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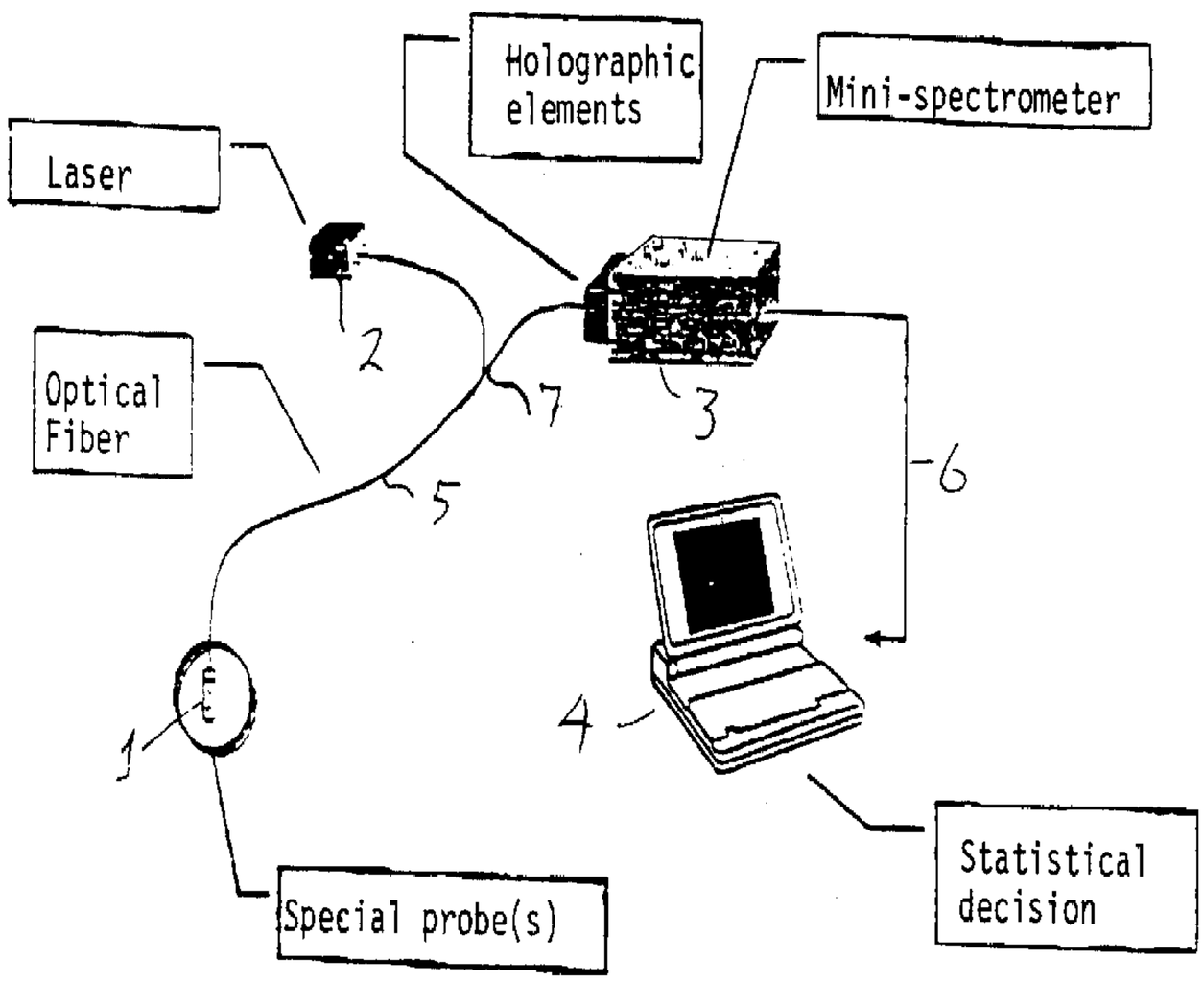
(54) **INSTRUMENT DE DETECTION DE SUBSTANCE DANS LES LIQUIDES**

(54) **INSTRUMENT FOR THE DETECTION OF SUBSTANCE IN FLUIDS**



(57) A porous light guiding structure (e.g. a porous optical element such as for example a glass fibre) may be used as a sensor probe for the detection of a substances) in a fluid (e.g. a liquid such as for example water).

