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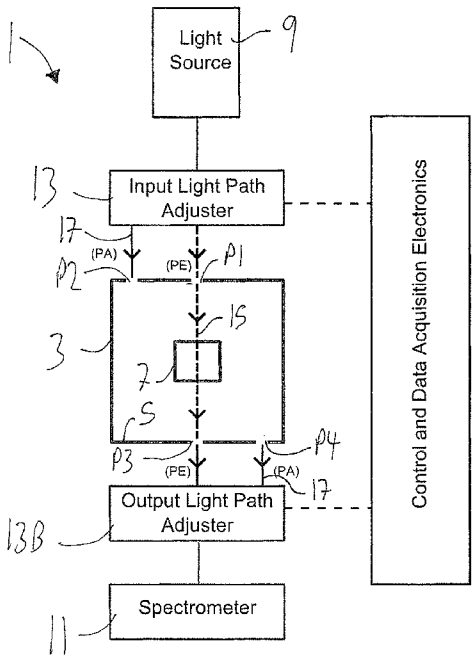


Figure 1

(57) Abstract: A spectrometer apparatus (1) is provided for measuring spectra of a liquid sample, such as a beverage such as wine. The apparatus (1) comprises an integrating cavity (3) comprising a reflective inner wall or walls (5), configured to receive a cuvette (7) containing the liquid sample within the integrating cavity (5). A combination of light inlet ports P1, P2 and light outlet ports P3, P4 are provided to receive light from at least one light source (9) and to deliver light to a spectrometer (11). A light path adjuster (13, 13B) is configured to selectively adjust a light path through the integrating cavity (5) such that at least two distinct light paths are provided; wherein when the light path adjuster (13, 13B) is in a first configuration, the apparatus (1) is in a transmission mode in which light from the light source follows a first light path (15) from the or one of the light inlet port(s) to the liquid sample such that the light from the light source irradiates the liquid sample directly before the light transmitted by the sample is transmitted through the or one of the light outlet port(s) and received by the spectrometer (11) for wavelength analysis of the light to provide an extinction spectrum of the liquid sample; and when the light path adjuster (13, 13B) is in a second configuration, the apparatus is in a diffusely reflecting mode in which light from the light source follows a second light path (17) from the or one of the inlet port(s) into the integrating cavity, is incident onto the reflective inner wall or walls of the integrating cavity and is diffusely reflected within the integrating cavity, such that the light from the light source irradiates the liquid sample before being transmitted through the or one of the light outlet port(s) and received by the spectrometer (11) for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the liquid sample.

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A SPECTROMETER APPARATUS FOR MEASURING SPECTRA OF A LIQUID SAMPLE USING AN INTEGRATING CAVITY

Field of the Invention

This invention relates to a spectrometer apparatus for measuring spectra of a liquid sample using an integrating cavity and in some embodiments, the invention relates to a UV-vis spectrometer apparatus for measuring turbid liquids.

Background

Standard UV-VIS spectroscopy is performed by shining a light source through a sample and measuring the transmitted light as a function of wavelength. The sample is generally a liquid that is contained within a square cuvette placed with the cuvette faces being perpendicular to the light beam. The transmitted light is then converted into an absorption spectrum which gives a measure of the absorbing power of the sample at every wavelength used. Absorbance can be used as a measure of the concentration of dissolved species (absorbance is proportional to concentration, known as the *Beer-Lambert Law)* or to identify the chemical content of a solution based on absorbance peaks of species at known wavelengths.

UV-VIS spectrometers are a standard instrument in analytical chemistry and can be used for both quantitative and qualitative analysis of liquids. UV-VIS spectrometers measure the spectrum of light directly transmitted by the sample, and determine the absorption spectrum based on the assumption that the only loss of light occurs due to absorption in the sample. This leads to the general requirement of brilliantly clear sample liquids in UV-VIS spectrometers.

In the more general case including turbid liquids, light is lost due to scattering by the sample, and UV-VIS spectrometers will measure the extinction spectrum instead of the absorption spectrum. In short:

$$\text{extinction} = \text{scattering} + \text{absorption}.$$

The intensity of light scattered generally is wavelength dependent, leading to a scattering spectrum. In UV-VIS spectrometers absorption and scattering spectra are superimposed and cannot be disentangled without separate knowledge of one of the two constituent spectra. In strongly scattering liquids (e.g. milk, paint, blood, wine) the light reaching the detector is diminished to a degree which renders the absorption spectrum component virtually indiscernible from the measured extinction spectrum, even if the scattering spectrum was known. For scattering/turbid samples standard UV-VIS is therefore of very limited general applicability, and if used, nonetheless requires sample pre-processing (e.g. filtration, centrifugation or other methods to remove the scattering species). Dilution of the sample is generally not helpful because it reduces both scattering and absorbance of the sample in the same proportion.

In summary, there is a significant range of samples where UV-VIS either does not work or time-consuming processing is required in order to allow analysis of cloudy solutions. Moreover, it can be impossible to separate out the relative contribution of scattering and absorption using standard UV-VIS spectroscopy.

Object of the Invention

It is therefore an object of the invention to provide a spectrometer apparatus which overcomes or at least ameliorates one or more disadvantages of the prior art, or alternatively to at least provide the public with a useful choice.

Further objects of the invention will become apparent from the following description.

Summary of Invention

Accordingly in one aspect the invention may broadly be said to consist in a spectrometer apparatus for measuring spectra of a liquid sample, the apparatus comprising:

an integrating cavity comprising a reflective inner wall or walls, and configured to receive a cuvette containing liquid sample within the integrating cavity,

wherein the integrating cavity comprises at least one light inlet port and at least one light outlet port, the or each light inlet port being configured to receive light from a light source and the or each light outlet port being configured to deliver light to a spectrometer;

the apparatus further comprising a light path adjuster configured to selectively adjust a light path through the integrating cavity such that at least two distinct light paths are provided; wherein

when the light path adjuster is in a first configuration, the apparatus is in a transmission mode in which light from the light source follows a first light path from the or one of the light inlet port(s) to the liquid sample such that the light from the light source irradiates the liquid sample directly before the light transmitted by the sample is transmitted through the or one of the light outlet port(s) and received by the spectrometer for wavelength analysis of the light to provide an extinction spectrum of the liquid sample; and

when the light path adjuster is in a second configuration, the apparatus is in a diffusely reflecting mode in which light from the light source follows a second light path from the or one of the inlet port(s) into the integrating cavity, is incident onto the reflective inner wall or walls of the integrating cavity and is diffusely reflected within the integrating cavity, such that the light from the light source irradiates the liquid sample before being transmitted through the or one of the light outlet port(s) and received by the spectrometer for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the liquid sample.

Such a spectrometer apparatus may in particular be used to obtain spectra being the absorption and extinction spectra of the sample, whereby using a suitable calibration procedure implemented by

one or more electronic data processors yields absorbance and extinction spectra that are defined for a given path length through the sample,

By providing an apparatus which can be used in each of the above configurations it is possible to obtain quantitative spectra where the path length of light through the sample in each configuration is well defined so that the data obtained in each configuration are relatable.

The apparatus may be configured such that, when in the second configuration, light from the second light path is transmitted:

a) directly from an inlet port onto the wall or walls of the integrating cavity; and/or

b) directly from an inlet port, onto and through the sample and subsequently onto the wall or walls of the integrating cavity.

Thus, when in the second configuration, the second light path may be transmitted from the inlet port either first through the sample or directly onto the cavity wall or walls. With either variant, the apparatus is configured such that the outlet port that is used in the second configuration does not look at the inlet port. In other words, the outlet port used in the second configuration "faces" the walls of the integrating cavity. An outlet port for example can be at 90° to an inlet port, or any other position on the integrating cavity. The relative position of the inlet port and outlet port used in the second configuration is such that the spectrometer does not collect the incident light or the light directly transmitted from the sample.

Preferably, when in the first configuration the inlet port is directly opposed from the outlet port such that , the first light path extends directly across the integrating cavity.

In another aspect of the invention there is provided a spectrometer apparatus for measuring spectra of a liquid sample, in particular where the spectra obtained are the absorption and extinction spectra of the sample, the apparatus comprising:

an integrating cavity comprising a reflective inner wall or walls, and configured to receive a cuvette containing liquid sample within the integrating cavity,

wherein the integrating cavity comprises at least one light inlet port and at least one light outlet port, the light inlet port being configured to receive light from a light source and the light outlet port being configured to deliver light to a spectrometer;

the apparatus further comprising a light path adjuster configured to selectively adjust a light path through the integrating cavity such that at least two distinct light paths are provided; wherein

when the light path adjuster is in a first configuration, the apparatus is in a transmission mode in which light from the light source follows a first light path from the light inlet port to the liquid sample such that the light from the light source irradiates the liquid sample directly before the light transmitted by the sample is collected via the light outlet port positioned directly opposite the inlet port and received by the spectrometer for wavelength analysis of the light to provide an extinction spectrum of the liquid sample; and

when the light path adjuster is in a second configuration, the apparatus is in a diffusely reflecting

mode in which light from the light source follows a second light path from the inlet port into the integrating cavity, and is incident onto either the reflective inner wall or walls of the integrating cavity or directly onto the liquid sample; wherein the light transmitted and/or scattered by the sample is transmitted through the outlet port, the apparatus being configured such that light directly transmitted and/or reflected by the sample is reflected by the inner wall or walls of the cavity before being transmitted through the outlet port, and received by the spectrometer for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the liquid sample.

Preferably, using a suitable calibration procedure yields absorbance and extinction spectra that are defined for a given path length through the sample,

A preferred implementation of the second configuration is to position the outlet port such that it directly faces an area of the cavity wall that the light from the inlet port does not directly illuminate.

The apparatus, used in both configurations and with a suitable calibration procedure, yields both the extinction and absorption spectrum of the liquid sample, where the path length through the sample in both said configurations is well defined, such that the spectra obtained give wavelength-dependent extinction and absorption coefficients of the sample respectively across the wavelength range of the light illuminating the sample.

The apparatus may comprise one or more integral light source(s), or the light source may be configured to be connected to one or more separate light source(s).

The apparatus may further comprise an integral or remote controller configured to control the light path adjuster to selectively adjust the path of light through the apparatus.

The controller is preferably configured to control the spectrometer, and in particular is configured to process the light received by the spectrometer for wavelength analysis of the light to provide the extinction and/or absorbance spectrum of the liquid sample contained in the cuvette. The spectrometer may be integral with the apparatus.

The controller or controllers may be configured to control one or more of:

a) switching between the first and second configurations;

b) acquiring spectra from the integrating cavity;

c) choosing operating conditions;

d) displaying spectra on a display of the apparatus, or of the controller, or in communication with the apparatus or controller;

e) saving data on a memory of the apparatus, or of the controller, or in communication with the apparatus or controller;

f) a user-interface of the apparatus, or of the controller, or in communication with the apparatus or controller, that interacts with the apparatus and allows a user to control the position of the light path adjustment mechanism.

The light path adjuster may comprise at least one movable optical element configured to manipulate light incident on the optical element from the light source, the light path adjuster being configured to adjust the movable optical element to selectively provide the first and second light paths.

The optical element may be adjustable by moving the optical element with respect to the integrating cavity from a first position in which the light travels along the first light path, and a second position in which the light travels along the second light path.

The integrating cavity comprises orthogonal longitudinal, vertical, transverse axes, and any one or more of the following positional characteristics of the optical element may be adjusted with respect to any one or more of the axes:

a) longitudinal position;
b) vertical position;
c) transverse position
d) orientation;
e) inclination.

A plurality of movable optical elements may be provided.

The movable optical element is preferably selected from any one or combination of:
a prism;
a lens;
a mirror;
a diffraction grating;
a fibre optic cable;
the light source;
a shutter.

The light path adjuster may additionally or alternatively comprise at least one fixed optical element which is not adjustable with respect to the integrating cavity. The fixed optical element may be configured to manipulate the light from the light source prior to the light inlet port. The fixed optical element may be configured to manipulate the light from the light outlet port.

The fixed optical element may be selected from any one or combination of:

a) a prism;
b) a lens;
c) a mirror;

d) a diffraction grating;
e) a fibre optic cable;
f) the light source.

The light path adjuster may comprise at least one electronic controller operative to effect selective operation of one or more light sources, to selectively provide the first and second light path.

The apparatus may comprise at least first and second light sources, the controller being configured to control each light source independently. The light sources could be switched on and off in a blinking or sequential fashion wherein in configuration one the first light source is switched on and in configuration two the second light source is on with the first off. The light sources may be controlled such that both or all light sources can be switched off, to acquire a dark spectrum.

The light path adjuster may be positioned:
a) between the light source and the light inlet port and/or
b) between the spectrometer and the light outlet port.

A plurality of light path adjustment mechanisms may be provided.

A plurality of light inlet ports may be provided, the light path adjuster being configured to provide the first light path by directing light from the light source through a first light inlet port, and to provide the second light path by directing light from the light source through a second light inlet port.

A plurality of light outlet ports may be provided, the first light path directing light from the integrating cavity through a first light outlet port, and the second light path directing light from the integrating cavity through a second light outlet port.

The integrating cavity may comprise any one of:
a) a diffusely reflecting spherical integrating cavity;
b) a cylindrical cavity;
c) a cuboidal or square cavity.

It will be appreciated that the integrating cavity may be any other shape or combination of shapes.

The integrating cavity may comprise an internal coating configured to provide any one or more of:
a) specular reflectance;
b) diffuse reflectance;
c) reflectance in the UV light spectrum;
d) reflectance in the visible light spectrum;
e) reflectance in the infra-red spectrum.

The light source may comprise any one or more of:

a) a quartz-halogen source;
b) an LED;
c) a laser;
d) any polychromatic source.

