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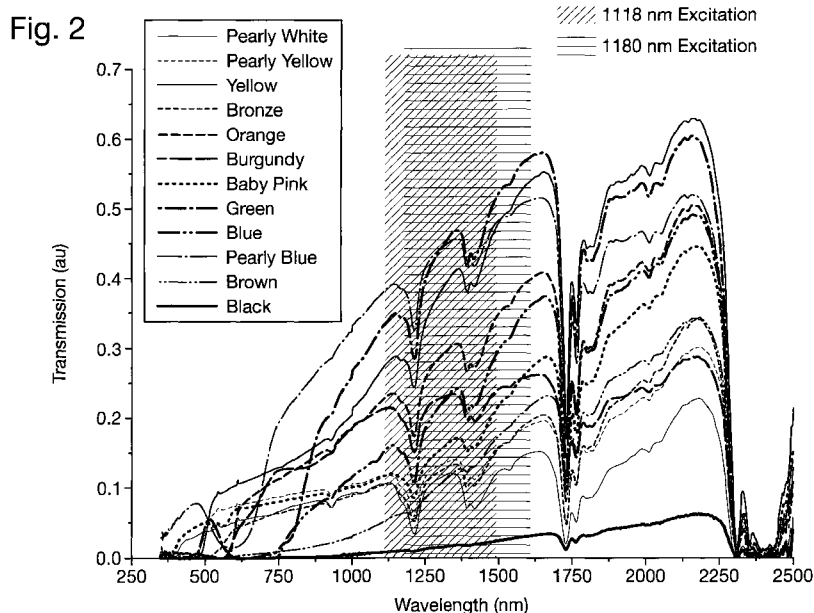
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(54) Title: IMPROVED RAMAN SPECTROSCOPY



(57) Abstract: The invention provides improved Raman spectroscopy based methods and apparatus for determining the characteristics of surfaces or sub-surfaces (i.e. behind a surface or barrier), particularly plastic surfaces. The method is particularly applicable to determining the characteristics of substances within containers, especially plastic containers.

Improved Raman Spectroscopy

This invention relates to improved methods for determining the characteristics of surfaces or sub-surfaces (i.e. behind a surface or barrier), particularly plastic surfaces. The method is particularly applicable to determining the characteristics of substances within containers, especially plastic containers.

Raman spectroscopy is generally undertaken with light sources of wavelengths in the visible or near infra-red regions, such as 532 nm (visible) or 785 nm (near infra-red). Since the intensity of the returned Raman signal is inversely proportional to the fourth power of the excitation wavelength, shorter wavelengths can provide stronger Raman scattering and better signal-to-noise ratio. However, irradiation at 532 nm results in a high level of fluorescence from the irradiated surface, which can overwhelm any Raman signal, and although irradiation with 785 nm suppresses the effect of fluorescence from materials in Raman spectra it is not completely eliminated, and can still create difficulties in identifying a material, especially with some plastic and glass materials. The use of a longer wavelength (1064nm) has been demonstrated to mitigate the problem of fluorescence further (fluorescence is reduced as the energy of the incident photons is reduced), however at such wavelengths absorption of light by the surface can become an issue, resulting in an incomplete Raman spectrum.

Spatially offset Raman Spectroscopy (SORS) is one technique that has been developed to produce spectra for materials behind surfaces or barriers, or contents inside containers, termed subsurface spectra. The technique exploits the fact that many materials are neither completely transparent to light nor completely block it, but that they tend to inelastic scatter light due to the Raman effect. In such a technique, two Raman spectra are recorded which contain different contributions from the surface/container and subsurface/contents. SORS is based on the generation of one spectra from light detected at the point of light irradiation,

and a second spectra from light detected at an offset position from that point. The two spectra are then subtracted using a scaled subtraction to produce a spectrum of the subsurface/contents, and potentially a spectrum of the material at the surface. Materials are identified by comparing the spectra to those of known materials. This approach enables
5 assessment of the characteristics of a material, such as the contents of a container, without physical contact with the material. For instance identification of drugs or dangerous chemicals at security check points such as in airports, allowing identification of the materials without sampling, which could expose those involved to a potentially hazardous substance. This approach to generating subsurface spectra can in particular suffer from the effects of
10 absorption by the surface, in addition to the problems from fluorescence, resulting in generation of incomplete or low quality spectra.

