Attenuated total reflectance sensing head
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ABSTRACT

An attenuated total reflectance (ATR) sensing head (10) for use in infra-red (IR) spectroscopy which includes a first IR transmissive body having a prismatic portion (12) which includes a sensing surface (42) for engagement with a sample material, and a second IR transmissive body (14). The prismatic portion (12) has firt IR input and output surfaces (40) which taper towards one another with increasing distance from the sensing surface, and is disposed in a recess formed in the second IR transmissive body, the latter having at least two surfaces (38) optically coupled to the first IR input and output surfaces (40). The angles of the surfaces of the first and second IR transmissive bodies cause polarised radiation to propagate through the ATR sensing head. This enables more accurate measurements to be made.

DESCRIPTION (OCR text may contain errors)

ATTENUATED TOTAL REFLECTANCE SENSING HEAD

CLAIMS (OCR text may contain errors)

Claims

The present invention relates to an attenuated total reflectance sensing head. It relates particularly, but not exclusively, to an attenuated total reflectance sensing head for use in mid-infrared spectroscopy.

Background Art

The absorption of infra-red radiation by a material gives extremely useful information about the molecular structure of that material. If infra-red radiation is directed through a material, some wavelengths will be absorbed and some will be transmitted. Analysis of the resulting absorption spectrum can reveal details about the molecular groups present in the material, and can therefore be used to identify the material. This technique is known as infra-red spectroscopy, and is commonly used in the pharmaceutical, agro- chemical, chemical and food industries to analyse substances.

Liquids absorb very strongly in the mid infra-red region of the electromagnetic spectrum, with optical path lengths through the liquid of more than a few tens of micrometers leading to complete absorption of the radiation. This means that it is extremely difficult to use conventional cuvettes to obtain absorption spectra. The attentuated total reflectance (or ATR) technique was developed to alleviate this problem, as well as enabling in-situ measurements to be carried out.

The basis of the ATR technique is that a crystal element is brought into contact with the material to be analysed. Infra-red radiation is passed through the crystal element and directed towards the crystal element/material interface at an angle greater than the critical angle. This leads to total internal reflection of the radiation and the formation of a non-propagating evanescent wave which extends into the material over a distance approximately equal to the wavelength of the radiation. In the presence of an absorbing medium the evanescent wave

(LR) spectroscopy which consists of or includes a first IR transmissive body having a prismatic portion (12) including a sensing surface (42) for engagement with a sample material, the prismatic portion (12) having first LR input and output surfaces (40) which taper towards one another with increasing distance from the sensing surface, and a second IR transmissive body (14) having at least two surfaces (38) optically coupled to said IR input and output surfaces (40), the second IR transmissive body

(14) being adapted, in use, to direct IR radiation into and away from the IR input and output surfaces respectively.

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2. An ATR sensing head (10) according to claim 1 wherein the second IR transmissive body (14) includes second IR output and second IR input surfaces (38) respectively optically coupled to the first IR input and first IR output surface (40).

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3. An ATR sensing head (10) according to claim 2 wherein the second IR transmissive body (14) includes a recess (18a) defined by at least said second LR input and second LR output surfaces (38) in which the prismatic portion (12) of the first LR transmissive body is disposed.

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4. An ATR sensing head (10) according to claim 3 wherein the first IR transmissive body (12) and the recess (18a) are of a complimentary shape.

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associated change in the totally internally reflected radiation. The totally internally reflected radiation is then monitored to yield the absorption spectrum of the material.

ATR crystal elements are commonly made of infra-red transmitting material such as zinc selenide, silicon or germanium, with zinc selenide being the most common. However, such crystals are not suitable for use with corrosive substances such as strong acids or bases and, due to their potential toxicity, they are also not suitable for use in the food industry. This problem is overcome by the use of an ATR element made of diamond, which is transparent to mid infra-red radiation. Diamond is also suitable as it can be used with corrosive substances, and is non-toxic. However, utilisation of diamond is not simple as the crystals are extremely expensive, and are therefore only used in relatively thin sheets.