The shape of the cuvette may be:
a) square;
b) plate-like;
c) cylindrical;
d) spherical;

The apparatus may be a UV-VIS spectrometer apparatus.

The apparatus may further comprise a sample holder configured to retain a cuvette containing liquid sample within the integrating cavity.

The light source may comprise first and second LED light sources, and the light path adjuster comprises a controller configured to control the first and second LED light sources such that when in the first configuration, the first LED light source is controlled to provide light on the first light path, and when in the second configuration the second LED light source is controlled to provide light on the second light path.

Light from each LED light source may be delivered to the integrating cavity via a respective fibre optic cable. Each LED light source may deliver light to a respective light inlet port. Each light path delivers light through a respective light outlet port.

The first LED light source may be associated with a collimation lens positioned between the first LED light source and the light inlet port associated with that LED light source

The apparatus may further comprise first and second outlet ports, and a beam splitter configured to selectively allow light from the first and second outlet ports to be transmitted to the spectrometer.

According to another aspect of the invention there is provided a spectrometer apparatus for measuring spectra of a liquid sample, the apparatus comprising:

an integrating cavity comprising a reflective inner wall or walls, and configured to receive a cuvette containing liquid sample within the integrating cavity,

wherein the integrating cavity comprises a first light inlet port and a second light inlet path at least one light outlet port, the first light inlet port being configured to receive light from a first LED light source and the second light inlet port being configured to receive light from a second LED light source, at least one light outlet port being provided and configured to deliver light to a spectrometer;

the apparatus further comprising a light path adjuster configured to selectively adjust a light path through the integrating cavity such that at least two distinct light paths are provided; wherein

when the light path adjuster is in a first configuration, the apparatus is in a transmission mode in which light from the first LED light source follows a first light path from the first light inlet port to the liquid sample such that the light from the first LED light source irradiates the liquid sample directly before the light transmitted by the sample is transmitted through the light outlet port and received by the spectrometer for wavelength analysis of the light to provide an extinction spectrum of the liquid sample; and

when the light path adjuster is in a second configuration, the apparatus is in a diffusely reflecting mode in which light from the second LED light source follows a second light path from the second inlet port into the integrating cavity, is incident onto the reflective inner wall or walls of the integrating cavity and is diffusely reflected within the integrating cavity, such that the light from the light source irradiates the liquid sample before being transmitted through the, or another, light outlet port and received by the spectrometer for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the liquid sample.

The spectrometer apparatus may be configured to measure spectra of a liquid sample selected from any one or more of the following:

a. Water;
b. Wine;
c. A beverage;
d. An edible liquid or partially liquid product.

According to a further aspect of the invention there is provided a method of measuring spectra of a liquid sample using the apparatus of any of the other aspects of the invention, comprising steps of:

a. activating the light source;
b. controlling the light path adjuster to be in the transmission mode or the diffusely reflecting mode; and
c. conducting wavelength analysis of the light transmitted through the light outlet port via the spectrometer for wavelength analysis of the light to provide an absorbance and/or extinction spectrum of the liquid sample contained in the cuvette.

Detailed Description of the Drawings

A number of embodiments of the invention will now be described by way of example with reference to the drawings in which:

Figure 1 is a schematic view of example components of a spectrometer apparatus in accordance with the invention;

Figures 2a and 2b are schematic views of a first embodiment of a spectrometer apparatus in accordance with the invention, in first and second configurations;

Figures 3a and 3b are schematic views of a second embodiment of a spectrometer apparatus in accordance

with the invention, in first and second configurations;

Figure 4 is a schematic view of a third embodiment of a spectrometer apparatus in accordance with the invention, simultaneously illustrating first and second configurations of the apparatus;

Figure 5 is a schematic view of a fourth embodiment of a spectrometer apparatus in accordance with the invention, simultaneously illustrating first and second configurations of the apparatus;

Figure 6 is a schematic view of a fifth embodiment of a spectrometer apparatus in accordance with the invention, simultaneously illustrating first and second configurations of the apparatus; and

Figure 7 is a schematic view of a sixth embodiment of a spectrometer apparatus in accordance with the invention, simultaneously illustrating first and second configurations of the apparatus.

Detailed Description

Throughout the description like reference numerals will be used to refer to like features in different embodiments.

With reference to Figure 1, a spectrometer apparatus 1 for measuring spectra of a liquid sample is provided which is configured to be able to measure multiple optical properties of a liquid sample, of which the properties are the wavelength dependent extinction and absorption coefficients of the liquid.

The apparatus 1 comprises an integrating cavity 3 comprising reflective inner walls 5, and configured to retain a cuvette 7 containing liquid within the integrating cavity 3, with light from a light source 9 being delivered into the cavity 3 via different light paths 15, 17 entering the cavity 3, the different light paths 15, 17 being selectively adjustable via a light path adjuster 13. The light path adjuster 13 is used to deliver the light into the cavity 3 through at least one inlet port P1, P2 along different paths depending on the configuration of the light path adjuster 13.

The apparatus 1 further comprises at least one light outlet port P3, P4 configured to deliver light to a spectrometer 11. In some examples, an output light path adjuster 13B is provided that controls the path of light from the integrating cavity 3 to the spectrometer 11.

In the first configuration, the apparatus 1 is in a transmission mode, where the input path adjuster 13 is positioned such that the light from the light source 9 entering the cavity 3 through an inlet port P1 so as to directly illuminate the liquid contained in the cuvette 7 and the outlet light path adjuster 13B is configured such that the light collected through an outlet port P3, and sent to the spectrometer 11 so that a proportion of light from the light source 9 is directly transmitted by the sample after illuminating the sample. In this configuration, the extinction spectrum of the sample is obtained.

In the second configuration, the apparatus 1 is in a diffusely reflecting mode, where the inlet light path adjuster 13 is positioned such that the light from the light source 9 entering the cavity 3

through an inlet port P2 can either directly illuminate the liquid contained in the cuvette 7 or can be incident on the cavity wall 5 and be diffusely reflected within the cavity 3 before interacting with the liquid sample. Furthermore in this second configuration, the outlet light path adjuster 13B is configured such that the light transmitted and/or reflected by the sample and collected through outlet port P4 and sent to the spectrometer 11 has undergone at least one reflection from the cavity walls 5 before entering the outlet port P4. In this configuration, the absorption spectrum of the sample is obtained, free from the effects of scattering by the liquid sample.

The means of switching between configuration modes is provided by one or more electronic controllers that select the configuration of both the inlet light path adjuster 13 and the outlet light path adjuster 13B (if provided), to obtain either the extinction or absorption spectrum of the liquid sample depending on the configuration mode that is selected.

The apparatus 1, and method of use of the apparatus 1, allows the measurement of the extinction and absorption spectrum of a liquid sample using a single apparatus and without movement of the liquid sample.

Referring now to Figures 2a, 2b, a first embodiment of a spectrometer apparatus 1 for measuring spectra of a liquid sample comprises an integrating cavity 3 comprising a reflective inner wall or walls 5, and configured to retain a cuvette 7 containing liquid sample within the integrating cavity 3. The integrating cavity 3 comprises at least one light inlet port P1, P2 and at least one light outlet port P3, P4, the light inlet port(s) P1, P2 being configured to receive light from a light source 9 and the light outlet port(s) P3, P4 being configured to deliver light to a spectrometer 11.

The apparatus 1 further comprises a light path adjuster 13 configured to selectively adjust a path of light through the integrating cavity 3 such that at least two distinct light paths 15, 17 are provided.

When the light path adjuster 13 is in a first configuration, the apparatus 1 is in a transmission mode in which light from the light source 9 follows a direct light path 15 from the, or one of the, light inlet ports P1, to the liquid sample such that the light from the light source 9 irradiates the liquid sample directly before being transmitted through the, or one of the, light outlet ports P3, P4 and received by the spectrometer 11 for wavelength analysis of the light to provide an extinction spectrum of the liquid sample in the cuvette 7.

When the light path adjuster 13 is in a second configuration, the apparatus 1 is in a diffusely reflecting mode in which light from the light source 9 follows a light path 17 from the, or one of the, inlet ports P1, P2 into the integrating cavity 3, and is either:

a) incident directly onto the reflective inner wall or walls 5 of the integrating cavity 3 and is diffusely reflected within the integrating cavity 3, such that the light from the light source 9 irradiates the liquid sample indirectly; or

b) incident directly (not shown) onto the liquid sample 7 such that the light from the light

source 9 irradiates the liquid sample directly and the light transmitted and/or reflected by the sample is diffusely reflected within the integrating cavity

The light is subsequently transmitted through the, or one of the, light outlet ports P3, P4 and received by the spectrometer 11 for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the cuvette 7.

The apparatus 1, and method of use of the apparatus, allows the measurement of the extinction and absorption spectrum of a liquid sample using a single apparatus and without movement of the liquid sample. The method consists of placing a liquid sample, which may be contained in a standard 1 cm square cuvette 7, in an integrating cavity 3 and delivering light to the sample either in a transmission or diffusely reflecting configuration. In the first configuration, the light transmitted by the sample is sent to a spectrometer 11 and an extinction spectrum is obtained, while in the second configuration light is diffusely reflected within the cavity 3 and interacts with the sample, so that the light scattered by the sample is not lost. In the second configuration the light may initially interact with the sample, or be incident directly on the walls of the cavity. The spectrum collected by the spectrometer 11 in the second configuration can then be related to the absolute absorption spectrum with suitable calibration and modelling. Switching between measurement configurations is provided via one or more adjustable optical elements L1-L5, M1-M4, configured to manipulate the light from the light source 9 prior to the light entering the integrating cavity 3. Such optical elements can comprise one or more shutters and/or moveable mirrors that control the light path through the integrating cavity 3, and as such allow both the extinction and absorption spectrum of the liquid to be obtained using a single apparatus 1.

The apparatus 1 suspends or supports a sample cuvette 7 within an integrating cavity 3, whereby the latter has a specific light inlet/outlet port configuration which, in combination with one or more optical elements, allows two distinct light-paths to be provided through the integrating cavity 3 between the light source 9 and spectrometer 11, and in particular the light detector of or connected to such a spectrometer.

The skilled person will appreciate that the first and second light paths through the integrating cavity 3 may be provided in a number of different ways, and by varying one or more of at least the following:

a. The number of, and/or position of inlet ports;
b. The number of, and/or position of outlet ports;
c. The number of, and/or position of, and/or type of, movable optical elements;
d. The number of, and/or position of, and/or type of any auxiliary fixed optical elements that may be used;
e. The relative position of the integrating cavity with respect to the light source and/or the spectrometer.

In practice the use of the apparatus 1 provides one or more of the following advantages:

- A method for performing standard UV-VIS measurements as in any other device available on the market with standard cuvettes.
- The ability to switch to an absorbance mode to remove any effects of scattering.
- Retrieval of both the extinction and absorbance spectra immediately, from the perspective of the user.
- Measurement of absorption and extinction spectra in a single instrument and without user intervention.
- Convenient sample replacement through a cavity port, akin to replacement in a standard UV-VIS instrument
- Provides a means to determine the absolute absorbance of turbid/scattering media

Different Inlet Ports

With reference to the first example of Figures 2a and 2b, light is transmitted from the light source 9 into the integrating cavity 3 along first light path 15 through one of two light inlet ports P, P2. When the apparatus 1 is in the first configuration, light enters through first light inlet port P1, and is directly incident on the liquid sample in the cuvette 7. The light transmitted by the liquid sample is collected via first light outlet port P3 and is processed in the same way a standard UV-VIS measurement would be done, by measuring the wavelength dependent extinction spectrum of the sample which determines the wavelength dependent extinction coefficient of the sample.

In the second configuration, the light from the light source is sent through P2 along second light path 17 and is directly incident on the reflective walls 5 of the cavity 3 first. The surface of the walls 5 of the cavity 3 is, to a good approximation, a perfect diffuse reflector *(lambertian surface).* The incident light thus spreads diffusely in the cavity 3 and illuminates and interacts with the sample. Light may be absorbed by the sample, but light scattered by the sample remains part of the diffuse illumination present in the cavity 3.

In the second configuration, the light is then collected via second light outlet port P4 that is specifically positioned such that as much as possible of the light directly transmitted or reflected by the sample does not enter outlet port P4 before it is reflected from the cavity walls 5, and is processed by the spectrometer 11, allowing the true absorbance spectrum of the sample to be determined, without spectral light loss due to scattering. Switching between extinction and absorbance modes is done via the light path adjuster without needing to change the sample position or any other optics of the apparatus.

The light path adjuster 13 thus adjusts the light received by the integrating cavity 3 from the light source 9 to provide a first light path 15 in which light is directly incident in the liquid sample and not on the walls 5 of the cavity 3, and a second light path 17 in which light is directly incident on the walls 5 of the cavity 3 but not on the liquid sample.

In the example of Figures 1a, 1b, the light path adjuster 13 comprises optical elements in the form of two transversely spaced part, angled set of inlet mirrors M1, M2 between the light source 9 and cavity 3, and a corresponding pair of transversely spaced part, angled set of outlet mirrors M3, M4 between the cavity 3 and the spectrometer 11. In this example, the cavity 3 comprises two transversely space apart light inlet ports P1, P2, and comprises two transversely space apart light outlet ports P3, P4. In this example, a plurality of lens L1-L5 are provided in different positions along the first and second light paths 15, 17. The light path adjuster also comprises a movable shutter S1 configured to open and close first outlet port P3.

One inlet mirror M1 and one outlet mirror M4 are both movable along the transverse axis of the cavity 3, whilst second inlet mirror M2 and second outlet mirror M3 are fixed and not movable. In the first configuration, both sets of mirrors are in a position in which they do not impede a notional path from the light source 9, first inlet port P1, the liquid sample, and the first outlet port P3. In this position light from the light source 9 is transmitted along a direct light path 15 and is directly incident on the liquid sample.