ABSTRACT OF THE DISCLOSURE

A porous light guiding structure (e.g. a porous optical element such as for example a glass fibre) may be used as a sensor probe for the detection of a substance(s) in a fluid (e.g. a liquid such as for example water).

INSTRUMENT FOR THE DETECTION OF SUBSTANCES IN FLUIDS

FIELD OF THE INVENTION

The present invention relates to sensor probe as well as an instrument (e.g. field instrument) for the detection of substances in a fluid (such as for example a liquid such as water). The substance(s) to be detected may for example be illicit materials and more specifically be illegal drugs in aqueous solutions. More particularly, the present invention relates to a porous probe element (e.g. fiber tip) which may be put in the liquid to be inspected; the probe may be associated with a standard fiber optic cable for carrying light from and to an analyzing instrument which may consist of a light source, monochromator, detector and associated signal detection and analysis electronics. The probe (e.g. fiber tip), which could also be any another form of light guiding structure, has been specially treated to create in the glass material a network of interconnected pores with a given pore size distribution. These pores have been previously treated so that they are partially filled with suitable metal particles; the metal is any suitable metal such as for example the metals of group Ib of the periodic table of elements, noble metals and the like. By suitably dosing this process, the porous fiber remains partially optically transparent and provides surface-enhancement of Raman scattering. The porous network of the probe (e.g. fiber tip) may also act as a time-diffusion discriminator for the various substances to be detected, in a manner analogous or similar to thin-layer-chromatography.

Although the present invention is discussed in particular terms with respect to the detection of illicit drugs, this is by way of example only. The present invention could of course be exploited in relation to any (organic) substances, in a liquid such as water for example. The invention may, for example, be exploited in relation to Raman spectroscopy. Using surface-enhanced Raman spectroscopy, sensitivity down to pico and femto-mole may be possible with modern CCD array detectors. Furthermore, the technique in accordance with the present invention also possess high information content

for establishing molecular identity since the spectra obtained are basically equivalent to high-resolution infrared vibrational spectra.

Rapid determination of the nature of suspect substances in an airport environment remains a difficult and challenging problem. Drug and explosive detection equipment using numerous techniques have been in existence for more than 10 years. The last few years have seen an increase in the number and types of detection systems being deployed in the field by numerous police and drug enforcement agencies. Continued interest in the application of new technology for the detection of drugs and explosives has led to the development of new instrumentation. However, there, still lack a general, low cost, field portable instrument that could be used by non-technical personnel for rapid assessment of suspicious materials or drug detection.

DESCRIPTION OF PRIOR ART

US Pat. No. 5,250,095 (SIGEL JR GEORGE ET AL) describes the use of a porous fiber as a chemical sensor. In this case, the pores are used as an optical chamber to contain the agent, which cause a change in the optical transmission of light by the agent. The SIGEL patent is very similar to standard spectroscopy techniques to detect and identify substances : it uses a tunable narrow-wavelength light source, an optical cell (the porous fiber) and a detector to measure the change in absorption of light as a function of wavelength.

US Pat. No. 3,904,422 (EATON ET AL) describes the use of porous glass, because of its inherent properties of inertness, optical transparency, and large surface area, as a chromatographic separation medium.

Nonetheless, the prior art has not disclosed the use of porous fiber tip by combining four important key functions : 1. The pores serve as a stable medium for the metal particles that will enhance the Raman signal, 2. The pores serve as a time-diffusion discriminator for the substances to be detected, 3. The porous fiber is the container for the substances to be analyzed, and 4. The porous fiber is the light guiding structure.

SUMMARY OF THE INVENTION

The present invention relates to a porous light guiding structure(e.g. fiber tip) which may, for example, be disposed at the end of a fiber optic cable. The fiber optic cable serves as the light guide from and to an optical/electronic processing unit that may comprise or consist of a light source, monochromator detector and associated signal detection and analysis electronics. The porous structure (e.g. fiber tip) may be placed in the fluid (e.g. liquid) to be analyzed that may contain one or more of the organic substances (e.g. illicit drugs) to be detected.

The present invention also relates to an instrument for the detection of substances in a fluid (e.g. to field instrument for the detection of illicit drugs).

The present invention in particular relates to surface-enhanced optical probes. These probes may, for example, enhance the Raman signal by a factor of one million or more. The probe may, for example, be an optic tip having pores filled or associated with a suitable metal.

Thus the present invention relates to the use of a porous light guiding structure (e.g. a porous optical element such as for example a glass fibre) as a sensor probe for the detection of a substance(s) in a fluid (e.g. a liquid such as for example water).