A problem with the use of thin flat ATR elements made of diamond, is that in general, at least two interacting internal reflections at approximately 45° at the ATR element/absorbing medium interface are required to effect adequate absorption. This, combined with the fact that the element is mounted at the end of a long narrow cylindrical probe for insertion into a reaction vessel, means that it is a non-trivial problem to pass the radiation into and out of the thin diamond element located at the end of the narrow probe. This is because the radiation must be directed towards the flat diamond ATR element at the required angle of incidence. This problem is alleviated by the use of cheaper ATR elements such as zinc selenide from which a corner cube prism can be made, thereby facilitating a simpler compact retro-reflector design.

A composite attenuated total reflectance (ATR) element is disclosed in US Patent No. 5,773,825 (Axiom Analytical Inc.). This ATR element is bi-layered

transmissive body (14) further includes at least third IR input (32a) and third LR output surfaces which, in use, respectively receive incoming TR radiation and transmit outgoing IR radiation, said third IR input and third IR output surfaces tapering towards one another with increasing distance from the source of incoming

IR radiation.

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6. An ATR sensing head (10) according to claim 5 wherein LR radiation, upon entering the second IR transmissive body (14), is reflected once at an LR reflecting surface (16e) before entering the first IR transmissive body.

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7. An ATR sensing head (10) according to any preceding claim wherein the radiation is reflected n times within the first IR transmissive body (12), where n is an odd integer, before exiting said first LR transmissive body.

8. An ATR sensing head (10) according to claim 7 wherein IR radiation, upon entering the second IR transmissive body (14) from the first IR transmissive body (12), is reflected once before exiting the second LR transmissive body.

9. An ATR sensing head (10) according any preceding claim wherein the second IR transmissive body (14) contains zinc selenide.

10. An ATR sensing head (10) according to any preceding claim wherein the first IR transmissive body (12) contains diamond.

used to support the diamond layer which is made of an infra-red transparent material such as zinc selenide. However, the width of the supporting zinc selenide layer has to be relatively wide in order to provide two interacting internal reflections at the ATR element/absorbing medium interface. This ATR element is therefore not suitable for use in a very narrow probe due to the shape of the two layers of the element.

An aim of the present invention is to provide an ATR sensing head suitable for use in the analysis of corrosive materials such as, for example, strong acids or bases. A further aim of the invention is to provide an ATR sensing head suitable for use in a narrow probe.

Disclosure of Invention

According to a first aspect of the invention there is provided an attenuated total reflectance sensing head as claimed in claims 1 to 10.

According to a second aspect of the invention there is provided a probe as claimed in claims 11 to 16.

Brief Description of Drawings

A number of embodiments of the invention will now be described, by way of example only, with reference to the accompanying Figures, in which:-

Figure 1 shows a cross-sectional view of a first attenuated total reflectance sensing head;

Figure 2a shows a perspective view of a portion of the first attenuated total reflectance sensing head;

radiation directing means for directing radiation towards the sensing head; and c) second radiation directing means for directing radiation away from the sensing head, wherein the sensing head is as claimed in any of claims 1 to 10.

12. A probe (22) according to claim 11 wherein the first radiation directing means includes at least one optical fibre (28 a).

13. A probe (22) according to claims 11 and 12 wherein the second radiation directing means includes at least one optical fibre (28b).

14. A probe (22) according to claims 12 and 13 wherein the first radiation directing means further includes a collimating lens (30a).

15. A probe (22) according to claims 13 and 14 wherein the second radiation directing means further includes a collimating lens (30b).

16. A probe (22) according to claim 11 wherein the first and second radiation directing means includes an elongated radiation-confining tube.

17. An ATR (10) sensing head substantially as described herein with reference to Figures 1, 2, 4 and 5 of the accompanying drawing.

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8. A probe (22) substantially as described herein with reference to Figure 3 of the accompanying drawing.