In parallel, when mirror M1 is out of the first light path 15, shutter S1 is simultaneously open, allowing light transmitted by the sample to exit the cavity 3 from the extinction light outlet port P3. Moveable outlet mirror M3 is also simultaneously positioned out of the first light path 15 such that the light exiting P3 can be focused directly onto the spectrometer 11 via lens L5.

In configuration *2,* the moveable inlet mirror M1 is placed in the light path between the light source 9 and the first inlet port P1, with mirror M1 being positioned at 45° to the light path such that the light is directed to the fixed mirror M2 which consequently allows the light to be focused into the absorption light inlet port P2 via the focusing lens L2. In this configuration, the light is incident directly onto the interior wall 5 of the cavity 3 and is diffusely reflected within the cavity 3. The light within the cavity 3 is then collected via the outlet port P4 using lens L4 and sent to the spectrometer. Light is prevented from exiting the cavity 3 via the first outlet port P3 because this has been closed by movable shutter S1.

In practice the use of the apparatus 1 provides one or more of the advantages stated above.

The apparatus 1 may comprise, or be in communication with, an electronic controller/ software configured to perform the measurement i.e. reference and sample measurement, acquisition time, integration time and display of obtained extinction, absorbance and scattering spectra.

Same Inlet Port

Referring now to Figure 3a and 3b, a second embodiment of apparatus 1 is provided with like features being given like references. In this example, the apparatus 1 is similar to that of Figure 2, but a single light inlet port P1 is provided. The light path adjuster 13 comprises a combined pinhole-lens system comprising pinhole PN1 and focusing lens L2 placed between the light source

9 and the inlet port P1 and the moveable shutter S1 placed after the outlet ports P3 and P4. In the first configuration, shown in Figure 3b the light path adjuster 13 is configured such that such that pinhole PN1 is aligned with the incoming light path and the light entering the inlet port P1 is essentially collimated and in this position light from the light source 9 is transmitted along a direct light path 15 and is directly incident on the liquid sample. In parallel, when pinhole PN1 is in the light path, shutter S2 is simultaneously closed allowing light transmitted by the sample to exit the cavity 3 from the extinction light outlet port P3. Moveable outlet mirror M3 is also simultaneously positioned out of the first light path 15 such that the light exiting P3 can be focused directly onto the spectrometer 11 via lens L5.

In configuration 2, the light path adjuster is 13 is positioned such that the input pinhole PN1 is out of the light path and the focusing lens L2 is in the light path and the incident light from the light source 9 is focused onto the inlet port P1 such that the light is transmitted along a direct light path to the sample but because it has been focused to a point at the inlet port position, the light is divergent such that the light illuminates the entire transverse width of the sample cuvette. In parallel, when focusing lens L2 is in the light path, the shutter S2 is simultaneously open, covering the outlet port P3 with moveable mirror M4 positioned at 45° to the light path, In this configuration, light scattered, transmitted and reflected by the sample is diffusely reflected within the cavity 3 which then allows light that has been diffusely reflected within the cavity 3 to exit the cavity 3 from the absorption outlet port P4. This light is then collected via the outlet port P4 using lens L4 and sent to the spectrometer via mirror M3 and moveable mirror M4.

Shutter Selection Avoiding Sample

Referring now to Figure 4, a third embodiment of apparatus 1 is provided with like features being given like references. In this example, the movable inlet mirror M1 has been replaced by an inlet shutter S2, and a second fixed inlet mirror M1. The outlet mirrors M3, M4 are together transversely movable from a position as shown in Figure 2 in which angled outlet mirror M3 is in the light path of outlet port P3 so as to direct light from first light path 15 onto second outlet mirror M4 and onto spectrometer 11. Outlet shutter S1 comprises a shutter aperture which is aligned with outlet port P3 in this first configuration. Inlet shutter S2 comprises a pair of transversely spaced apart shutter apertures. In the first configuration the shutter S2 is positioned such that one of the shutter apertures is aligned with inlet port P1, but with inlet port P2 closed. Angled, fixed inlet mirrors M1, M2 direct light to inlet port P1.

In the second configuration inlet shutter S2 is moved transversely such that inlet port P1 is closed and inlet port P2 aligned with one of the inlet shutter S2 apertures such that light from light source 9 is transmitted directly into inlet port P2. Outlet mirrors M3, M4 are moved transversely so that mirror M3 is not in the light path between outlet port P4 and spectrometer 11.

Shutter Selection Straight Through Sample

With reference to Figure 5, fourth embodiment of apparatus 1 is provided with like features being

given like references. In this example, the apparatus 1 is similar to that of Figure 4, but no inlet mirrors are provided. The inlet shutter S2 is provided adjacent an inlet lens L6. Transverse adjustment of the position of the inlet shutter S2 aligns one or other shutter aperture with the inlet lens L6 and the light source. One inlet shutter aperture is relatively small, and the other is relatively large. By adjusting which aperture is aligned with the light source, in combination with lens L6, it is possible for both light paths 15, 17 to be directly incident on the liquid sample, with the first light path passing through the sample and exiting the cavity via outlet port P3, and the second light path also passing through the liquid sample but diffusing into contact with the walls 5 of the cavity 3 before exiting cavity 3 via second outlet port P4, when outlet shutter S1 closes first outlet port P3.

Referring now to Figure 6, a fifth embodiment of apparatus 1 is provided with like features being given like references. In this example, the apparatus 1 is similar to that of Figure 3a and 3b but the manipulation of the optical path for two different configurations is provided via off-axis parabolic (OAP) mirrors instead of lenses and flat mirrors. There are furthermore two inlet ports P1, P2 provided in this embodiment. In this example, the OAP M1 comprises a mirror, placed between the light source 9 and the first inlet port P1, with a hole drilled through the center, parallel to the incident light path, while OAP M2 has no hole drilled and redirects light with an angle, in this example, of 60°, between the light source 9 and the second inlet port P2. The light path adjuster comprises two moveable shutters S1, S2 on the inlet and outlet side of the integrating cavity 3, that move in parallel and depending on their position, block light incoming and outgoing from either ports P1 and P3 simultaneously, or P2 and P4 simultaneously.

In the first configuration, the light path adjuster is positioned such that the light reflected and focused from OAP M2 is blocked from entering the cavity 3 via second inlet port P2, such that only the light passing through the hole in OAP M1 enters the cavity 3 via first inlet port P1, and is transmitted along a direct light path 15. This light is directly incident on the liquid sample 7. In parallel, on the outlet side of the cavity 3, the shutter S2 of the light path adjuster is positioned such that second outlet port P4 is closed and light diffusely reflected within the cavity 3 does not reach the spectrometer 11. In parallel, first outlet port P3 is open, such that the light transmitted by the sample 7 can exit the first light outlet port P3, transmitted through the hole drilled in OAP M3 parallel to the light path, and can be focused directly onto the spectrometer 11 via lens L5.

In the second configuration, the shutter S1 of the light path adjuster is positioned such that the light passing through the hole in OAP M1 is blocked from entering the cavity 3 via inlet port P1. As such, the divergent light reaching OAP M1 is collimated and redirected 90° by OAP M1 onto OAP M2 from which it is then focused and redirected at 60° to the to a point at second inlet port P2. The light entering the cavity 3 is then divergent such that the light illuminates the entire transverse width of the sample cuvette, while not allowing any light to be directly transmitted onto the first light inlet port P1. In parallel, on the outlet side of the cavity 3, the shutter S2 of the light path adjuster is positioned such that outlet port P3 is closed and light directly transmitted by the

sample 7 does not reach the spectrometer 11. In parallel, outlet port P4 is open, such that the light scattered, transmitted and reflected by the sample 7 is diffusely reflected within the cavity 3 after which it leaves the cavity 3 via second outlet port P4. This divergent light is then collected via OAP M4, collimated and redirected at 90° by OAP M4, onto OAP M3 from which it is redirected at 90° and focused directly onto the spectrometer 11 by OAP M3.

Referring now to Figure 7, a sixth embodiment of apparatus 1 is provided with like features being given like references. In this example, the manipulation of the optical path for two different configurations is provided via a pair of fibre optic cables 21, 23, each of which is associated with a respective light source 25, 27, and with a respective inlet port P1, P2. Each light source 25, 27 may comprise a respective LED source 25, 27 which with an associated LED electronic controller 29 comprise the light adjuster in this example, whereby the provision of light to inlet port P1 or P2 is controlled by suitable activation and deactivation of the LED sources 25, 27 by the controller 29.

In this example, the fibre optic cable 21 supplies light directly to first inlet port P1. Fibre optic cable 23 supplies light to second inlet port P2 via a collimation lens 30.

An outlet mirror 32 and beam splitter 33 are provided between outlet ports P3, P4 and the spectrometer 11 and are configured to allow selectively allow light from first and second outlet ports P3, P4 to reach spectrometer 11 in dependence upon in which configuration the apparatus is operating.

In the first configuration, the apparatus 1 is in a transmission mode in which the light path adjuster, namely the controller 29 is controlled such that light is provided from LED source 25, via first fibre optic cable 21 to inlet port P1. Light entering the cavity 3 through inlet port P1 directly illuminates the liquid contained in the cuvette 7 and the outlet light path adjuster, namely outlet mirror 31 and splitter 33, are configured such that the light collected through outlet port P3, and sent to the spectrometer 11, includes a proportion of light from the first LED source 25 is directly transmitted by the sample after illuminating the sample. In this configuration, the extinction spectrum of the sample is obtained.

In the second configuration, the apparatus 1 is in a diffusely reflecting mode, where the controller 29 controls second LED source 27 to provide light via second fibre optic cable 23 to the second inlet port P2. Light from the LED source 25 entering the cavity 3 through inlet port P2 can either directly illuminate the liquid contained in the cuvette 7 or can be incident on the cavity wall 5 and be diffusely reflected within the cavity 3 before interacting with the liquid sample. In this second configuration, the outlet mirror 31 and/or splitter 33 are configured such that the light transmitted and/or reflected by the sample and collected through second outlet port P4 and sent to the spectrometer 11 has undergone at least one reflection from the cavity walls 5 before entering the outlet port P4. In this configuration, the absorption spectrum of the sample is obtained, free from the effects of scattering by the liquid sample.

The use of independently controllable LED light sources each of which feed a particular inlet port P1, P2 may result in a somewhat simpler apparatus which requires less separate movable and/or fixed optical elements to control the light entering sphere 3, and to allow the apparatus to operate in the first and second configurations.

In this embodiment, inlet port P2 is non-parallel with inlet port P1, such that light enters the cavity via inlet port P2 at an angle inclined to the major axes of the cavity. The position/angle of the port P2 should be chosen so as to minimise the chance for any fresnel reflections from the cuvette 7 exiting through the transmission port P3, P4 upon first reflection when the light hits the cuvette 7. The angle of the light path through port P2 can be selected accordingly.

The movable and/or fixed optical elements may, in an apparatus 1, be selected from:

a. a prism;
b. a lens;
c. a mirror;
d. a diffraction grating;
e. a fibre optic cable;
f. the light source.

Example Components

Provided below is, a non-limiting outline of example components that can be used with some examples of apparatus 1:

- **Light source 9**: A tungsten halogen lamp providing light for excitation from 350-900 nm, purchased from ThorLabs.
- **Moveable Mirrors** (M1, M4, in the example of Figures 1 and 2): Standard optical mirrors mounted 45° to the light path, that can be translated into and out of the beam path for choosing either the first or second configurations. Purchased from ThorLabs.
- **Fixed Mirrors** (M2, M4, in the example of Figures 1 and 2): Standard optical mirrors mounted 45° to the light path that can be translated into and out of the beam path for choosing either the first or second configurations. Purchased from ThorLabs.
- **Delivery Lens** (L2, in the example of Figures 1 and 2): Standard convex lens of defined focal length used for the second configuration to focus the incoming light through inlet port P2 onto the cavity walls 5 for absorption measurements. Purchased from ThorLabs.
- **Integrating Cavity 3:** 50 mm internal diameter spherical integrating cavity with diffusely reflecting inner walls. The sphere has four ports (P1-P4) drilled in the walls for light delivery and collection and a custom drilled sample port on the north pole for suspending the cuvette 7 in the centre of the cavity 3. The integrating cavity 3 is purchased from Avian Technologies. The sphere geometry may be bespoke, to suit the application with which apparatus 1 is used. The cavity 3 may be non-spherical, and could be cylindrical or cuboidal. The coating of walls 5 may have different types of surface reflectivity, including specular and diffuse reflectance or combinations

thereof in the UV, visible, or infrared region or combinations thereof.

- **Sample Holder/Cuvette 7**: The cuvette 7 is held in the apparatus 1 via a holder that clamps around the cuvette 7 and also allows the cuvette 7 to be suspended within the cavity 3 at a fixed position. The following cuvette geometries may be provided: standard (1 cm square), thin or plate-like(10 x 1 mm), cylindrical, spherical (combinations are possible too, e.g. cylindrical with a flat region)
- **USB Spectrometer 11**: Analyzes the intensity of the light leaving the cavity 3 as a function of wavelength, allowing a spectrum to be obtained and displayed on, for example, a computer screen. This may be a standalone device powered and interfaced via USB connection to a controller in the form of a laptop/computer. Light detection may be as per a standard spectrometer with dispersive optics and detection via CMOS, CCD, diode-array, or scanning-monochromator.
- **Electronics**: The movable mirrors are driven by stepper motors, and controlled by programmable micro-controller with stepper motor driver board. Both micro-controller and the USB spectrometer are attached to a controller such as a mini-computer internal to the apparatus 1. The purpose of the mini-computer is two-fold, i) it facilitates communication with the spectrometer 11 and with the motor driver, and *ii)* it provides a web-based graphical user interface. This facilitates interaction with the apparatus 1 in that there is no need for the user to install special software, and no need for the developer to maintain operating-system dependent custom software.
- **Light sources**: standard UV-VIS (i.e. Halogen, Xenon, Deuterium lamps), LEDs of any sort, lasers, combinations of all these; and any polychromatic source with attached monochromator for wavelength selection.
- **Delivery optics:** assemblies of standard optical components such as lenses, mirrors, shutters, diffraction gratings, optical fibers, or any combinations thereof.
- **Light-path switching**: Motorised linear stage(s) and/or shutter(s).