Therefore, there is a need for improved methods that can overcome the limitations of both fluorescence and absorption. It is an aim of the present application to provide an improved Raman Spectroscopy method, and especially one that overcomes the problems of both
15 fluorescence and absorption in the production of surface and sub-surface Raman spectra.

Accordingly in a first aspect, the present invention provides a method of producing a Raman spectrum which reduces or omits the effect of surface absorption in the spectrum comprising:

irradiating the surface with light of a first wavelength, collecting scattered light, and
20 generating a first Raman spectrum from the light collected;

irradiating the surface with light of a second wavelength, collecting scattered light, and generating a second Raman spectrum from the light collected,

wherein the first and second wavelength are selected such that the Raman shifted ranges of the first Raman spectrum and second Raman spectrum are adjacent or overlap, and have

further been selected such that the first and second Raman spectrum can be combined to reduce or omit the effect of absorption peaks in either spectra resulting from the surface; and combining the first Raman spectrum and second Raman spectrum to produce a third Raman spectrum representative of the surface, which third Spectrum reduces or omits the effect of absorption from the surface.

In one embodiment, the first and second wavelengths are both greater than 1000 nm.

In a preferred embodiment, the method is for producing a Raman spectrum of a sub-surface which reduces or omits the effect of absorption from the surface in the spectrum. The surface may for example be a container, and sub-surface may be the contents of a container.

In one embodiment, the method utilises spatially offset Raman Spectroscopy (SORS).

Such a method for producing a sub-surface Raman spectrum using SORS which reduces or omits the effect of absorption from the surface in the spectrum, may comprise:

- a. Irradiating the surface with light of a first wavelength at a first position;
- b. Collecting scattered light from the first position, and a second position spatially offset from the first position;
- c. Spectrally separating at least a portion of the collected light from each position to produce two Raman spectra from the light collected at each point;
- d. Through scaled subtraction of the two spectra producing a first Raman spectrum representative of the sub-surface;
- e. Repeating steps a to d with light of a second wavelength to produce a second Raman spectrum representative of the sub-surface, wherein both the first and

second wavelength are greater than 1000 nm, and the two wavelengths are selected such that the Raman shifted ranges of the first Raman spectrum and second Raman spectrum are adjacent or overlap, and have further been selected such that the first and second Raman spectrum can be combined to reduce or omit the effect of absorption peaks in either spectra resulting from the surface; and

- f. Combining the first Raman spectrum and second Raman spectrum to produce a third Raman spectrum representative of the sub-surface, which third spectrum reduces or omits the effect of absorption from the surface.

- 10 The method is in particular directed to producing a Raman spectrum of the contents (sub-surface) of a container (surface) which reduces or omits the effect of absorption from the container material in the spectrum, thus providing an improved SORS method for generating a Raman spectrum of a substance, through a barrier or container, which comprises supplying incident light of two or more different wavelengths to the surface of the container.
- 15 Combining Raman spectra from incident light of different wavelengths preferably requires the output wavelength ranges to overlap to enable the baselines to be matched and the intensity of the spectral features to be scaled. Spectral matching algorithms used to identify materials use peak position and relative peak intensity.

- Raman Spectroscopy that provides an output in the stokes shifted Raman region 500-2300cm⁻¹ is preferred as many key features which allow for identification of materials occur in this range. The Raman region of 0-3000cm⁻¹ is however desirable as it contains additional features.