Figures 3 a and b show a cross-sectional view of a probe and the first attenuated total reflectance sensing head;

Figure 4 shows a cross-sectional view of a second attenuated total reflectance sensing head; and

Figure 5 shows a cross-sectional view of another attenuated total reflectance sensing head. Detailed Description of Preferred Embodiments

Referring to Figure 1, there is shown a cross-sectional view of an attenuated reflectance sensing head (10a) which comprises a first TR transmissive portion (12) made of diamond, and a second, supporting IR transmissive portion (14) made, for example, of zinc selenide. As shown in Figure 2a, the zinc selenide portion (14) is a rectangular solid block with a front face (16a), back face (16b) (not shown), upper face (16c), and lower face (16d), the rectangular solid having a truncated wedge-shaped cut-away portion extending from the upper face (16c) of the rectangular block towards the centre of the block to form an upper recess (18a), and a larger truncated wedge-shaped cut-away portion extending from the lower face (16d) of the rectangular block towards the centre of the block to form a lower recess (18b). Both cut-away portions extend from the front face (16a) to the back face (16b) of the block.

The diamond portion (12) of the sensing head (10a) is of a complimentary shape to, and is disposed within, upper recess (18a) (i.e., it is a hexahedron having a trapezoid vertical cross-section). It is separated from the zinc selenide portion (14) by a small air gap (20) at its lower surface (44). This arrangement is shown in Figure 2b. The tapered surfaces of the diamond and the zinc selenide portions of the sensing head are in optical contact. These surfaces may be coated with an anti-reflection coating, if required.

The probe (22) in which the sensing head (10a) is disposed is formed from an elongated tube of circular cross-section. The ATR sensing head (10a) is located at its distal end. As shown in Figures 3a and 3b, the ATR sensing head (10a) is kept in place by way of a lip (24) located at the end of the probe. The lip (24) protects the zinc selenide portion (14) from, but exposes the diamond portion (12) to, the material under test. A sealing member (26) is disposed on the underside of the lip (24) to prevent material from entering the probe (22) and coming into contact with the supporting portion (14). In the present example, the sealing member is in the form of a ring.

Referring again to Figure 1, during operation of a spectroscope utilising the present invention, infra-red radiation is optic connections (28a,b). The radiation is then collimated by a first lens (30a) into the lower recess (18b) and onto a sloped lower inner surface (32a) of the zinc selenide portion (14), whereupon a portion of the radiation (34) is refracted into the zinc selenide portion, and a portion of the radiation (36) is reflected back into the lower recess.

The angle of slope, θ , of the lower inner surface (32a) of the zinc selenide portion (14) is such that the infra-red radiation (36) reflected by this surface is at right angles to the refracted infra-red radiation (34). As a result, the refracted beam (34) is polarized so that only parallel polarized radiation propagates through the ATR sensing head (10a), and virtually all of the perpendicularly polarized radiation is reflected. This occurs as a consequence of the radiation incident upon the lower inner sloped surface (32a) being at the Brewster (or polarizing) angle, i , where tan i = n , and n is the refractive index of the material from which the second portion (14) is made. A polarized beam of infra-red radiation gives more accurate attenuated total reflection spectra than non-polarised beams because the depth of the evanescent wave into the absorbing medium, and hence the fraction of light absorbed, is polarisation dependent. The required angle, θ , of slope of the lower inner surface (32a) is approximately equal to that required to yield a refracted beam of 45° off the original direction of the radiation. This angle of 45° is the desired angle for propagation of the radiation through the sensing head.

The refracted beam of radiation (34) passes through the zinc selenide towards the outer surface (16e) of the second portion (14). The outer surfaces (16e,f) (i.e., the side faces of the rectangular block) of the zinc selenide portion (14) are substantially parallel to the original direction of propagation of the infra-red beam. The refracted radiation (34) is totally internally reflected at the outer surface (16e) of the zinc selenide portion (14), at an angle, φ_x , of 45°. However, the outer surface (16e) could be mirrored so that total internal reflection does not have to take place at this surface. After being reflected, the beam (34) passes through the zinc selenide towards the upper recess (18a).

The inner surfaces (38) of the zinc selenide portion which define the upper recess (18a) are also sloped. The angle of the slope is such that the beam exits from the zinc selenide portion (14) of the sensing head and enters the diamond portion (12) at an angle, φ_2 , of 90° to both the upper inner surface (38) of the zinc selenide portion, and the sloping side surface (40) of the diamond portion. This ensures that refraction across the diamond/zinc selenide interface does not occur. An index matching fluid may also be used at this interface to improve optical coupling.