Parameters/Variables

There are a number of physical and geometrical parameters/variables which are factors in the design and operation of an apparatus 1 as described above, which include any one or more of the following:

- **Cavity Surface reflectivity** ρ is the ratio of reflected to incident light rays. For the operation of the cavity in line with apparatus 1, is the reflectivity must be close to unity, i.e. the walls 5 comprise highly reflective material. The apparatus 1 further requires the reflectivity to be strongly diffuse (Lambertian).
- **Port fraction** f is the ratio of the surface area of all cavity ports P1-P4 to the total surface area of the walls 5 of the cavity 3. A ray of light randomly traversing the cavity 3 thus has a chance f to escape.
- **Enhancement factor** *M:* approximately encodes the number of diffuse cavity surface reflections a ray will undergo before either absorbed by the walls of the cavity or leaving via a port. In the ideal case of an empty spherical cavity we have $M = \frac{\rho}{1-\rho(1-f)}$.
- **Chance to hit the sample** μ: a purely geometric factor, states the probability for a ray

which diffusely reflected off the cavity surface to interact with the sample cuvette.

- **Path-length** L is the average length of the path a ray of light takes within the sample volume. L is large if M and i are large.

Apparatus Calibration/Measurements/Control Overview

The following factors form the basis for the apparatus 1 in order to obtain error free spectra:

Relating to absorbance measurements:

- The controller determines the absolute absorption cross-section of samples inserted into an integrating cavity; this requires accurate calibration of measureable intensities against known standards.
- Input port positions for absorbance: There are two options for the placement of this port:
  - i) Avoiding direct illumination of the sample improves reproducibility of measurements as it is less sensitive on the exact geometric replacement of the sample cuvette. The disadvantage of this approach is that some light reaches the detector (determined by μ) without interacting with the sample, even for a fully absorbing sample, which limits the range of measurable optical density.
  - *ii)* Alternatively all incident rays can be made to pass through the sample. This solves the problem of saturating absorbance and allows the measurement of strongly absorbing samples. In this case the detection port needs to collect from a section of the cavity wall which does not receive light from direct or reflected illumination.
- Detection port positions for absorbance: The field of view of the detection port must not intersect the sample, instead it should gather light only from the cavity surface. This minimizes the dependence of the measurement on the scattering properties of the sample.
- Geometric optimization of the setup: the average pathlength in the sample, L, can be approximated by the ratio of the sample volume and the cavity volume, $rV = V_{sample}/V_{cavity}$: multiplied by the average chord length in the cavity, $\bar{c} = 4V_{cavity}/A_{cavity}$ (where A_{cavity} is the surface area of the cavity), and by the enhancement factor M. The approximate pathlength $L = rV\bar{c}M$ governs the lower limits of the detectable optical density; for example, for low-absorbance samples it is desirable to maximise L: *i)* M becomes maximal for a cavity surface reflectivity $\rho \rightarrow 1$ and cavity port fraction $f \rightarrow 0$, *ii)* rV increases with the relative sample volume and approaches one as the sample fills the sphere entirely, *iii)* $\bar{c}$ *is* maximal for a spherical cavity. A spherical cavity filled entirely by the sample, with maximal surface reflectivity and minimal port openings may be an optimal setup for detection of ultra-low concentrations.
- It is not straight-forward to choose a combination of parameters (cavity and sample geometries, port locations, numerical apertures, etc.) which fit the requirements of validity, reproducibility, and user-convenience. The design choices may be a non-trivial compromise. For example, the apparatus 1 described above is suited for standard cuvettes, including cuvettes with short optical pathlength for strongly absorbing liquids.

Relating to combined extinction-absorbance measurements:

- extinction measurements are performed inside an integrating cavity; this comes with geometric constraints in that the sample walls must be perpendicular to the incident beam, which

requires a square or flat-walled cuvette. Cuvettes with curved surfaces (e.g. cylindrical) are also possible, but would require specialised optics to counter the refractive effects.

- The numerical aperture available in both delivery and detection needs to be constrained in order to avoid diffuse illumination of the sample and to minimize detection of multiple-scattering light.
- Combined delivery and detection optics capable of switching between the absorption and extinction pathways are required. The arrangement of these pathways must ensure that they do not affect each other.

Apparatus Calibration/Measurements/Control Example Detail

Detail of an example calibration method that could be used to calibrate a spectrometer apparatus as described above, is set out in the attached Appendix.

The spectrometer apparatus may be configured to measure spectra of a liquid sample selected from any one or more of the following:

a. Water;
b. Wine;
c. A beverage;
d. An edible liquid or partially liquid product;
e. Paint;
f. Water, such as seawater;
g. Nanoparticles;
h. Emulsions;
i. Blood

In one example the spectrometer apparatus may therefore be a wine testing apparatus.
The above list is non-limiting.

Unless the context clearly requires otherwise, throughout the description, the words "comprise", "comprising", and the like, are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense, that is to say, in the sense of "including, but not limited to".

Although this invention has been described by way of example and with reference to possible embodiments thereof, it is to be understood that modifications or improvements may be made thereto without departing from the scope of the invention. The invention may also be said broadly to consist in the parts, elements and features referred to or indicated in the specification of the application, individually or collectively, in any or all combinations of two or more of said parts, elements or features. Furthermore, where reference has been made to specific components or integers of the invention having known equivalents, then such equivalents are herein incorporated as if individually set forth.

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

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Appendix - Example Calibration Method

Calibration Procedure for Combined Extinction and Absorbance Spectrometer

Background

In a standard UV-VIS transmission measurement, the extinction, $E(\lambda)$, of a sample being measured is related to the extinction coefficient, α_{E} of the sample and the path length through the sample, κ, by the Beer-Lambert Law, given as

$$E(\lambda) = -\log_{10} T(\lambda) = \kappa \alpha_{\mathrm{E}}, \tag{1}$$

where $T(\lambda)$ is the ratio of transmitted to incident light at a given wavelength. If the extinction is due to a particular analyte (such as a dye molecule) in the sample, the extinction coefficient is then proportional to the concentration of analytes, c and the *molar extinction coefficient* of the analyte, $\bar{\epsilon}_{E(\lambda)}$. Thus when the path length is well known then the measured extinction, $E(\lambda)$ is directly proportional to the sample extinction coefficient, which can be used to compute the concentration of the analyte through

$$E(\lambda) = \kappa c \bar{\epsilon}_{E(\lambda)}, \tag{2}$$

This illustrates the quantitative power of UV-VIS measurements, because for a standard UV-VIS setup, the path length is well defined by the length of the cuvette used, which is in general 1 cm. In reality extinction is the sum of scattering and absorption of the sample and thus $\bar{\epsilon}_{E(\lambda)}$ can be separated into two contributions: one from absorption and one from scattering. These are then called the molar absorption coefficient, $\bar{\epsilon}_{A(\lambda)}$ and the scattering coefficient $\bar{\epsilon}_{S(\lambda)}$ respectively. This leads to the Beer-Lambert expression of

$$E(\lambda) = \kappa c(\bar{\epsilon}_{A(\lambda)} + \bar{\epsilon}_{S(\lambda)}). \tag{3}$$

This allows three general cases where the sample can be:

1. *absorbing only*, i.e. $\bar{\epsilon}_{A(\lambda)} \neq 0$ and $\bar{\epsilon}_{S(\lambda)} = 0$
2. *scattering only*, i.e. $\bar{\epsilon}_{A(\lambda)} = 0$ and $\bar{\epsilon}_{S(\lambda)} \neq 0$
3. *absorbing and scattering*, i.e. $\bar{\epsilon}_{A(\lambda)} = 0$ and $\bar{\epsilon}_{S(\lambda)} \neq 0$

For the majority of samples, case 1 applies, where $\bar{\epsilon}_{E(\lambda)} = \bar{\epsilon}_{A(\lambda)}$, and Equation 2 can be used to determine the concentration of the analyte or the molar absorption coefficient. However when case 3 is applicable, standard UV-VIS configuration cannot be used as it is very difficult to separate the contributions from scattering and absorbance independently. Thus if the analyte of interest has an $\bar{\epsilon}_{A(\lambda)}$ but is embedded within a liquid that has a non zero $\bar{\epsilon}_{S(\lambda)} \neq 0$, then the concentration of the analyte cannot be determined via an extinction measurement due to the contribution of scattering. The solution to this problem is to embed the sample within an integrating cavity as described in the original invention, to remove the effects of scattering on the measured signal.

Integrating Cavity Path Length

In a non-standard transmission configuration, such as that shown below, where the sample is embedded within an integrating cavity such that the light interacting with the sample is diffusely reflected within the cavity by the cavity walls, the path length in the sample is no longer simply defined as the thickness of the cuvette because the light may pass many times through sample and at different angles before leaving the cavity and entering the spectrometer. As such, it is no longer valid to use Equation 2 to determine the molar absorption coefficient of the sample (limiting ourselves here to case 1 for the sake of argument). With $\bar{\epsilon}_{S(\lambda)} = 0$ and writing $E(\lambda)$ as $A_{\mathrm{R}}(\lambda)$, the *measured absorbance* in the cavity is instead given by

$$A(\lambda)_{\mathrm{MEAS}} = \kappa_{\mathrm{eff}}(A_{\mathrm{R}}(\lambda)) A_{\mathrm{R}}(\lambda), \tag{4}$$

where $\kappa_{\mathrm{eff}}(A(\lambda))$ is the *effective cavity path length* and $A_{\mathrm{R}}(\lambda)$ is the "real absorbance" signal that would be measured in a standard transmission measurement for a path length of 1 cm. $\kappa_{\mathrm{eff}}(A_{\mathrm{R}}(\lambda))$ is explicitly a function of wavelength (due to the non-flat reflectivity of the cavity material) and $A_{\mathrm{R}}(\lambda)$. Rearranging Equation 4 gives

$$\boxed{\kappa_{\mathrm{eff}(A_{\mathrm{R}}(\lambda))} = \frac{A(\lambda)_{\mathrm{MEAS}}}{A_{\mathrm{R}}(\lambda)},} \tag{5}$$

showing that it is straightforward to determine the cavity path $\kappa_{\mathrm{eff}}(A_{\mathrm{R}}(\lambda))$ as a function of wavelength and sample (real) absorbance by measuring a range of absorbing samples in both transmission and absorption mode (as is described in the original invention) and taking the ratio of $A(\lambda)_{\mathrm{MEAS}}$ to $A_{\mathrm{R}}(\lambda)$.

method for determining the cavity path length is required so that the measured absorbance in this configuration, A_{MEAS}, can be converted into the equivalent absorbance that would be measured in a 1 cm path length transmission setup. Consequently, once the path length is known, A_{MEAS} can be corrected for the increase (or decrease) in path length compared to the transmission setup and Equation 2 can be applied to determine the absorption coefficient (or concentration) of the analyte.

Integrating Cavity Calibration

The approach outlined for determining the effective cavity path length is implemented below using the setup described in the orginal invention and using the dye Eosin B as the analyte. A concentration series of the dye is measured to determine the path length across a range of sample absorbances. In all cases, $(A_R(\lambda))$ is the "real" absorbance measured in the transmission mode and $A(\lambda)_{MEAS}$ is the measured absorbance in the absorbance mode and $\kappa_{eff}(A_R(\lambda))$ is the absorption and wavelength dependent path length in the cavity. The details of the measurements are described in the Methods section.

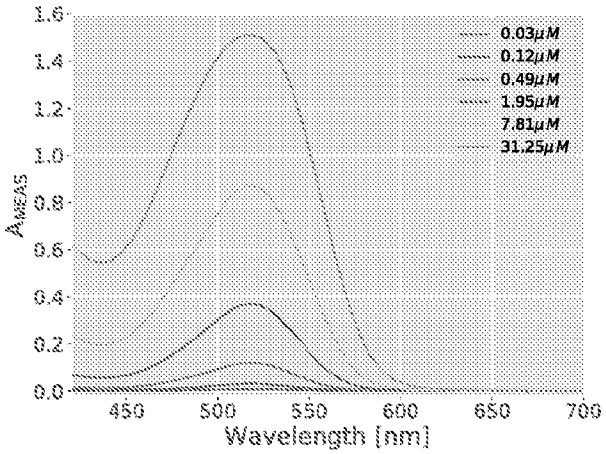


FIG. 1. Absorption spectra $(A(\lambda)_{MEAS})$ of Eosin B concentration series in absorption mode.