- Wavelengths of 1000nm or greater have been shown to mitigate the effect of fluorescence from the surface and sub-surface which occurs at shorter wavelengths. The selection of suitable wavelengths is also likely to depend on the intensity of the Raman effect available,

since the intensity of the Raman effect decreases with longer wavelengths. One suitable range may be 1000 nm to about 1750 nm.

The Applicant has found that irradiation of a surface with incident light sources of two wavelengths ≥ 1000 nm, can be used to produce two Raman spectra of a sub-surface, which when combined can reduce or omit the effects of absorption in the final spectrum, and thus consequently produce a more representative, sharper or more complete spectrum of the sub surface. The reduction of the effect of absorption in the spectrum should improve the likelihood of matching the spectrum of the contents with comparative spectra in libraries, such as those using matching algorithms.

- 10 Suitable wavelengths can be identified through interrogation of the absorption characteristics, and absorption spectra, of the surface and/or subsurface constituents or materials. The wavelengths may be selected by identifying and avoiding absorption peaks that occur in the Raman shifted region of the surface (container) transmission spectra.

- 15 Accordingly, in a second aspect, the present invention provides a method for selecting two wavelengths for the method of the first aspect to reduce or omit the effect of absorption from a surface in a Raman spectrum, preferably of the subsurface, comprising;

- 20 a. Irradiating the surface at a plurality of wavelengths,
- b. Collecting scattered light for each wavelength;
- c. Spectrally separating the collected scattered light to produce a transmission spectrum for the surface at each wavelength; and
- d. Selecting two wavelengths, preferably above 1000 nm, which display adjacent or overlapping Raman shifted regions, and can be combined to produce a Raman spectrum, preferably of the subsurface, which reduces or omits the effect of absorption from the surface, as compared to separate

Raman spectra, preferably for the subsurface, at the two separate wavelengths.

The method is in particular directed to selecting two wavelengths to reduce or omit the effect of absorption from the material of a container in a Raman spectrum of the contents of that container.

The Applicant has in particular identified and selected wavelengths suitable for overcoming problems of absorption when interrogating containers produced from high-density polyethylene (HDPE), a common household plastic.

The transmission spectra profiles of HDPE have been interrogated to select ranges of excitation wavelengths suitable for producing spectra of container contents that can be combined to reduce or omit the effects of the absorption of the HDPE container. Essentially to enable any areas of absorption interference in the two spectra to be reduced or preferably omitted, and the two resulting spectra combined due to the adjacency or preferably overlap of the spectral regions.

Two Raman excitation wavelengths suitable for use with HDPE containers are 1118 nm and 1180 nm, chosen such that the resulting Stokes shifted Raman spectrum occurs within the spectral ranges 1255 nm – 1362 nm and 1500 – 1700 nm where there are no HDPE absorption features, resulting in absorption free Stokes shifted Raman spectrum from 506 – 1602 cm^{-1} and 1808 – 3062 cm^{-1} .

Table 1. Raman shift at 1255, 1362, 1500, and 1700 nm, for excitation wavelengths 1118 and 1180 nm.

Excitation wavelength	Raman shift at 1255 nm	Raman shift at 1362 nm	Raman shift at 1500 nm	Raman shift at 1700 nm

1118 nm	976 cm ⁻¹	1602 cm ⁻¹	2278 cm ⁻¹	3062 cm ⁻¹
1180 nm	506 cm ⁻¹	1132 cm ⁻¹	1808 cm ⁻¹	2592 cm ⁻¹

Multiple Raman excitation wavelengths can be selected to produce incomplete Stokes shifted Raman spectra within absorption free spectral windows. These multiple Raman spectra can then be fused together to produce a more complete Raman spectrum, such as

5 one with greater spectral coverage.

The data in Table 2 demonstrates that use of multiple excitation laser wavelengths between 1000 nm – 1255 nm can be used to produce Stokes shifted Raman spectra from 0 – 4117 cm⁻¹ for HDPE by accessing the absorption free spectral windows.