The length of the upper face (42) of the diamond portion (12) of the sensing head which comes into contact with the internally reflected three times, as shown in Figure 1. Two of these reflections occur at the diamond/sample interface. Again, the lower surface of the diamond part (12) may be mirrored so that total internal reflection is not an absolute requirement.

After the third total internal reflection, the radiation passes back into the zinc selenide portion (14) of the sensing head. The exit route of the infra-red beam is in the opposite direction to the input route. The radiation exits the ATR sensing head (10a) and enters the lower recess (18b). The exiting radiation is focused onto a fibre optic connection (28b) by a further lens (30b), and is directed to the main spectrometer for further processing and subsequent analysis.

Another embodiment of the invention is shown in Figure 4. The structure of the ATR sensing head (10b) is the same as the aforedescribed ATR sensing head (10a), except that the lower surface (44) of the diamond (12) is in contact with the zinc selenide portion (14) of the sensing head. In addition, the lower surface (44) of the diamond and/or the adjacent zinc selenide portion of the sensing head can be coated with a highly reflective layer of, for example, gold to reflect IR radiation at this coated surface.

For ATR sensing heads (10a) and (10b), the second portion (14) can be made from a material other than zinc selenide, but there will now be a different angle of slope, θ , of the inner surface (32) in order for the beam to be reflected by 45° at the outer surface (16e). It can be shown that the angle, θ , of the slope of the lower inner surface (32a) of the second portion (14) which is composed of a material of refractive index n_2 , in order to provide a 45° refracted beam, is given by:

$$\theta = 180 - \tan^{-1}\left(\frac{1}{1-\frac{\sqrt{2}}{n_2}}\right).$$

Note that where the second portion (14) of the sensing head is made of a material with a different refractive index to zinc selenide, the Brewster condition will not be satisfied, and therefore the radiation will only be partially polarized.

A further embodiment of the invention is shown in Figure 5. Here, the attenuated total reflectance sensing head (10c) case, the second portion (14) of the sensing head has a rectangular cut-away portion in the upper face (16c) of the block, rather than a truncated wedge. As before, the diamond portion (12) of the ATR sensing head (10c) is of a complimentary shape to, and sits in, upper recess (18a).

As zinc selenide and diamond have virtually the same refractive index over the mid infra-red region, where the second portion (14) of the sensing head is made of zinc selenide there will be no significant refraction of the infra-red beam as it travels across the zinc selenide/diamond interface. At this interface (i.e. where the infra-red beam enters and leaves the diamond portion) the zinc selenide and the diamond should be in optical contact. If they are not in optical contact, total internal reflection would occur in the zinc selenide portion, and the radiation would be unable to propagate from the zinc selenide to the diamond. The angle, θ , of the slope of the lower inner surface (32a) of the zinc selenide portion is the same as for the aforedescribed ATR sensing heads (10a,b), i.e., 112.45°. To obtain the reflection of the beam within the diamond portion (12) of the sensing head, the second portion (14) may have an air gap (20) behind the diamond, or the lower surface (44) of the diamond may be coated with a highly reflective coating, as discussed previously.

Where the second portion (14) of the ATR sensing head (10c) is made of a material which does not have the same refractive index as diamond, refraction of the infra-red beam will occur as it crosses the supporting crystal/diamond interface. If the angle of incidence, θ_i , within the diamond (12) is required to be 45°, which is desirable, then the angle, θ , of the slope of the lower inner surface (32a) of the second portion (14) of the sensing head can be shown to be given by:

$$\theta = 180 - \tan^{-1}\left(\frac{\frac{n_1}{n_2}\sin(45)}{\cos\left(\sin^{-1}\left(\frac{n_1}{n_2}\sin(45)\right)\right) - \frac{1}{n_2}}\right)$$