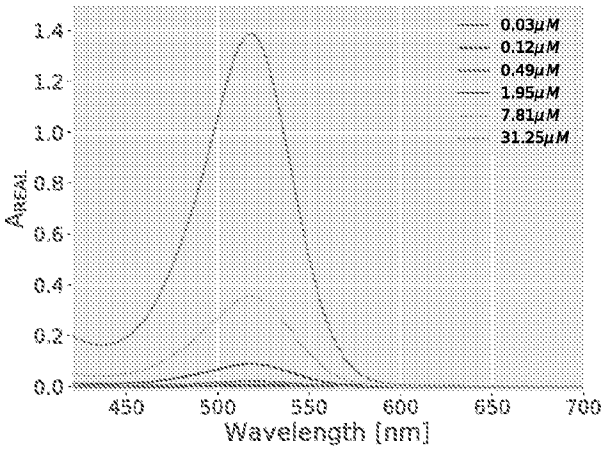


FIG. 2. Absorption spectra $(A(\lambda)_R)$ of Eosin B concentration series in transmission mode.

The $A(\lambda)_{MEAS}$ and $(A_R(\lambda))$ spectra obtained using the invention described for an Eosin B concentration series are shown in Figures 1 and 2, where the concentration of dye in each measurement is indicated. While the spectra look similar in both configurations, there is a clear difference in the magnitudes of the measured spectra at each concentration. As expected from the Beer Lambert Law, in the extinction configration (not shown), with no scattering present, the $(A_R(\lambda))$ scales linearly with absorption coefficient. In the cavity configration however, it is clear that magnitude quickly deviates from being linearly proportional to concentration, owing to the non linear response of the cavity path length to increasing absorbance.

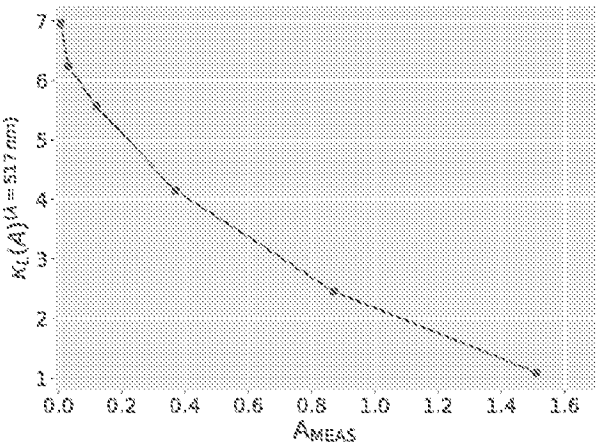


FIG. 3. $\kappa_{eff}(A_R(\lambda))$ at 517 nm as a function of measured absorbance, $A(\lambda)_{MEAS}$.

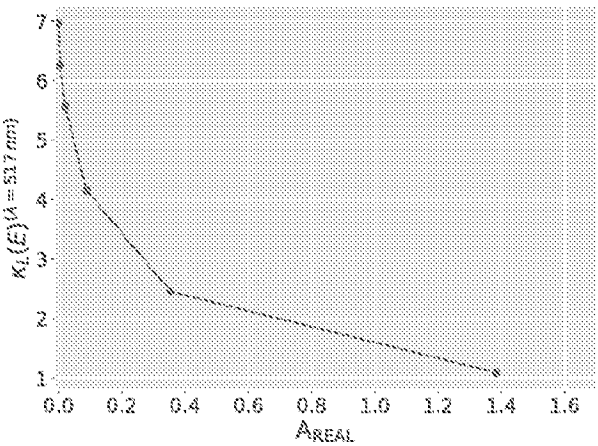


FIG. 4. $\kappa_{eff}(A_R(\lambda))$ at 517 nm as a function of real absorbance, $A(\lambda)_R$.

Using the data in Figures 1 and 2, $\kappa_{eff}(A_R(\lambda))$ can be calculated at any wavelength by taking the ratio of $A(\lambda)_{MEAS}$ and $A_R(\lambda)$ as given by Equation 4. The path length factor at 517 nm obtained from the Eosin data

is plotted in Figure 3 against measured absorbance, A_{MEAS} and against real absorbance, A_{R} in Figure 4. The intermediate values of $\mathbf{L}(\lambda, \alpha_a)$ are then found via linear interpolation between the measured data points shown. The cavity path length has then been successfully determined at a single wavelength in the range of A_{REAL} between 0.001 1.39. For the paticular cavity geometry used, at 517 nm, $\kappa_{\mathrm{eff}}(A_{\mathrm{R}}(\lambda = 517))$ reaches a maximum value of 7 cm at the lowest absorbance ($A_{\mathrm{MEAS}} = 0.007$) and decreases to a minimum of 1.1 cm at the highest absorbance ($A_{\mathrm{MEAS}} = 1.51$). The method for obtaining $\kappa_{\mathrm{eff}}(A_{\mathrm{R}}(\lambda))$ can be extended to all wavelengths where the dye absorbs sufficiently.

Cavity Path Length in the Presence of Scattering

The effects of scattering on $A(\lambda)_{\mathrm{M}}$ (and thus $\kappa_{\mathrm{eff}}(A_{\mathrm{R}}(\lambda))$) when the sample has a non-zero scattering coefficient are shown for two cases in Figures 5 6. It is clear that in both cases where the dye concentration is significantly different, the presence of scattering in the solution has negligible effect on the measured absorbance spectrum illustrating that the cavity path length is insensitive to sample scattering. Thus the calibration method outlined above for zero-scattering can be applied to samples of arbitraty scatteirng coefficients. The corresponding extinction ($A(\lambda)_{\mathrm{R}}$) spectra for the 488 nm Eosin series are shown in Figure 7, where the scattering due to the silica particles is evident in the broad Rayliegh type spectrum exhibited (note the underlying Eosin absorbance profile partly visbile in some the spectra where scattering and absorbance are comparable).

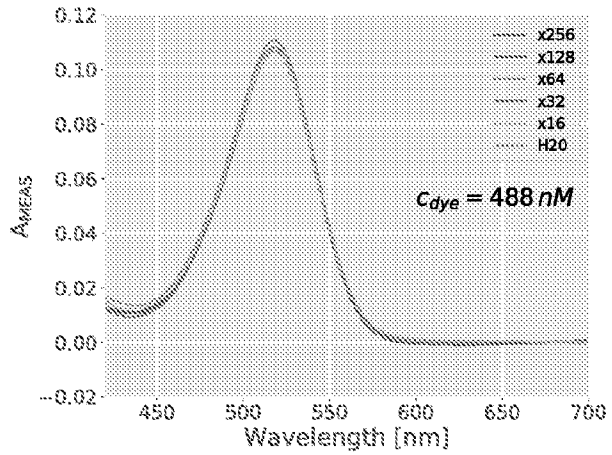


FIG. 5. $A(\lambda)_{\mathrm{MEAS}}$ spectra of 488 nM Eosin in solutions of increasing scattering coefficients, where the dilution of the silica particles from stock is indicated in the legend.

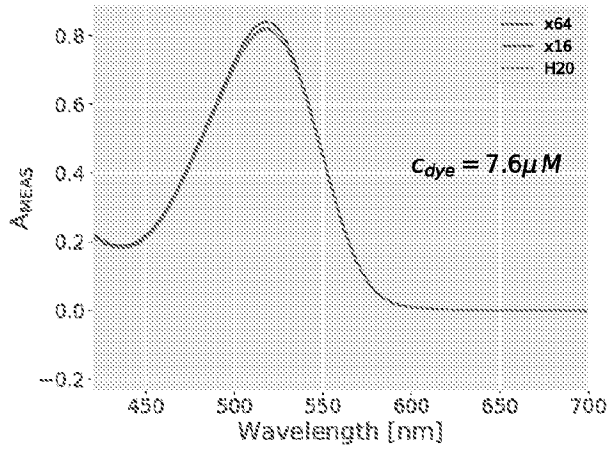


FIG. 6. $A(\lambda)_{\mathrm{MEAS}}$ spectra of 7.8μM Eosin in solutions of increasing scattering coefficients, where the dilution of the silica particles from stock is indicated in the legend.

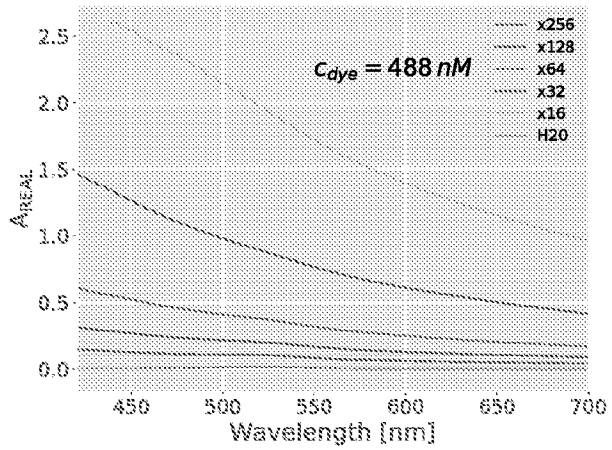


FIG. 7. Corresponding extinction spectra,$A(\lambda)_{\mathrm{R}}$, for the 488 nM Eosin + silica concentration series, where the dilution of the silica particles from stock is indicated in the legend.

I. APPLYING CAVITY CALIBRATION TO AN ARBITRARY SOLUTION:

The calibrated cavity spectrometer, characterised by $\kappa_{\mathrm{eff}}(A(\lambda))$, can now be used to quantitatively determine the extinction and (real) absorption spectra of an arbitrary sample with an absorbance within the range for which $\kappa_{\mathrm{eff}}(A(\lambda))$ has been measured. This is illustrated in Figures 8 and 9, where two food dyes, Blue1 and Red 3 respectively, with different absorption spectra were measured in the cavity spectromter. The dyes absorb at significantly different wavelengths and thus are ideal to test the validity of the calibration method. Using a suitable mathematical model that computes $\kappa_{\mathrm{eff}}(A(\lambda))$ based on the Eosin calibration data, the measured ab-

sorbance, $A(\lambda)_{\mathrm{M}}$, can be recalibrated to yield the *calibrated absorbance*, which, as shown in the figures is almost identical to the real absorbance, $A(\lambda)_{\mathrm{R}}$ (obtained via the transmission mode measurment). These two cases illustrate the validity of the proposed approach for returning the equivalent absorption spectrum in transmission mode from the measured absorbance in absorbance mode. Thus for a sample with arbitrary scattering coefficient, the approach is still valid and will correctly yield the sample's real absorbance spectrum, $A(\lambda)_{\mathrm{R}}$, along with its extinction spectrum, $E(\lambda)_{\mathrm{R}}$ simultaneously.

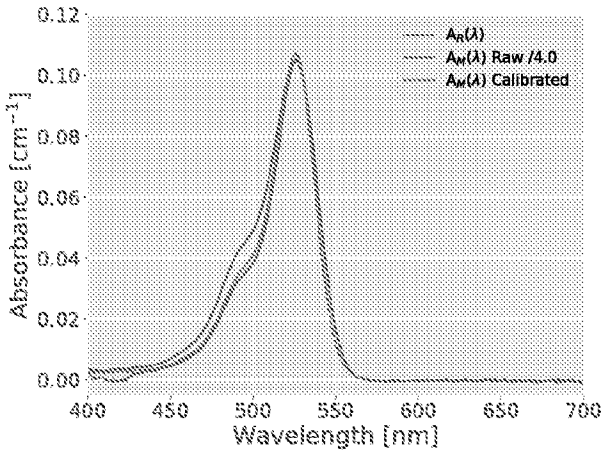


FIG. 8. $A(\lambda)_{\mathrm{R}}$ spectrum of 1.25μM Blue1 in H20 along with the raw absorbance spectrum, $A(\lambda)_{\mathrm{M}}$, scaled by a factor of 4 for comparison, and the calibrated version of $A(\lambda)_{\mathrm{M}}$.

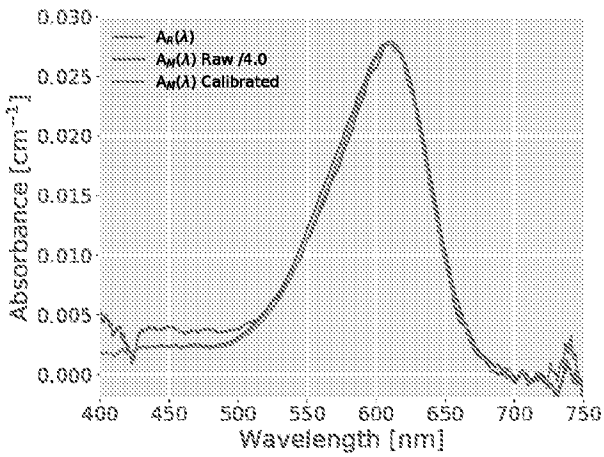


FIG. 9. $A(\lambda)_{\mathrm{R}}$ spectrum of 1.25μM Red 3 in H20 along with the raw absorbance spectrum, $A(\lambda)_{\mathrm{M}}$, scaled by a factor of 4 for comparison, and the calibrated version of $A(\lambda)_{\mathrm{M}}$.

APPENDIX A - MEASUREMENT PROCEDURE

The following steps are used to perform a full measurement of a sample using the invention:

1. The user sets the spectrum integration time and the total number, N, of spectral acquisitions required for the measurement. For each step (reference, sample and dark), the average spectrum is computed by taking the average of the N spectra acquired.

2. The software is used to set the instrument to absrobance mode.

3. A reference spectrum is acquired by placing 2 mL of reference solution (water in this case) contained in a 1 cm x 1 cm cuvette within the cavity and measuring the intensity of transmitted light in absorbance mode, registered by the software as $I_{\mathrm{R}}^{A}(\lambda)$.

4. The software is used to switch the instrument to extinction mode.

5. The same reference solution is measured in extinction mode, with the intensity of the transmitted light registered by the software as $I_{\mathrm{R}}^{E}(\lambda)$.

6. The cuvette is removed, the reference solution is removed and replaced with the 2 mL of the sample solution, i.e. the dye at the lowest concentration used. The cuvette is replaced into the cavity in the same position as the reference solution.