Table 2. Multiple excitation wavelengths between 1000 nm and 1340 nm, and their

10 respective Raman shifts at 1255, 1362, 1500, and 1700 nm, where there are no HDPE absorption features.

Excitation Wavelength	1255 nm	1362 nm	1500 nm	1700 nm
1000	2032	2658	3333	4118
1020	1836	2462	3137	3922
1040	1647	2273	2949	3733
1060	1466	2092	2767	3552
1080	1291	1917	2593	3377
1100	1123	1749	2424	3209
1118	976	1602	2278	3062
1120	960	1586	2262	3046

1140	804	1430	2105	2890
1160	653	1279	1954	2738
1180	506	1132	1808	2592
1200	365	991	1667	2451
1220	229	855	1530	2314
1240	96	722	1398	2182
1260	-32	594	1270	2054
1280	-156	470	1146	1930
1300	-276	350	1026	1810
1320	-392	234	909	1693
1340	-505	121	796	1580

Raman shift is calculated using the following expression:

$$\Delta\omega = (1/\lambda_0 - 1/\lambda_1)$$

Where ω is the Raman shift expressed in wavenumbers, λ_0 is the excitation wavelength and
5 λ_1 is the Raman spectrum wavelength.

The technique however also applies to any material which is at least partially opaque including most common liquid containers, at least partially transparent glass and plastics including HDPE and Polyethylene terephthalate (PET).

The technical benefit of an improved method (method of the first aspect) of identifying
10 substances in HDPE containers improves the time and efficiency of systems for identifying substances in common containers.

Two collection points, for example at the point of incidence and at one point spatially offset from the point of incidence, are sufficient to produce spectral data for SORS. In other cases more collection points spatially offset from each other may be used and the spectral data combined to yield more accurate or more complete data to determine the characteristics of the sub-surface and/or surface.

Two wavelengths of incident light are sufficient to produce spectral data that can be combined to reduce or omit the effects of absorption. More wavelengths may however be used and the spectral data combined to yield more accurate or more complete data to determine the characteristics of the sub-surface and/or surface.

10 The method may further comprise steps of identifying the material using a processor and library matching algorithms.

Thus, with this method spectroscopic information can be obtained that can be interpreted to establish the contents of a container without exposure to the contained substance. The present invention uses multiple wavelengths in the longer SWIR range to allow Raman features of the contained substances to be obtained which could otherwise be unavailable due to reabsorption of scattered light.

The power density of the light source/laser is maintained in a range to optimise scattering without melting/damaging the container/barrier.

The spatially offset measurement point in SORS is preferably at an optimum distance from the point of incidence of the light source, which for these wavelengths is typically between 2 - 5 mm.

With the present invention for substances in a container, the collection of Raman spectra from points spatially offset from the point of incidence of the probe laser results in a series of spectra (2 or more). The series of spectra taken contain different relative contributions of the

Raman signals generated from the container material and the substance contained. In repeating the process for a second wavelength a different set of data is produced. This enables more representative spectra of the contained substance to be obtained by applying numerical processing to the two resulting spectra to produce a spectrum representative of the substance which can be matched to data to identify the substance.

In a third aspect, the present invention provides an apparatus suitable for performing the method of the first aspect comprising means for providing two wavelengths of light, preferably of greater than 1000 nm.

The means for providing the two wavelengths of light may be two separate light sources, such as two lasers.

The wavelengths of light may be 1118 nm and 1180 nm, though numerous other wavelengths are possible.

The apparatus may comprise a processor for undertaking scaled subtraction of spectra, and/or for combining spectra to reduce or omit the effect of absorption from the surface, or container.

The present invention will now be described with reference to the following non-limiting examples and drawings in which

Figure 1 illustrates transmission spectra of a number of coloured HDPE containers from household products in which Raman shifted regions from excitation at 785 nm, 1064 nm and 1240 nm are overlaid for comparison; and

Figure 2 illustrates transmission spectra of coloured HDPE containers from household products in which Raman shifted regions from excitation at 1118 nm and 1180 nm are overlaid for comparison.