The present invention further provides a fiber optic probe adapted for use with a source of excitation energy having a single wavelength and means for analyzing the emission of a sample comprising a porous light guiding structure having metal particles being disposed within the pores of said structure.

The present invention also relates to a detection instrument for the detection of a substance in a fluid comprising a) an excitation light source for irradiating a sample with

light of a single wavelength; b) a sample part where said sample is irradiated with said excitation light so as to generate scattered light; c) an optical/electronic processing means for producing an electronic signal indicative of the presence of a substance (e.g. comprising a photoreceiving part comprising a monochromator, a photodetector for detecting said scattered light etc.) and wherein said sample part comprises a porous light guiding structure, metal particles being disposed within the pores of said structure. The electronic signal may for example be sent on to processing means such as a computer for analysis and readout of the presence of a substance.

In accordance with the present suspicious materials could be detected using a small flexible fiber optic probe head. This type of second-generation SERS has recently become feasible with rapid progress in several key technologies: Miniature fiber optic probes; large amplification of the signals thanks to specially designed surface-enhanced probes; use of powerful spectrally narrow near-infrared laser diodes; efficient ultra-narrow holographic notch filters and miniature spectrometers.

The SERS is very attractive not only because of its sensitivity but because it can identify trace of compounds in complex environmental samples.

Traditional analytical techniques are good for bulk materials but are not sensitive enough for modern security applications. Using surface-enhanced Raman spectroscopy, sensitivity down to pico and femto-mole is possible with modern CCD array detectors. Furthermore, the technique also possess high information content for establishing molecular identity since the spectra obtained are basically equivalent to high-resolution infrared vibrational spectra. Traditional Raman spectroscopy has long been a powerful analytical tool. However, it was limited to the laboratory because of the requirement for very powerful laser and sophisticated spectrometer. The discovery of the surface-enhanced effect has allowed the use of small laser diodes and working in the near infrared eliminates the problems of fluorescence associated with visible laser excitation. Surface-enhanced Raman spectroscopy (SERS) is likely to be one of the most sensitive methods

for chemical detection. Unfortunately, SERS does not lend itself to quantitative analysis or easy field used because the active surfaces required are short-lived and difficult to reproduce. The object of the present invention promises to circumvent these difficulties with the use of a porous fiber tip as a stable surface-enhanced medium.

The first step in creating the special porous fiber tip is to start with a rod of borosilicate glass that is melted and stretched to the desired diameter. These fibers are then heat treated to create the phase separation of the glass and then leached in an acid solution. What is left is a network of pores in silica glass. Once the fiber tip is porous, metal particles are deposited in the pores by chemical means. The metallic particles can be of copper, gold or silver. They are deposited by the reduction of the corresponding salt, directly inside the pores. The salt can be deposited on the surface of the pores by immersing the porous glass in a solution of the salt and the reductor. The reduction reaction is then induced by heat or by photochemical means.

The pore size distribution and the spatial extent of the porous section are other properties that can be controlled in order to tailor the time-diffusion and light guiding properties of the porous tip. For example, in the case of fiber and its circular symmetry, it is relatively easy to vary the size of the porous section so that only the cladding is porous and the core remains solid. In that case, the light that is mostly guided in the core, nevertheless interacts with the pores through the evanescent field of the guided mode. Other geometry of the guiding structure can also be accommodated in this matter. Controlling the spatial extent of the porous section and the pore size distribution also has a direct impact on the diffusion properties for the substances to be detected. This way the porous fiber can act as a miniature chromatograph since different substances will diffuse at different rates within the fiber tip. This phenomena is particularly interesting in situation where it is required to distinguish between several substances in the same aqueous medium. A time analysis of the optical signature, surface-enhanced Raman or fluorescence spectra or any other type of spectrum, can be mathematically processed using well known chemometrics procedures to give information not available from a single time-invariant spectrum. As

a compound to be detected diffuse inside the porous glass, the corresponding Raman emission becomes more and more important until an equilibria is reached, which corresponds to the complete filling of the pores. Since the diffusion constant of molecules in porous glass differs from one compound to another, the ratio of the various Raman peaks corresponding to various molecules will vary with time. The acquisition of several spectra between the time of immersion of the probe until the equilibria is reached gives rise to a matrix of spectra. Analysis of the rank of this matrix allows the calculation of the number of compounds present in the solution. The presence of a specific compound can also be determined by the method of target testing (E.R. Malinowski, Factor Analysis in Chemistry, John Wiley&Son, NY,1991).