7. In extinction mode, the intensity of the light transmitted by the sample is measured, registered by the software as $I_{\mathrm{S}}^{E}(\lambda)$

8. The software is used to switch the instrument to absorbance mode and the intensity of the light transmitted by the sample is measured, registered by the software as $I_{\mathrm{S}}^{A}(\lambda)$.

9. The software is set to dark mode (i.e. the light source is switched off) and a dark spectrum is measured, registered by the software as $I_{\mathrm{D}}(\lambda)$.

10. Steps 5-7 are repeated for the entire set of samples in the dilution series, from the lowest concentration of dye to the highset, where new reference samples are taken in between if lamp drift is an issue.

The extinction and (measured) absorption spectra of the n^{th} sample are then computed as:

$$E^{n}(\lambda) = -\log_{10}\left(\frac{I_S^E(\lambda) - I_D(\lambda)}{I_R^E(\lambda) - I_D(\lambda)}\right), \qquad (6)$$

and

$$A_M^n(\lambda) = -\log_{10}\left(\frac{I_S^E(\lambda) - I_D(\lambda)}{I_R^E(\lambda) - I_D(\lambda)}\right), \quad (7)$$

where n is the sample number in the dilution series, meaning $n = 1$ is the lowest concentration and $n = n$ is the highest concentration.

For the extinction and absorption spectra shown (zero scattering case), each spectrum is then post processed by first subtracting a constant background. In the case of Eosin B, this is done by taking the average value of of each spectrum in the 700 to 750 nm, where the dye does not absorb. Each spectrum is then smoothed to remove noise by using a Savitzky-Golay filter with a box width of 61 and a polynomial of order 2. The measured absorption spectrum is then converted into the real absorption spectrum as outlined above using Equation 5, yeilding 2 spectra, namely the extinction $E(\lambda)$ and the real absorption, $A_R(\lambda)$ spectra.

APPENDIX B - EXPERIMENTAL DETAILS

Eosin B, sourced from SigmaAldrich, samples were prepared by diluting a stock of 500 μM in water. The stock solution was prepared from the powder as received. Scattering solutions of 300 nm silica particles were prepared by dilution from a stock solution of 50 mg mL^{-1} aqueous solutions as received from the supplier. Sacttering solutions were then mixed with equal volumes of Eosin B to achieve the desired final dye+scattering concentration. Implicit in this approach is the assumption that the dye molecule and the scattering particles do not interact, either through electrostatic adsorption of the molecules to the particle surface or through chemical interaction. For this reason, it is desirable to use a dye that has the same charge as the particle surface; in the case here, Eosin B is negatively charged and the silica particles have a COOH surface group that will be negatively charged in solution, so there should be no interaction between both species, as evidenced by the similarity between the dye absorbance spectrum in dissolved in H20 and in the silica solutions. All samples were prepared immediately prior to measurement in the instrument. After each sample was measured in a dilution series, cuvettes were washed thoroughly with water, then ethanol, then water as required and a new water reference was taken if needed.

REFERENCES

CLAIMS

1. A spectrometer apparatus for measuring spectra of a liquid sample, the apparatus comprising:

an integrating cavity comprising a reflective inner wall or walls, and configured to receive a cuvette containing liquid sample within the integrating cavity,

wherein the integrating cavity comprises at least one light inlet port and at least one light outlet port, the or each light inlet port being configured to receive light from at least one light source and the or each light outlet port being configured to deliver light to a spectrometer;

the apparatus further comprising a light path adjuster configured to selectively adjust a light path through the integrating cavity such that at least two distinct light paths are provided; wherein

when the light path adjuster is in a first configuration, the apparatus is in a transmission mode in which light from the light source follows a first light path from the or one of the light inlet port(s) to the liquid sample such that the light from the light source irradiates the liquid sample directly before the light transmitted by the sample is transmitted through the or one of the light outlet port(s) and received by the spectrometer for wavelength analysis of the light to provide an extinction spectrum of the liquid sample; and

when the light path adjuster is in a second configuration, the apparatus is in a diffusely reflecting mode in which light from the light source follows a second light path from the or one of the inlet port(s) into the integrating cavity, is incident onto the reflective inner wall or walls of the integrating cavity and is diffusely reflected within the integrating cavity, such that the light from the light source irradiates the liquid sample before being transmitted through the or one of the light outlet port(s) and received by the spectrometer for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the liquid sample.

2. The apparatus of claim 1 arranged such that, when in the second configuration, light from the second light path is transmitted:

a. directly from the inlet port onto the wall or walls of the integrating cavity; and/or

b. directly from the inlet port, onto and through the sample and subsequently onto the wall ficor walls of the integrating cavity.

3. The apparatus of claim 1 or claim 2 wherein the inlet port used in the first configuration is directly opposed from the outlet port used in the first configuration such that, when in the first configuration, the first light path extends directly across the integrating cavity.

4. The apparatus of any one of claims 1to 3 further comprising the light source.

5. The apparatus of any one of the preceding claims further comprising a controller configured to control the light path adjuster to selectively adjust the path of light through the apparatus.

6. The apparatus of claim 5 wherein the controller is an integral part of the apparatus and is in direct communication with the apparatus.

7. The apparatus of claim 5 wherein the controller is remote from the apparatus and is configured to be in wireless communication with a transceiver of the apparatus.

8. The apparatus of any one of claims 5 to 7 wherein the controller is configured to control the spectrometer, and in particular is configured to process the light received by the spectrometer for wavelength analysis of the light to provide the extinction and/or absorbance spectrum of the liquid sample contained in the cuvette.

9. The apparatus of claim 5 further comprising the spectrometer.

10. The apparatus of any one of claims 5 to 9 wherein the controller is configured to control one or more of:

a. switching between the first and second configurations;
b. acquiring spectra from the integrating cavity;
c. choosing operating conditions;
d. displaying spectra on a display of the apparatus, or of the controller, or in communication with the apparatus or controller;
e. saving data on a memory of the apparatus, or of the controller, or in communication with the apparatus or controller;
f. a user-interface of the apparatus, or of the controller, or in communication with the apparatus or controller, that interacts with the apparatus and allows a user to control the position of the light path adjustment mechanism.

11. The apparatus of any one of the preceding claims wherein the light path adjuster comprises at least one movable optical element configured to manipulate light incident on the optical element from the light source, the light path adjuster being configured to adjust the movable optical element to selectively provide the first and second light paths.

12. The apparatus of claim 11 wherein the optical element is adjustable by moving the optical element with respect to the integrating cavity from a first position in which the light travels along the first light path, and a second position in which the light travels along the second light path.

13. The apparatus of claim 12 wherein the integrating cavity comprises orthogonal longitudinal, vertical, transverse axes, and any one or more of the following positional

characteristics of the optical element may be adjusted with respect to any one or more of the axes:

a. longitudinal position;
b. vertical position;
c. transverse position
d. orientation;
e. inclination.

14. The apparatus of any one of claims 11 to 13 wherein a plurality of movable optical elements are provided.

15. The apparatus of claim 11 wherein the movable optical element is selected from:

a. a prism;
b. a lens;
c. a mirror;
d. a diffraction grating;
e. a fibre optic cable;
f. the light source.

16. The apparatus of any one of claims 11 to 15 wherein the light path adjuster comprises at least one fixed optical element which is not adjustable with respect to the integrating cavity.

17. The apparatus of claim 16 wherein the fixed optical element is configured to manipulate the light from the light source prior to the light inlet port.

18. The apparatus of claim 16 or claim 17 wherein the fixed optical element is configured to manipulate the light from the light outlet port.

19. The apparatus of any one of claims 16 to 18 wherein the fixed optical element is selected from:

a. a prism;
b. a lens;
c. a mirror;
d. a diffraction grating;
e. a fibre optic cable;
f. the light source.

20. The apparatus of any one of the preceding claims wherein the light path adjuster comprises at least one electronic controller operative to effect selective operation of one or more light sources, to selectively provide the first and second light path.

21. The apparatus of claim 20 comprising at least first and second light sources, the controller

being configured to control each light source independently.

22. The apparatus of any one of the preceding claims wherein the light path adjuster is positioned between the light source and the light inlet port.

23. The apparatus of any one of the preceding claims wherein the light path adjuster is positioned between the spectrometer and the light outlet port.

24. The apparatus of any one of the preceding claims wherein a plurality of light path adjustment mechanisms are provided.

25. The apparatus of any one of the preceding claims wherein a plurality of light inlet ports are provided, the light path adjuster being configured to provide the first light path by directing light from the light source through a first light inlet port, and to provide the second light path by directing light from the light source through a second light inlet port.

26. The apparatus of any one of the preceding claims wherein a plurality of light outlet ports are provided, the first light path directing light from the integrating cavity through a first light outlet port, and the second light path directing light from the integrating cavity through a second light outlet port.

27. The apparatus of any one of the preceding claims wherein the integrating cavity comprises any one of:

a. a diffusely reflecting spherical integrating cavity;
b. a cylindrical cavity;
c. a cuboidal or square cavity.

28. The apparatus of any one of the preceding claims wherein the integrating cavity comprises an internal coating configured to provide any one or more of:

a. specular reflectance;
b. diffuse reflectance;
c. reflectance in the UV light spectrum;
d. reflectance in the visible light spectrum;
e. reflectance in the infra-red spectrum.

29. The apparatus of any one of the preceding claims wherein the light source comprises any one or more of:

a. a quartz-halogen source;
b. an LED;
c. a laser;
d. any polychromatic source.

30. The apparatus of any one of the preceding claims wherein the shape of the cuvette is:

a. square;
b. plate-like;
c. cylindrical;
d. spherical;

31. The apparatus of any one of the preceding claims being a UV-VIS spectrometer apparatus.

32. The apparatus of any one of the preceding claims further comprising a sample holder configured to retain a cuvette containing liquid sample within the integrating cavity.

33. The apparatus of any one of the preceding claims wherein the light source comprises first and second LED light sources, and the light path adjuster comprises a controller configured to control the first and second LED light sources such that when in the first configuration, the first LED light source is controlled to provide light on the first light path, and when in the second configuration the second LED light source is controlled to provide light on the second light path.

34. The apparatus of claim 33 wherein light from each LED light source is delivered to the integrating cavity via a respective fibre optic cable.

35. The apparatus of claim 33 or 34 wherein each LED light source delivers light to a respective light inlet port.

36. The apparatus of any one of claims 33 to 35 wherein each light path delivers light through a respective light outlet port.

37. The apparatus of any one of claims 33 to 36 wherein the first LED light source is associated with a collimation lens positioned between the first LED light source and the light inlet port associated with that LED light source

38. The apparatus of any one of claims 33 to 37 further comprising first and second outlet ports, and a beam splitter configured to selectively allow light from the first and second outlet ports to be transmitted to the spectrometer.

39. A spectrometer apparatus for measuring spectra of a liquid sample, in particular where the spectra obtained are the absorption and extinction spectra of the sample, the apparatus comprising:
an integrating cavity comprising a reflective inner wall or walls, and configured to receive a cuvette containing liquid sample within the integrating cavity,
wherein the integrating cavity comprises at least one light inlet port and at least one light outlet port, the light inlet port being configured to receive light from a light source and the light outlet port being configured to deliver light to a spectrometer;
the apparatus further comprising a light path adjuster configured to selectively adjust a light path through the integrating cavity such that at least two distinct light paths are provided; wherein:
when the light path adjuster is in a first configuration, the apparatus is in a transmission mode in

which light from the light source follows a first light path from the light inlet port to the liquid sample such that the light from the light source irradiates the liquid sample directly before the light transmitted by the sample is collected via the light outlet port and received by the spectrometer for wavelength analysis of the light to provide an extinction spectrum of the liquid sample; and

when the light path adjuster is in a second configuration, the apparatus is in a diffusely reflecting mode in which light from the light source follows a second light path from the inlet port into the integrating cavity, and is incident onto either the reflective inner wall or walls of the integrating cavity or directly onto the liquid sample;

wherein light transmitted and/or scattered by the sample is transmitted through the outlet port, the apparatus being configured such that light directly transmitted by the sample is reflected by the inner wall or walls of the cavity before being transmitted through the outlet port, and received by the spectrometer for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the liquid sample.

40. A spectrometer apparatus for measuring spectra of a liquid sample, the apparatus comprising:

an integrating cavity comprising a reflective inner wall or walls, and configured to receive a cuvette containing liquid sample within the integrating cavity,

wherein the integrating cavity comprises a first light inlet port and a second light inlet path at least one light outlet port, the first light inlet port being configured to receive light from a first LED light source and the second light inlet port being configured to receive light from a second LED light source, at least one light outlet port being provided and configured to deliver light to a spectrometer;

the apparatus further comprising a light path adjuster configured to selectively adjust a light path through the integrating cavity such that at least two distinct light paths are provided; wherein

when the light path adjuster is in a first configuration, the apparatus is in a transmission mode in which light from the first LED light source follows a first light path from the first light inlet port to the liquid sample such that the light from the first LED light source irradiates the liquid sample directly before the light transmitted by the sample is transmitted through the light outlet port and received by the spectrometer for wavelength analysis of the light to provide an extinction spectrum of the liquid sample; and

when the light path adjuster is in a second configuration, the apparatus is in a diffusely reflecting mode in which light from the second LED light source follows a second light path from the second inlet port into the integrating cavity, is incident onto the reflective inner wall or walls of the integrating cavity and is diffusely reflected within the integrating cavity, such that the light from the light source irradiates the liquid sample before being transmitted through the, or another, light outlet port and received by the spectrometer for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the liquid sample.

41. The spectrometer apparatus of any one of the preceding claims configured to measure

spectra of a liquid sample selected from any one or more of the following:

a. Water;

b. Wine;

c. A beverage;

d. An edible liquid or partially liquid product.

