à 500 nm, une première longueur d'onde λ_1 est déterminée comme la longueur d'onde la plus courte dans cette plage pour laquelle A_w et A_o sont tous deux inférieures à une valeur représentant la limite supérieure de la plage linéaire de l'équipement utilisé pour mesurer A_w et A_o, une deuxième longueur d'onde λ_2 est déterminée comme la longueur d'onde la plus grande dans cette plage pour laquelle A_w et A_o sont tous deux supérieures à une valeur représentant le bruit dans ledit équipement, et ladite correction de la capacité d'absorption mesurée est effectuée par ladite régression des moindres carrés de la capacité d'absorption de la paraffine mesurée à A_o, λ et λ^2 sur la plage de longueurs d'onde de λ_1 à λ_2, ladite valeur représentant la limite supérieure de la plage linéaire de l'équipement utilisé pour mesurer A_w et A_o est de 3,0 AU et ladite valeur représentant le bruit dans ledit équipement est de 0,002 AU.

6. Procédé selon la revendication 3, dans lequel les longueurs des trajectoires optiques l_w et l_o dans la paraffine contenant l'huile et dans l'huile déparaffinée, respectivement, sont variables, au moins l'une de ces longueurs de trajectoire étant modifiée jusqu'à ce que les capacités d'absorption mesurées A_w et A_o soient les mêmes et la quantité d'huile α_{ow} de la paraffine étant ensuite déterminée à partir de ladite formule pour α_{ow} où $R_{wo} = l_o/l_w$.

7. Procédé selon la revendication 3, dans lequel l_o est choisie comme étant égale à une longueur de trajectoire optique minimum $l_{min} \geqq 0{,}5$ mm, et on choisit une longueur d'onde λ pour laquelle la capacité d'absorption de l'huile déparaffinée sur la longueur de la trajectoire l_{min} est égale à une valeur maximum spécifiée $\lambda_{max} \leqq 3$, pour l'absorption de l'huile déparaffinée à une longueur d'onde λ, ladite valeur maximum ne dépassant pas la limite supérieure de linéarité de l'équipement utilisé pour mesurer A_o, et dans lequel la longueur de la trajectoire optique est modifiée pour déterminer une longueur de trajectoire optique 1 pour laquelle la capacité d'absorption de l'huile déparaffinée est égale à A_{max} et la quantité d'huile α_{OW} de la paraffine est déterminée à partir de ladite formule pour α_{ow} ou $R_{wo} = l_{min}/l$.

8. Procédé selon la revendication 3, dans lequel un solvant est ajouté aux échantillons de la paraffine contenant l'huile et de l'huile déparaffinée avant que le stade (i) ne soit effectué et dans lequel la quantité d'huile α_{ow}, exprimée par une fraction pondérale de la paraffine, est déterminée à partir de la formule :

$$\alpha_{ow} = R_{wo}K_1/\{K_2 - R_{wo}K_3\}$$

où

$R_{wo} = a_w/a_o$
$K_1 = \{Z_{ow} + (W_{sw}/W_w)Z_{os}\}$
$K_2 = \{1 + (W_{so}/W_o)Z_{os}\}$
$K_3 = (1-Z_{ow})$

et où

Z_{ow} = rapport de la densité de l'huile à la densité de la paraffine,
Z_{os} = rapport de la densité de l'huile à la densité du solvant,
W_{sw} = poids du solvant ajouté pour diluer l'échantillon de paraffine,
W_w = poids de l'échantillon de paraffine,
W_{so} = poids du solvant ajouté pour diluer l'échantillon d'huile déparaffinée,
W_o = poids de l'échantillon, et

et dans laquelle la capacité d'absorption mesurée A_w de la paraffine contenant l'huile est corrigée au spectre d'absorption KA_o (où K(<1) est une constante de proportionnalité) pour le spectre d'absorption auquel contribue l'absorption par des contaminants moléculaires dans la paraffine contenant l'huile et/ou la diffusion par la phase dispersée présente dans la paraffine contenant l'huile, ladite correction étant effectuée en déterminant les coefficients K, B_o, B_1 et B_2 de la formule $A_w = KA_o + B_o + B_1\lambda + B_2\lambda^2$ où l'expression

$B_o + B_1\lambda + B_2\lambda^2$ représente approximativement ledit spectre d'absorption de contribution, par une régression des moindres carrés de la capacité d'absorption de la paraffine mesurée à A_o, λ et λ^2 et en utilisant la valeur déterminée du coefficient K pour déterminer la quantité d'huile α_{ow} de la paraffine à partir de ladite formule pour α_{ow}, où $R_{wo} = Kl_o/l_w$, l_o et l_w étant respectivement les longueurs des trajectoires optiques à travers l'huile déparaffinée et la paraffine.