Examples

Optimising Wavelengths for Generating Sub-surface Raman Spectra

- 5 Problem: Detecting the contents of a bottle without sampling the potentially hazardous material.

SORS is one method that has been demonstrated as providing a solution to this technical challenge for some contents and container combinations. However, whilst SORS allows through-barrier detection, fluorescence from the container and/or contents can still be
10 problematic. This fluorescence can mask at least the weaker Raman chemical fingerprint signals of the contents, thereby preventing detection.

Using a longer excitation wavelength that falls outside (or on the tail) of the fluorescence absorption band can help to mitigate against fluorescence from the container and/or contents, and the Applicant has shown that a single wavelength of 1064 nm can be used to
15 overcome or reduce sample fluorescence in the Raman spectra, as opposed to shorter wavelengths typically used in commercial Raman devices (e.g. 785 nm).

Despite promising results obtained using 1064 nm, some unrepresentative spectra were obtained for detection through some materials, particularly plastics such as HDPE.

Absorption peaks present in the container absorption spectra that occur in the Raman
20 shifted region can affect the completeness or quality of any spectrum, and especially can affect scaled subtraction and result in unrepresentative sample spectra being obtained. These unrepresentative spectra can cause problems for identification, such as through library matching algorithms.

The Applicant has considered these problems.

Having regard to Figure 1 and Figure 2, in an attempt to identify an optimal excitation wavelength for HDPE, a range of commercially available lasers of different wavelengths was considered. The Raman shifted region between 0 – 2250 cm^{-1} resulting from these different
5 excitation wavelengths are overlaid onto the transmission spectra of the HDPE containers to evaluate their potential for improving the quality or completeness of sub-surface Raman spectra.

It is clear from Figures 1 and 2 that all of the SWIR wavelengths considered generate Raman shifted ranges that overlap with absorption features, such as the features resulting
10 from absorption at approximately 1200-1250 nm, 1370-1480 nm, and 1700-1850 nm from the HDPE containers. Therefore, it is highly likely that use of these wavelengths would result in the production of unrepresentative spectra.

Use of an even longer SWIR wavelength would also result in a further reduction in resultant Raman scatter.

15 Transmission spectra were recorded from 69 container materials and from the results, it was concluded that no single available laser wavelength ≥ 1000 nm will avoid absorption peaks from HDPE plastic containers.

The Applicant has identified that a dual wavelength system can however overcome these problems, using at least two wavelengths ≥ 1000 nm, targeted at parts of the transmission
20 spectra where no absorption features occur (e.g. 1255 – 1362 nm and 1500 – 1700 nm for HDPE containers), and as a good example use of the excitation wavelengths of 1118 nm and 1180 nm to cover the Raman shifted ranges 506 – 1602 cm^{-1} and 1808 – 3062 cm^{-1} for HDPE, and produce a more complete spectra free of interference from absorption. This approach overcomes the issues of container and/or contents fluorescence, and avoids

absorption peaks present in the transmission spectra of the barriers/containers of interest, which lead to unrepresentative spectra being obtained.

The Applicant has identified that an apparatus having two excitation wavelengths ≥ 1000 nm can be used to generate more representative or complete sub-surface spectra and

- 5 especially overcome fluorescence from the contents/container and absorption of Raman scattered light by the container, which problems have been shown to result in the production of incomplete or unrepresentative spectra, that in particular can cause problems for library matching algorithms.