The description has so far concentrated on the fabrication and use of the fiber tip, which is the most novel aspect of this invention. This fiber tip can be fabricated in large quantity at relatively low cost so that it need not be reused after a test if this simplifies the procedure. In that case, it is a simple matter to devise a cheap interconnection between the fiber tip and the rest of the instrument. A simple mechanical splice of the type used for multimode fibers would be appropriate to attach the fiber tip to the fiber optic cable that is itself connected to the bulk of the instrument.

The bulk of the instrument is composed of a light source, a monochromator or light analyzing apparatus, a detector and associated electronics and a microcomputer for data analysis. In the case of surface-enhanced Raman spectroscopy, the light source would be a laser diode emitting near 800 nm as this is a small convenient and powerful source for this type of application. Other sources are possible of course as this would be obvious to anyone in the field. The source is injected in the transport fiber through a 2x2 coupler. The output port of this same coupler is then used to bring the light reflected by the fiber tip to the monochromator. The monochromator, or other light analyzing apparatus, is used to disperse the light in order to analyze its spectral components. If the fiber tip is designed as a SERS probe of the type described above, the spectrum will be representative of the infrared-active vibrational bands of the substances present in the

aqueous medium in which the probe is immersed. The time-variant nature of this spectrum will provide the necessary discrimination that will allow the identification of several substances. The identification of these substances is helped by the use of a microcomputer and appropriate software that will compare the measured spectra with a database of known substances.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention and its advantages will be more easily understood after reading the following non-restrictive description of an example embodiment thereof, made with reference to the following drawings, where :

Figure 1 is a schematic representation of the field instrument for the detection of illicit drugs showing the major components of the instrument.

Figure 2 is a schematic representation of a porous fiber tip used as a probe.

Figure 3 is a schematic representation of a different configuration for the fiber tip probe.

Figure 4 is a schematic representation of different forms the guiding structure can take.

Figure 5 is a graph illustrating the time-dependent diffusion process present with porous glass.

The present invention relates to an instrument, which, for example, may be used to detect illicit drugs in aqueous medium. The optical probe generally includes a porous optical waveguide whose pores contain surface-enhanced metallic particles and whose pore size distribution is designed to allow time-diffusion separation of the substances to be detected. In the preferred embodiment, the waveguide is an optical fiber and the spectral analysis is done using Raman spectroscopy. However, other forms of waveguide are

possible and the metallic particles can be replaced with chromophores in which case the fluorescence spectrum is analyzed and not the Raman spectrum.

The following description will initially review the basic principles and objects of the invention before describing an example embodiment thereof.

The optical probe is connected to a light source and light analyzing instrument through a fiber optic cable and 2x2 coupler. This probe is put in the aqueous medium, urine for example, to be analyzed. This aqueous medium could contain a fix number of illicit drugs in small concentrations whose presence we whish to determine. The fiber tip is constructed from porous glass whose pores contain an active surface-enhancing substance like metallic particles. The fiber tip also allows light from the transport fiber to interact with the substances adsorbed on the metallic particles and light scattered from these centers to be guided back to the analyzing instrument through the same transport fiber. The light source and the light analyzing system, a laser diode and monochromator with CCD array in the preferred embodiment, are those normally used for SERS (surface-enhanced Raman spectroscopy). The characteristics of the pores, size and spatial distributions, are tailored to favor a time-controlled diffusion of the substances to be detected inside the porous portion of the fiber tip. Because different, substances will have different diffusion time constant, this can be used to identify several substances in a mixture using well known chemometrics analysis techniques.

The performance of this invention relies heavily on the use of a porous glass structure whose parameters can be well controlled. The porous waveguides may, for example, be fabricated from borosilicate glasses using standard techniques put forward some time ago (US Pat. 2,286,275, HOOD H.P. AND NORDBERG M.K.). First, the borosilicate glass is put in the form of a fiber or other waveguide structure by standard glass manipulation. The glass is then reheated to a temperature below the melting point to induce a phase separation. Once cool down, the waveguide is treated in a diluted acid for several hours to dissolve the alkaline-borate crystals and leave behind, a structure of interconnected pores in a matrix of pure silica. If one desires a waveguide with just the porous cladding and a solid, non-porous core, then the immersion in the acid bath should last only a few

minutes. The time of immersion allows controlling the depth of the porous region. The control of the size distribution of the pores is done through the initial glass composition and the time-heat profile of the initial reheat treatment.