where n_x is the refractive index of diamond, and n_2 is the refractive index of the material from which the second portion (14) of the sensing head is made. The glancing angle, φ , at the outer side walls (16e,f) of the second portion (which is equivalent to the angle of incidence, φ , off normal at the supporting part /diamond interface) is then given by:

n. φ = sin ^{l} — sin(45) , where φ = φ_x = φ_2 - ^{n}2

In the aforedescribed embodiments of the invention, it is shown that three reflections occur within the diamond portion (12) of the sensing head. However, it is possible to have g reflections, where g is an odd integer which will usually be either 1, 3 or 5. For the embodiments shown in Figures 1 and 4 (i.e., where the diamond (12) has a trapezoid vertical cross-section), for a diamond portion of thickness t, we can generalise that for g reflections, the outer length of the diamond portion L_0 and inner length L_i is given by the following:

L, = {g - l)x t and L_0 = {g + l)x t .

For the embodiment of the invention shown in Figure 5 (i.e., where the diamond portion (12) has a rectangular vertical cross-section), the relationship between the length, L, and the thickness, t, of the diamond portion which must be satisfied for 45° infra-red radiation propagation therethrough, is given by: $L \geq (g + 2) \times t$.

For the aforedescribed embodiments of the invention, the surface (46) of the second portion (14) of the sensing head which defines the upper boundary of the lower recess (18b) may be roughened. This stops reflections from the bottom of the diamond portion (12) from being specularly reflected at this surface. If this surface is not roughened, it could possibly lead to specular reflections being detected by the infra-red detector, giving false readings.

The advantages of the aforedescribed ATR sensing heads (10a,b,c) are: 1) polarisation of infra-red radiation incident upon the ATR sensing head (10a,b,c) occurs automatically for a zinc selenide supporting portion without the need for additional polarisers; and 2) the shape of the ATR sensing head (10a,b,c) means that a narrow probe can be used.

Variation may be made to the aforementioned embodiments without departing from the scope of the invention. For example, the surfaces (32) of the second portion of the sensing head where refraction occurs are sloped. The sides (16e,f) of the second portion where reflection occurs are flat. The remaining outer surfaces of the second portion of the sensing head could be curved, leading to a cylindrical second portion with two flats polished on the outer sides.

A further variation to the embodiment shown in Figure 5 is that the second portion (14) of the sensing head could have only one (lower) recess formed therein which receives incoming IR radiation. In this case, the diamond (12) could have a rectangular cross section and may extend across the whole upper surface (16c) of the second portion of the sensing head.

be made from any material transparent to the wavelength of interest. It could, for example, be zinc sulphide or germanium.

Another possible variation to the aforementioned embodiments is that the lower inner surfaces (32) of the second portion (14) of the sensing head could be coated with an anti- reflection coating. This would prevent losses due to reflection of infra-red radiation at the ATR sensing head (10a,b,c) surfaces, but the infra-red beam will not be polarised.

PATENT CITATIONS

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Citing Patent	Filing date	Publication date	Applicant	Title
US20150136986 *	2 May 2013	21 May 2015	Hamamatsu Photonics K.K.	Prism member, terahertz-wave spectroscopic measurement device, and terahertz-wave spectroscopic measurement method

* Cited by examiner

CLASSIFICATIONS

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Cooperative Classification	G01N21/3563, G01N21/35, G01N21/552
European Classification	G01N21/55B

LEGAL EVENTS

Date	Code	Event	Description
7 Mar 2002	AL	Designated countries for regional patents	**Kind code of ref document:** A1 **Designated state(s):** GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG
7 Mar 2002	AK	Designated states	**Kind code of ref document:** A1 **Designated state(s):** AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU CZ DE DK DM DZ EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW
2 May 2002	121	Ep: the epo has been informed by wipo that ep was designated in this application	
22 Aug 2002	DFPE	Request for preliminary examination filed prior to expiration of 19th month from priority date (pct application filed before 20040101)	
10 Jul 2003	REG	Reference to national code	**Ref country code:** DE **Ref legal event code:** 8642

Date	Code	Event	Description
19 Jan 2005	NENP	Non-entry into the national phase in:	**Ref country code:** JP