42. A spectrometer apparatus substantially as described herein and as shown in the accompanying drawings.

43. A method of measuring spectra of a liquid sample using the apparatus of any one of claims 1 to 41, comprising steps of:

a. activating the light source;

b. controlling the light path adjuster to be in the transmission mode or the diffusely reflecting mode; and

c. conducting wavelength analysis of the light transmitted through the light outlet port via the spectrometer for wavelength analysis of the light to provide an absorbance spectrum of the liquid sample contained in the cuvette.

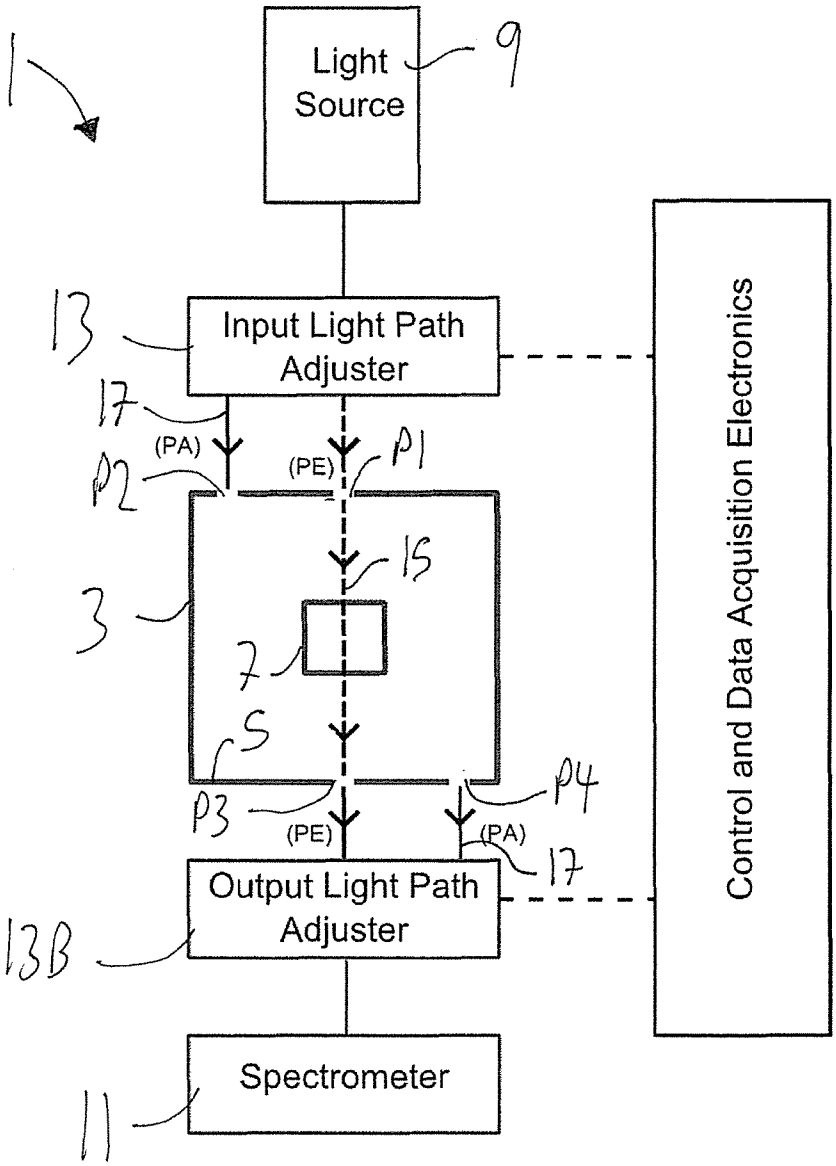

1
Light Source
9
13
Input Light Path Adjuster
17
(PA)
(PE)
P1
P2
15
3
7
5
P3
P4
(PE)
(PA)
17
Output Light Path Adjuster
13B
Spectrometer
11
Control and Data Acquisition Electronics