Thus for example a starting borosilicate glass may have a composition of 60 % SiO_2, 30 % B_2O_3, 4 % K_2O and 2 % Al_2O_3 (percentages are by weight). It is pulled, at 700 degrees celsius, to form a fibre having a diameter of 230 microns. After the glass is made porous by a process as described herein (i.e. heat treatment and chemical attack) the glass may for example have a specific surface of 330 m^2/g and an average pore size of 1.35 nm; The specific surface may for example range from 200 to 550 m^2/g and the average pore size may range from .5 to 5 nm.

Once this porous glass network is fabricated, the pores must be partially filled with metallic particles that will enhance the Raman effect. One example to produce silver particles in porous glass would be as follows: First, solutions of silver nitrate and sodium citrate are mixes together. Porous fibers are then immersed in that solution for one hour and then dried. The fibers are then placed in an oven and the temperature is slowly raised to 100 celsius and left there for 3 hours. The fibers are finally rinsed and dried and kept in a pure nitrogen atmosphere until used.

Thus for example in the case of the deposition of silver particles the process may proceed as follows:

A silver nitrate solution (10^{-4} mole/litre) is mixed with a sodium citrate solution (10^{-4} mole/litre) to obtain 200 ml of solution. The porous fibers are then immersed in the solution for 1 hour after which the impregnated fibers are removed and excess solution removed therefrom. The fibers are then placed in a drying oven and the temperature of the oven is slowly raised to 100 °C. The fibers are left in the oven for 3 hours then rinsed in distilled water for 15 minutes. The fibers are finally dried and kept in dry nitrogen before their use.

With reference to Figure 1, there is shown a diagram of a possible field instrumentation

for the detection of illicit drugs using the above described optical probe. The light source 2 is coupled via the fiber optic coupler 7 to the transport fiber 5 which brings the light to the probe 1. Light generated in the probe 1 is sent back to the transport fiber 5, the coupler 7 and finally arrives at the light analysis instrument 3. The signals from the detector 3 are sent to the computer 4 via an electrical pathway 6.

Referring back to figure 1 the system components are all fiber coupled so there is no critical alignment and the packaging is simplified. The light source may be a well-packaged single frequency laser diode with medium power (in the 10 to 20 mWatt range). The light analyses instrumentals 3 may be a spectrometer associated with collimating optics, a holographic element or filter and focusing optics. The holographic notch filter effectively eliminates the strong signals coming from the scattered laser light. This allows use of a single grating miniature spectrometer with CCD array readout. The fiber is used as both the transmitter and collector. The tip of the fiber is a miniature surface-enhanced probe that consists of a specially treated porous glass structure. Finally, computer software will do the spectral processing using a database and specially designed statistical tools.

The CCD-array detector is a charge-coupled-detector array; one such detector is the model DV420-BV from Andor Technologies of MA USA which offers 128 pixels x 1024 pixels and can be easily fitted to many spectrometers or monochromators.

An example of a suitable light analysing instrument is the Aries Model FF500 imaging spectrograph from Aries MA USA. It has a focal length of 500 mm and a f# of f/4. It can be equipped with a grating having 1200 lines per millimetre.

The light source may be a narrow band laser diode or other equivalent laser source. One example of a good laser source is the laser diode Model LD1050 from Power Technology Inc. of MA USA. It emits at 785 nm with a total power of 60 mwatt.

In actual measurement, the optical probe 1 is placed in the solution to be analyzed as shown in Figure 2. The fiber probe itself can have different configurations, and Figure 3 illustrates two such possibilities: A completely porous waveguide or just the porous

cladding. Figure 4 illustrates that the waveguide need not be an optical fiber but other configurations are possible. Finally, Figure 5 shows a practical example of the time-diffusion process in porous glass. In this particular case, the transmission of a porous optical fiber is monitored at a single wavelength while the fiber is being exposed to a vapor of acetone. The time varying transmission signal demonstrates that the vapor diffuses in the structures in about one minute and half. After this time the concentration of acetone is homogeneous in the porous fibre.

We claim:

1. The use of a porous light guiding structure (e.g. a porous optical element such as for example a glass fibre) as a sensor probe for the detection of a substance(s) in a fluid (e.g. a liquid such as for example water).