Claims

1. Method of producing a Raman spectrum which reduces or omits the effect of surface absorption in the spectrum comprising:

irradiating a surface with light of a first wavelength, collecting scattered light, and generating

5 a first Raman spectrum from the light collected;

irradiating the surface with light of a second wavelength, collecting scattered light, and generating a second Raman spectrum from the light collected,

wherein the first and second wavelength are greater than 1000 nm and are selected such that the Raman shifted ranges of the first Raman spectrum and second Raman spectrum are
10 adjacent or overlap, and have further been selected such that the first and second Raman spectrum can be combined to reduce or omit the effect of absorption peaks in either spectra resulting from the surface; and

combining the first Raman spectrum and second Raman spectrum to produce a third Raman spectrum, which third Spectrum reduces or omits the effect of absorption from the surface.

15 2. A method according to Claim 1 for producing a Raman spectrum of a sub-surface which reduces or omits the effect of surface absorption in the spectrum.

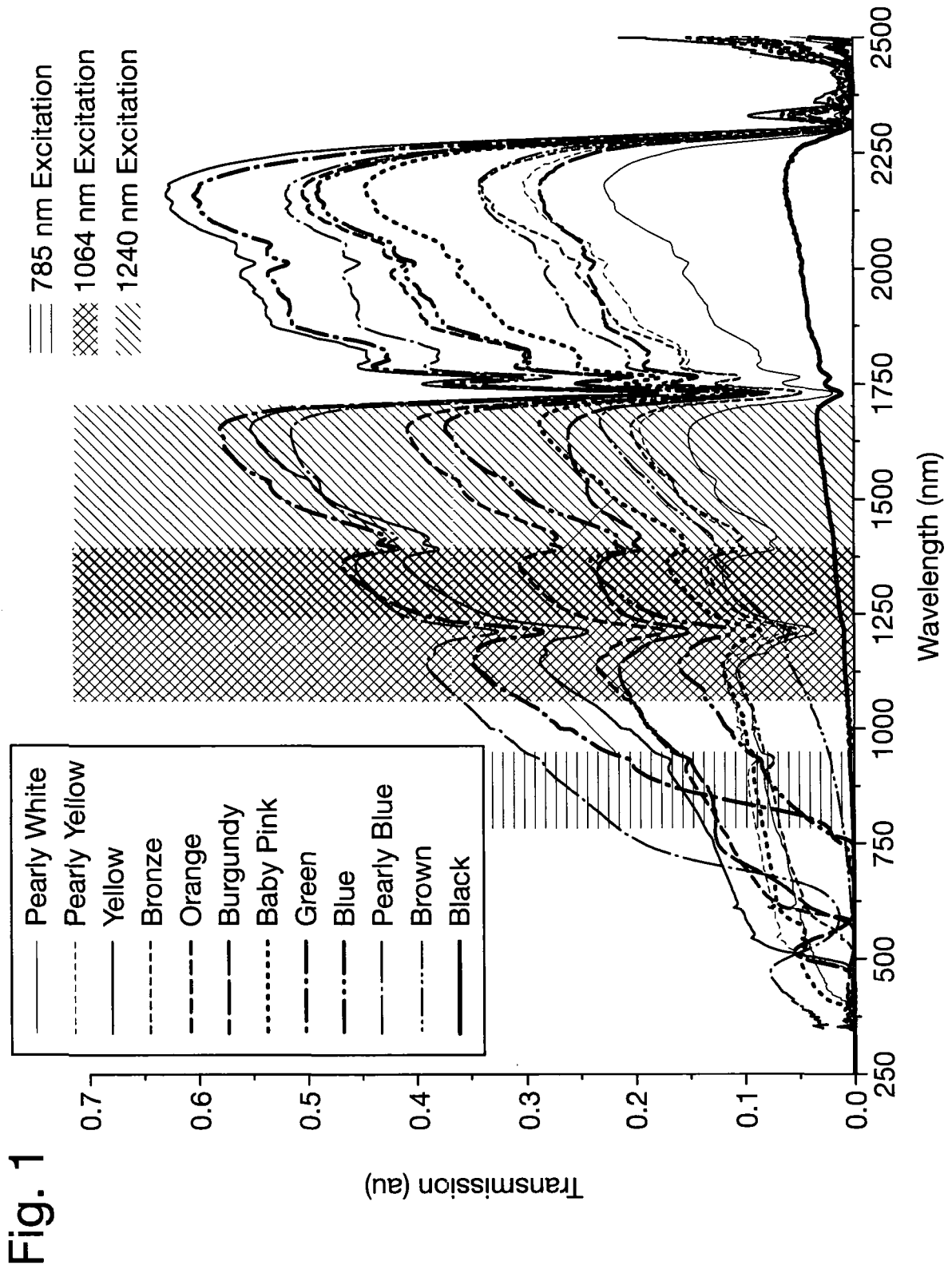
3. A method according to Claim 2, wherein the surface is a container, and the sub-surface is the contents of the container.