Figure 1

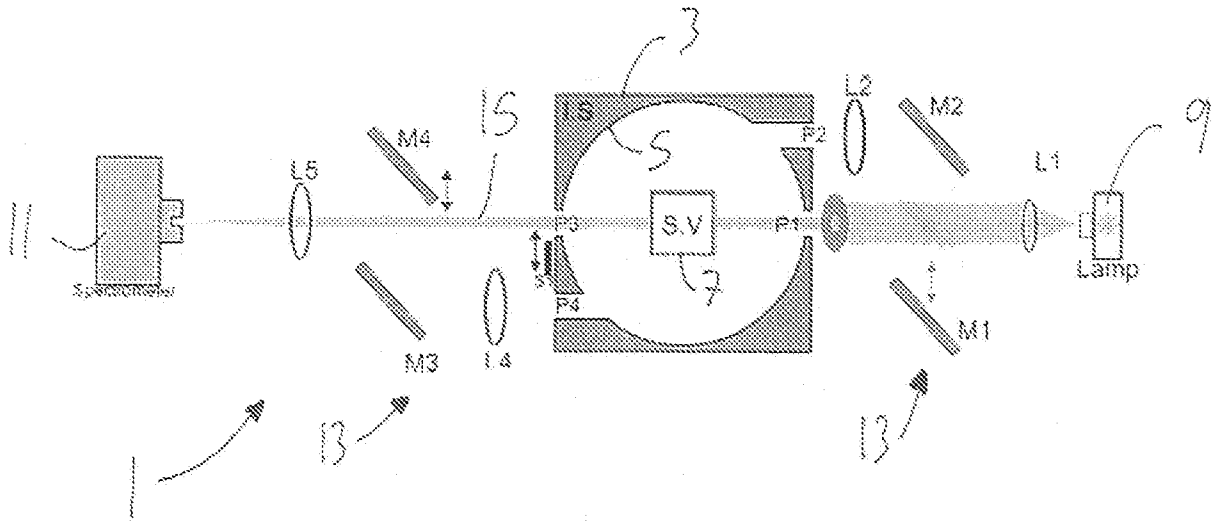


Figure 2a

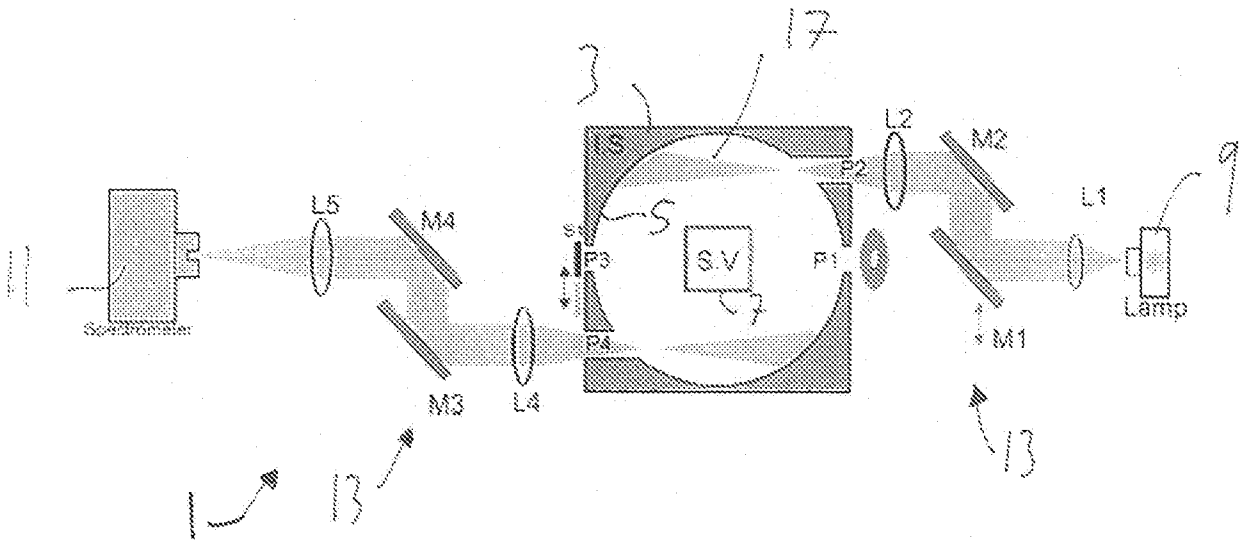


Figure 2b

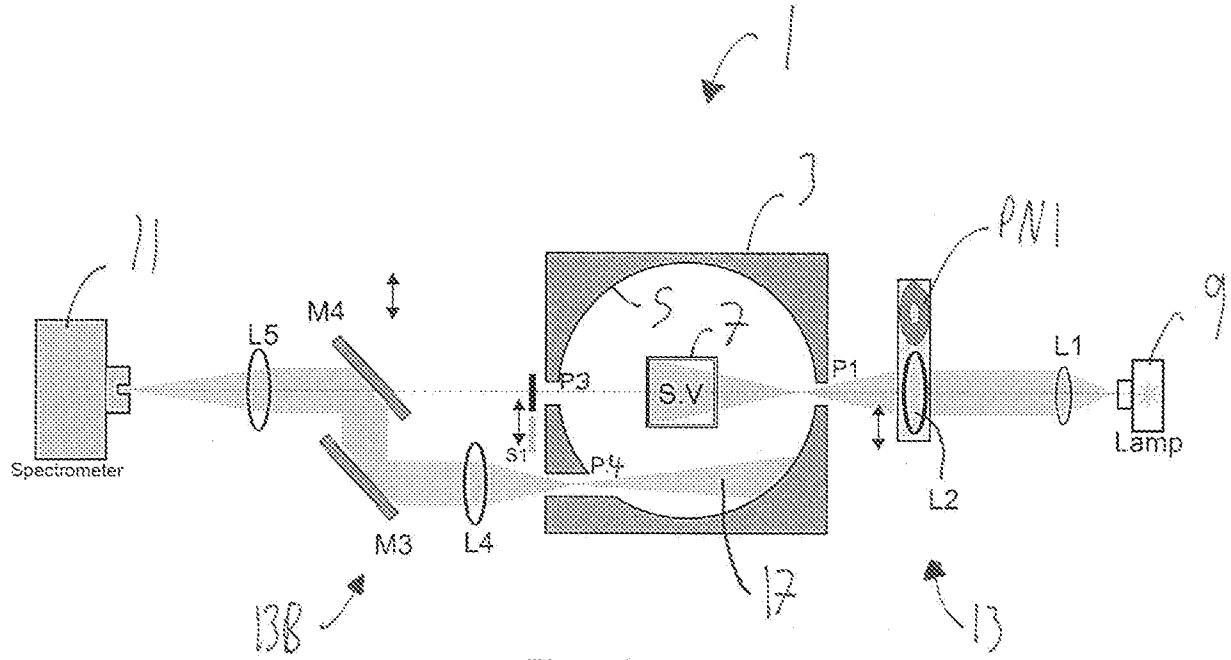


Figure 3a

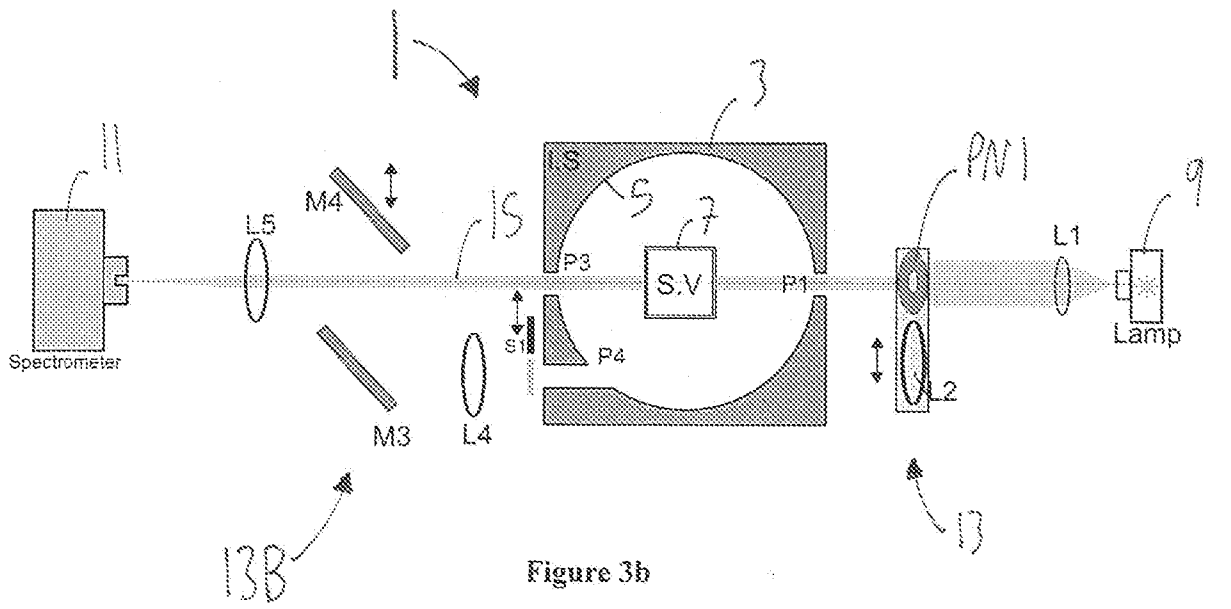


Figure 3b

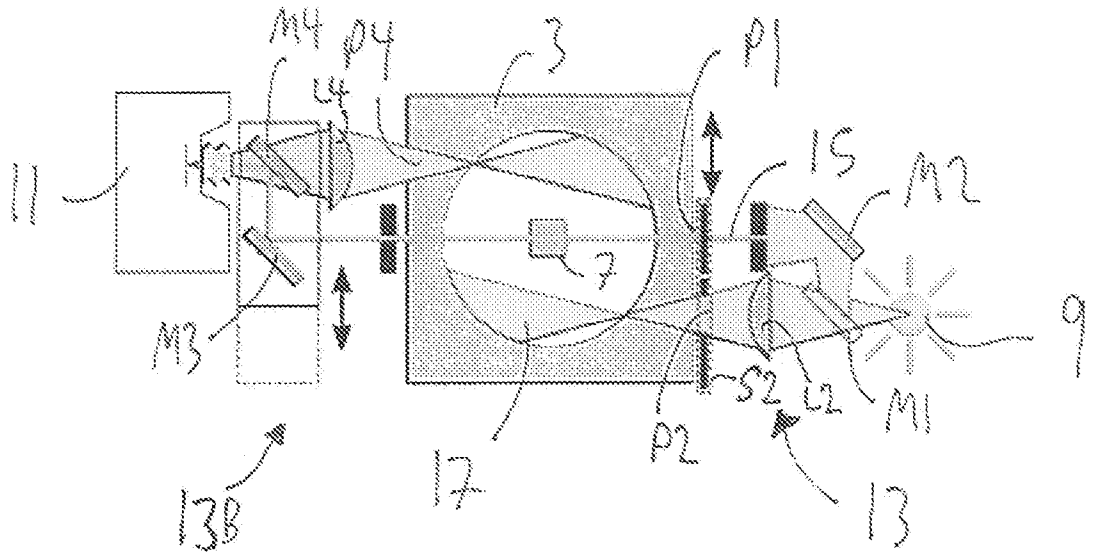


Figure 4

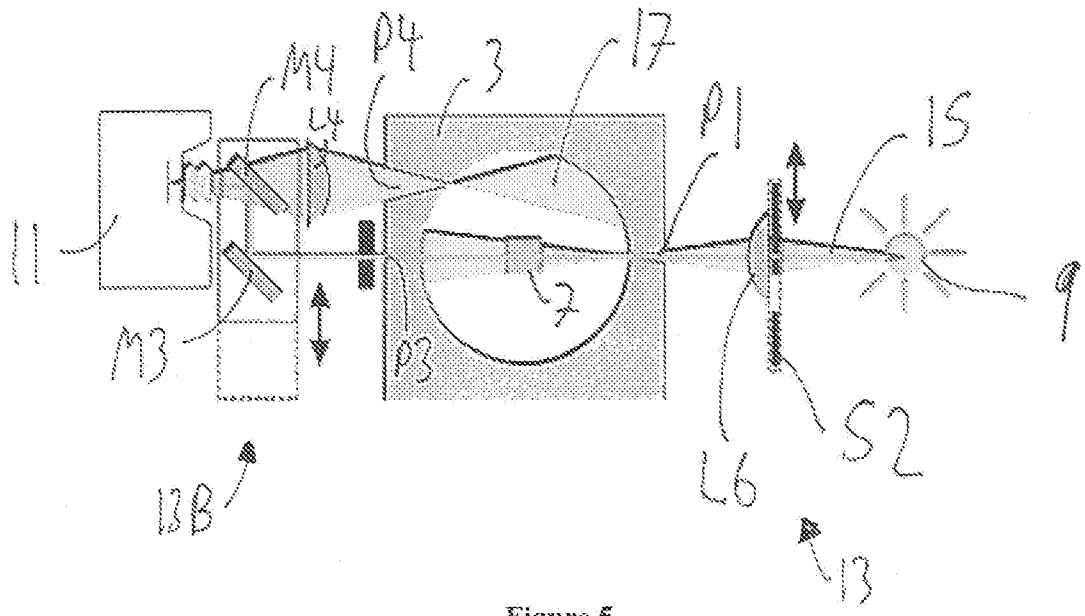


Figure 5

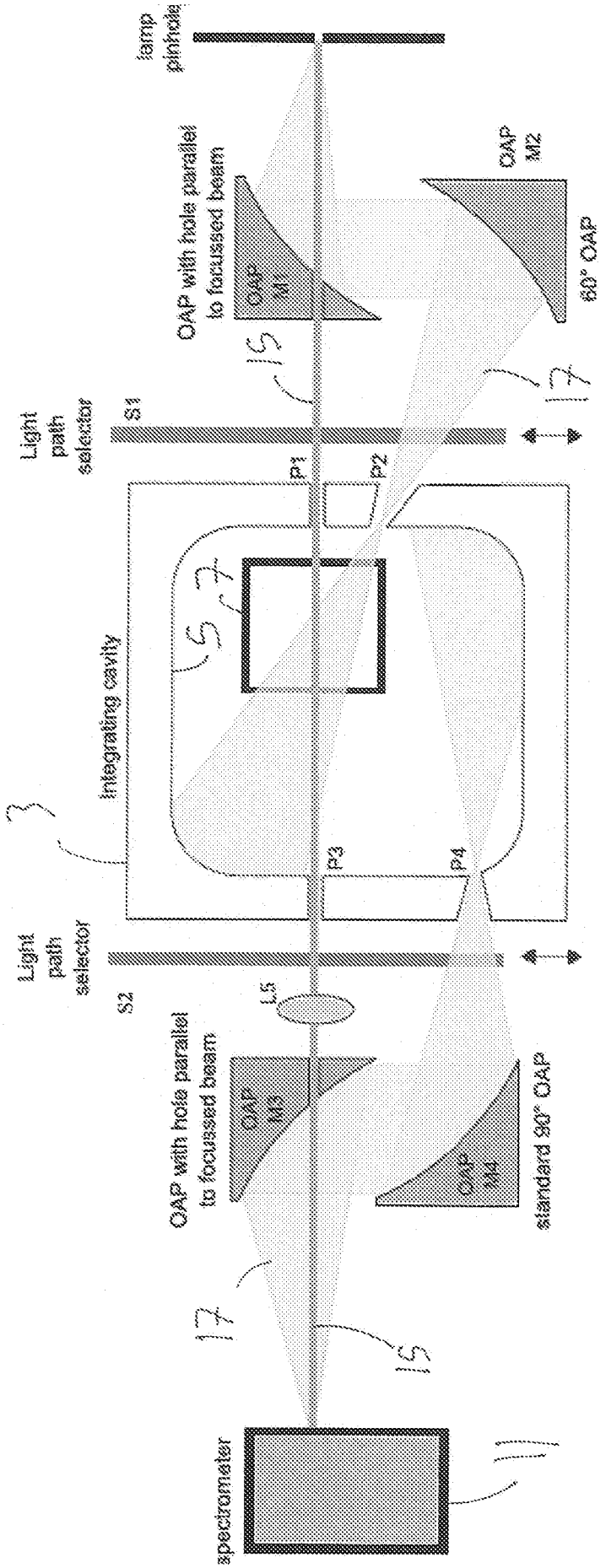

lamp pinhole
OAP with hole parallel to focussed beam
OAP M1
OAP M2
60° OAP
15
17
Light path selector
S1
P1
P2
integrating cavity
3
S
P3
P4
Light path selector
S2
L5
OAP with hole parallel to focussed beam
OAP M3
OAP M4
standard 90° OAP
17
15
spectrometer
11

Figure 6

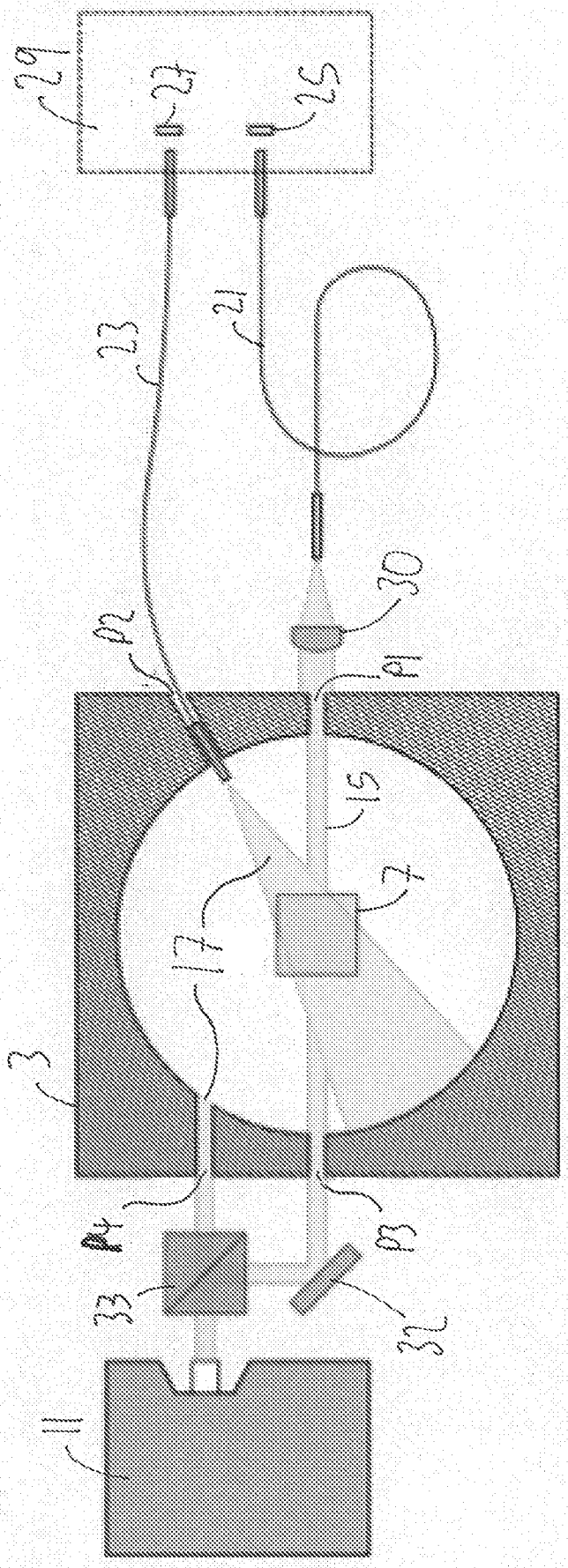


Figure 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2017/050131

A. CLASSIFICATION OF SUBJECT MATTER

G01J 3/02 (2006.01) G01N 21/25 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PATENW: IPC/CPC G01J3/0254, G01N2201/065 and Keywords(extinction, absorption, liquid, fluid, scatter, spectrum) and like terms; Applicant/Inventor search

Google Patents/Scholar: spectrometer, integrating, sphere, cavity adjust light path, absorption, extinction, fluid, spectra, turbid and like terms

Applicants/Inventors names searched in internal databases provided by IP Australia

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 December 2017	14 December 2017
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Andrew Walker AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262223676

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2017/050131

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:

because they relate to subject matter not required to be searched by this Authority, namely:

the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including

2. ☒ Claims Nos.: **42**

because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

See Supplemental Box

3. ☐ Claims Nos:

because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/NZ2017/050131**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7057730 B2 (FRY et al.) 06 June 2006 Abstract; Figures 2-4	
A	US 2010/0309463 A1 (LUCKE et al.) 09 December 2010 Abstract	
A	US 2011/0226961 A1 (OSAWA et al.) 22 September 2011 Abstract; Figures 1-4	
A	EP 2315004 B1 (HAMAMATSU PHOTONICS KK) 20 March 2013 Abstract; Figures 1-8	
A	WO 2005/100955 A1 (MAGYAR TUDOMÁNYOS AKADÉMIA SZEGEDI BIOLÓGIAI KÖZPONT) 27 October 2005 Abstract; Figures	
A	WO 2012/020440 A1 (CONSIGLIO NAZIONALE DELLE RICERCHE) 16 February 2012 Abstract; Figure 1	
A	Nelson, N. B., and Prézelin B. B. "Calibration of an integrating sphere for determining the absorption coefficient of scattering suspensions." Applied Optics 32.33 (1993): 6710-6717. See whole document especially Abstract and pages 1-3	

Supplemental Box

Continuation of **Box II**

Claim 42 does not comply with Rule 6.2(a) because it relies on references to the description and/or drawings.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/NZ2017/050131**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 7057730 B2	06 June 2006	US 2004141179 A1	22 Jul 2004
		US 7057730 B2	06 Jun 2006
		AU 2003290994 A1	15 Jun 2004
		WO 2004046701 A2	03 Jun 2004
US 2010/0309463 A1	09 December 2010	US 2010309463 A1	09 Dec 2010
US 2011/0226961 A1	22 September 2011	US 2011226961 A1	22 Sep 2011
		US 8415639 B2	09 Apr 2013
		CN 102192786 A	21 Sep 2011
		CN 102192786 B	29 Oct 2014
		JP 2011196735 A	06 Oct 2011
		JP 5640257 B2	17 Dec 2014
		KR 20110105349 A	26 Sep 2011
		KR 101781219 B1	22 Sep 2017
		TW 201135197 A	16 Oct 2011
		TW I500912 B	21 Sep 2015
EP 2315004 B1	20 March 2013	EP 2315004 A1	27 Apr 2011
		EP 2315004 B1	20 Mar 2013
		CN 102066910 A	18 May 2011
		CN 102066910 B	09 Jan 2013
		JP 2010008362 A	14 Jan 2010
		JP 5148387 B2	20 Feb 2013
		KR 20110040743 A	20 Apr 2011
		KR 101716902 B1	15 Mar 2017
		US 2011098962 A1	28 Apr 2011
		US 8525989 B2	03 Sep 2013
		WO 2010001700 A1	07 Jan 2010
WO 2005/100955 A1	27 October 2005	WO 2005100955 A1	27 Oct 2005
		HU 0401709 A2	28 Nov 2005
		HU 227140 B1	30 Aug 2010
WO 2012/020440 A1	16 February 2012	WO 2012020440 A1	16 Feb 2012

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/NZ2017/050131**

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Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.