2. A fiber optic probe adapted for use with a source of excitation energy having a single wavelength and means for analyzing the emission of a sample comprising a porous light guiding structure having metal particles being disposed within the pores of said structure.

3. A detection instrument for the detection of a substance in a fluid comprising a) an excitation light source for irradiating a sample with light of a single wavelength; b) a sample part where said sample is irradiated with said excitation light so as to generate scattered light; c) an optical/electronic processing means for producing an electronic signal indicative of the presence of a substance comprising a photodetector for detecting said scattered light and wherein said sample part comprises a porous light guiding structure, metal particles being disposed within the pores of said structure.

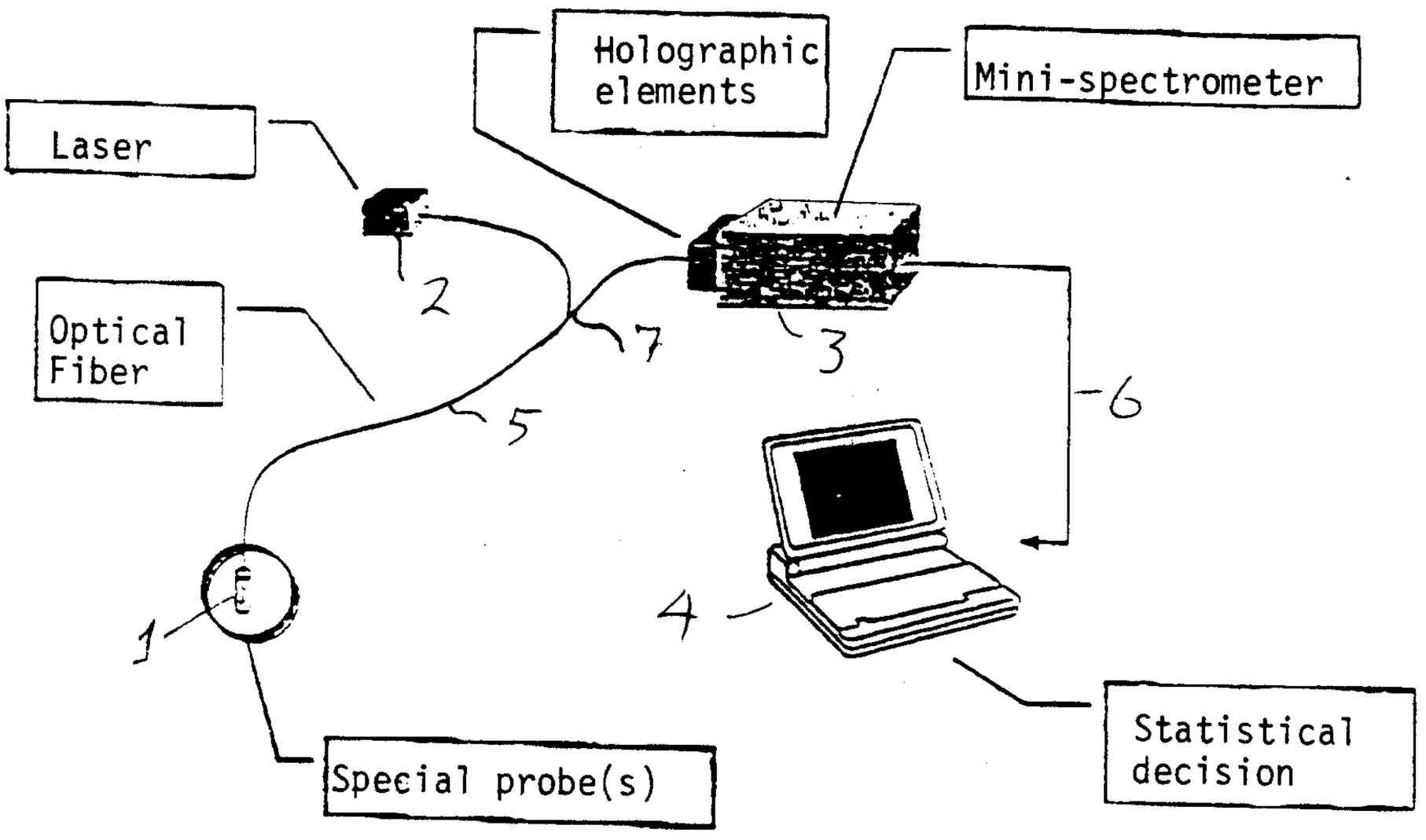

Holographic elements
Mini-spectrometer
Laser
2
7
3
Optical Fiber
5
6
1
4
Special probe(s)
Statistical decision