9. Appareil de détermination spectroscopique de la quantité α_{Nn} d'un constituant N d'un mélange de fluides O dans un autre constituant n du mélange après séparation dudit mélange en lesdits constituants 1, ..., M (où n, N≦ M) et où, en raison d'une séparation imparfaite, ladite quantité α_{Nn} du constituant N reste présente avec le constituant séparé n, ledit appareil comprenant :
(i) des moyens agencés pour déterminer la capacité d'absorption a_N dudit premier constituant séparé N à une longueur d'onde sélectionnée ou à de multiples longueurs d'onde sur une plage de longueurs d'onde sélectionnées dans laquelle le constituant N présente une absorption de lumière, et agencés également pour déterminer la capacité d'absorption a_n dudit autre constituant séparé n avec ladite quantité α_{Nn} des constituants N présents à la même longueur d'onde sélectionnée ou sur la même plage de longueurs d'onde sélectionnée, et
(ii) des moyens de calcul pour calculer la quantité α_{Nn} dudit premier constituant N présent avec le constituant séparé n à partir d'une expression mathématique qui contient, ou qui équivaut à une expression qui contient les capacités d'absorption a_n et a_N où les capacités d'absorption sont exprimées uniquement sous la forme du rapport a_n/a_N.

10. Appareil de séparation d'un mélange de fluides O en une série de constituants 1, ..., M (M ≧ 2), comprenant :
(i) un séparateur pour effectuer la séparation, et
(ii) un appareil spectroscopique selon la revendication 9, dans lequel lesdits moyens de calcul sont encore agencés de manière à commander le séparateur afin de minimiser les variations entre la quantité calculée α_{Nn} et une valeur souhaitée pour cette quantité.

11. Appareil de détermination spectroscopique de la quantité α_{NO} d'un constituant N d'un mélange de fluides O dans le mélange de fluides lui-même, après la séparation dudit mélange en lesdits constituants 1, ... M (où N ≦ M), ledit appareil comprenant :
(i) des moyens pour déterminer la capacité d'absorption a_N dudit premier constituant séparé N à une longueur d'onde sélectionnée ou à de multiples longueurs d'onde sur une plage de longueur d'onde sélectionnée dans laquelle le constituant N présente une absorption de lumière et agencés également pour déterminer la capacité d'absorption a_O dudit mélange de fluides O à la même longueur d'onde sélectionnée ou sur la même plage de longueurs d'onde sélectionnée, et
(ii) des moyens de calcul agencés pour calculer la quantité α_{NO} dudit premier constituant N à partir d'une expression mathématique qui contient, ou qui équivaut à une expression qui contient les capacités d'absorption a_n et a_N, dans laquelle les capacités d'absorption sont exprimées uniquement sous la forme du rapport a_O/a_N.

12. Appareil selon la revendication 9, 10 ou 11, dans lequel le moyen de mesure de la capacité d'absorption est pourvu d'un moyen d'échantillonnage susceptible de fonctionner sous le contrôle des moyens de calcul pour acheminer de manière répétée et en séquence des parties des constituants n et N à partir des moyens de séparation à travers les moyens de mesure des capacités d'absorption, pour permettre de déterminer les capacités d'absorption a_n et a_N des constituants n et N.

13. Appareil selon la revendication 9, 10 et 11, dans lequel les moyens de mesure des capacités d'absorption sont pourvus de sondes optiques à fibres, chacune étant agencée pour détecter l'intensité de la lumière qui est passée à travers un constituant respectif n des M constituants résultant de la séparation et pour guider la lumière détectée aux moyens de mesure des capacités d'absorption qui sont agencés pour mesurer la capacité d'absorption de la lumière reçue des sondes optiques à fibres en séquence sous la commande des moyens de calcul.