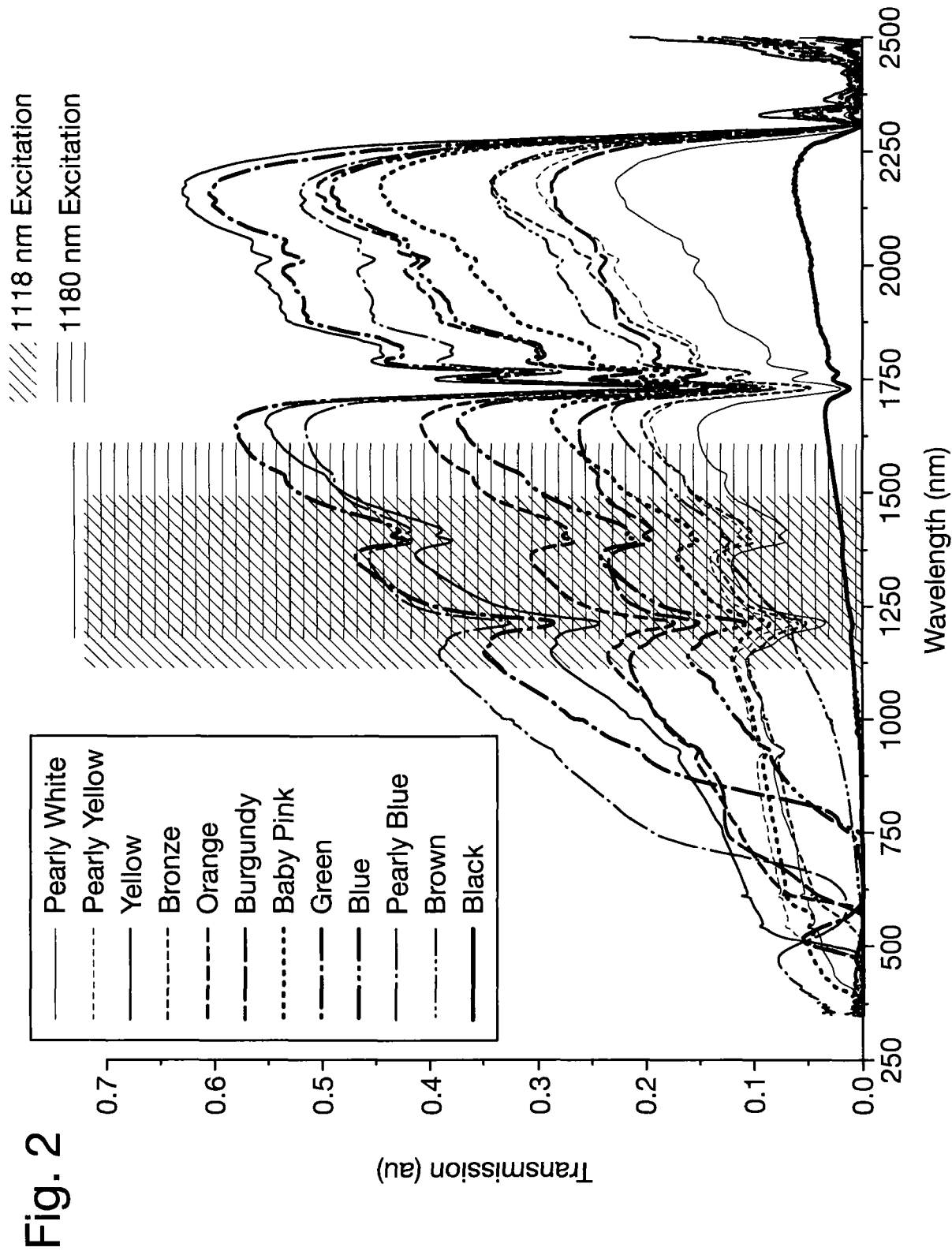
4. A method according to Claim 3 for producing a Raman spectrum of the contents of a
20 container which reduces or omits the effect of absorption from the container material in the spectrum, comprising:

- a. Irradiating the surface of the container with light of a first wavelength at a first position;
 - b. Collecting scattered light from the first position, and a second position spatially offset from the first position;
 - 5 c. Spectrally separating at least a portion of the collected light from each position to produce two Raman spectra from the light collected at each point;
 - d. Through scaled subtraction of the two spectra producing a first Raman spectrum representative of the sub-surface;
 - 10 e. Repeating steps a to d with light of a second wavelength to produce a second Raman spectrum representative of the sub-surface, wherein both the first and second wavelength are greater than 1000 nm, and the two wavelengths are selected such that the Raman shifted ranges of the first Raman spectrum and second Raman spectrum are adjacent or overlap, and have further been selected such that the first and second Raman spectrum can be combined to
15 reduce or omit the effect of absorption peaks in either spectra resulting from the surface; and
 - f. Combining the first Raman spectrum and second Raman spectrum to produce a third Raman spectrum representative of the sub-surface, which third Spectrum reduces or omits the effect of absorption from the surface.
- 20 5. A method according to Claims 1 to 4, wherein the first wavelength is about 1118 nm, and the second wavelength is about 1180 nm.
 6. A method for selecting two wavelengths for the method of Claims 1 to 4 to reduce or omit the effect of absorption from a container material in a Raman spectrum comprising;

- a. Irradiating the surface at a plurality of wavelengths,
 - b. Collecting scattered light for each wavelength;
 - c. Spectrally separating the collected scattered light to produce a transmission spectrum for the surface at each wavelength; and
 - 5 d. Selecting two wavelengths above 1000 nm which display adjacent or overlapping Raman shifted regions, and can be combined to produce a Raman spectrum of the subsurface which reduces or omits the effect of absorption from the surface, as compared to separate Raman spectra for the subsurface at the two separate wavelengths.
- 10 7. An apparatus suitable for performing the method of Claims 1 to 6, comprising means for providing two wavelengths of light of greater than 1000 nm.
 8. An apparatus according to Claim 7, wherein the means for providing two wavelengths are two separate lasers.
 9. An apparatus according to Claim 8, wherein the first of the two lasers provides a
15 wavelength of about 1118 nm, and the second of the two lasers provides a wavelength of about 1180 nm.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/000133

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/65
ADD.

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)
G01N

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)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	page 15, line 4 - page 38, last line; figures	1-9
Y	----- SHREVE A P ET AL: "EFFECTIVE REJECTION OF FLUORESCENCE INTERFERENCE IN RAMAN SPECTROSCOPY USING A SHIFTED EXCITATION DIFFERENCE TECHNIQUE", APPLIED SPECTROSCOPY, THE SOCIETY FOR APPLIED SPECTROSCOPY. BALTIMORE, US, vol. 46, no. 4, 1 April 1992 (1992-04-01), pages 707-711, XP000264023, ISSN: 0003-7028, DOI: 10.1366/0003702924125122 the whole document ----- -/--	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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Name and mailing address of the ISA/

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Politsch, Erich

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/000133

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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