Figure 1

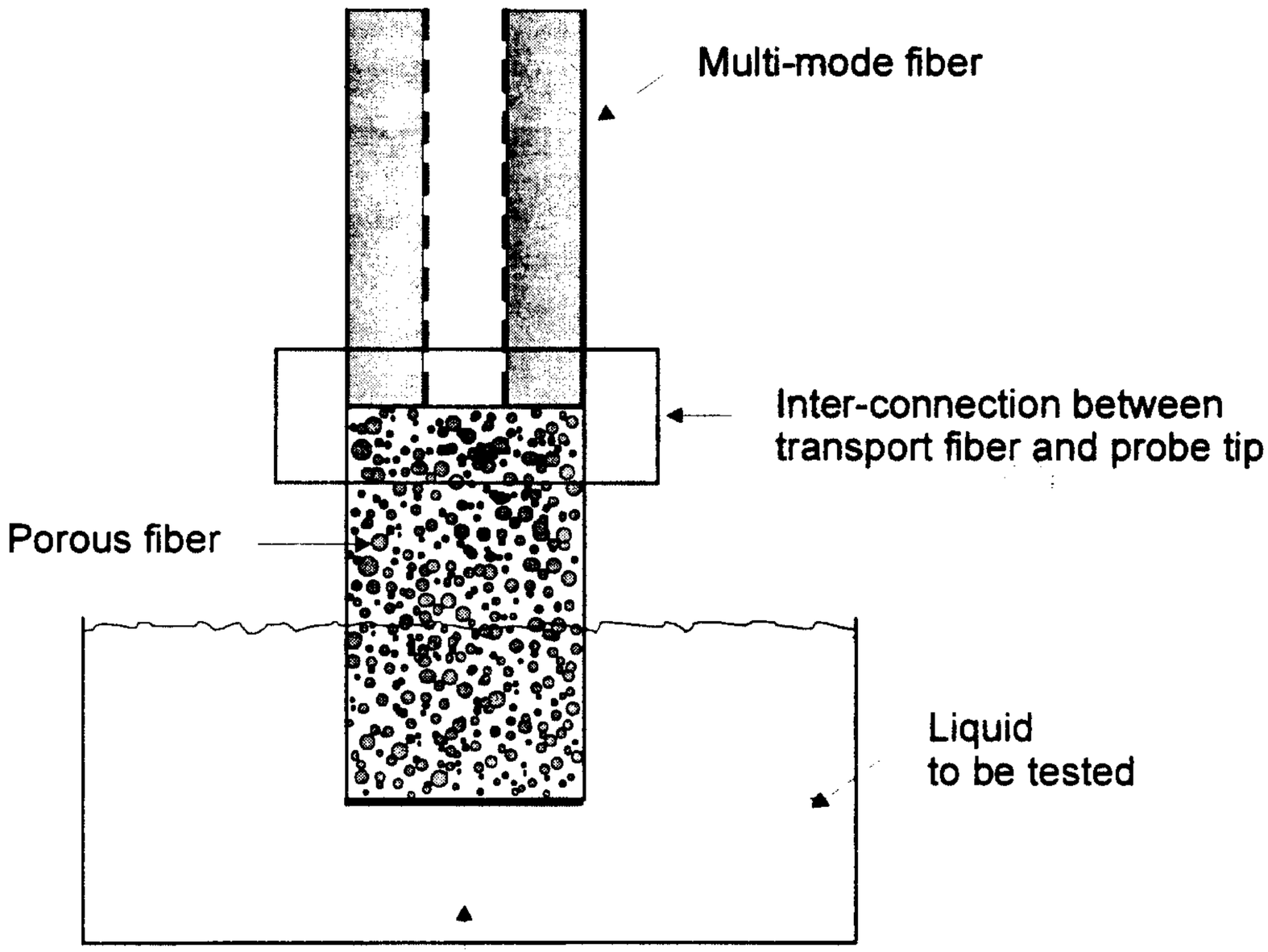

Multi-mode fiber
Inter-connection between
transport fiber and probe tip
Porous fiber
Liquid
to be tested
100 % Reflecting coating

Figure 2

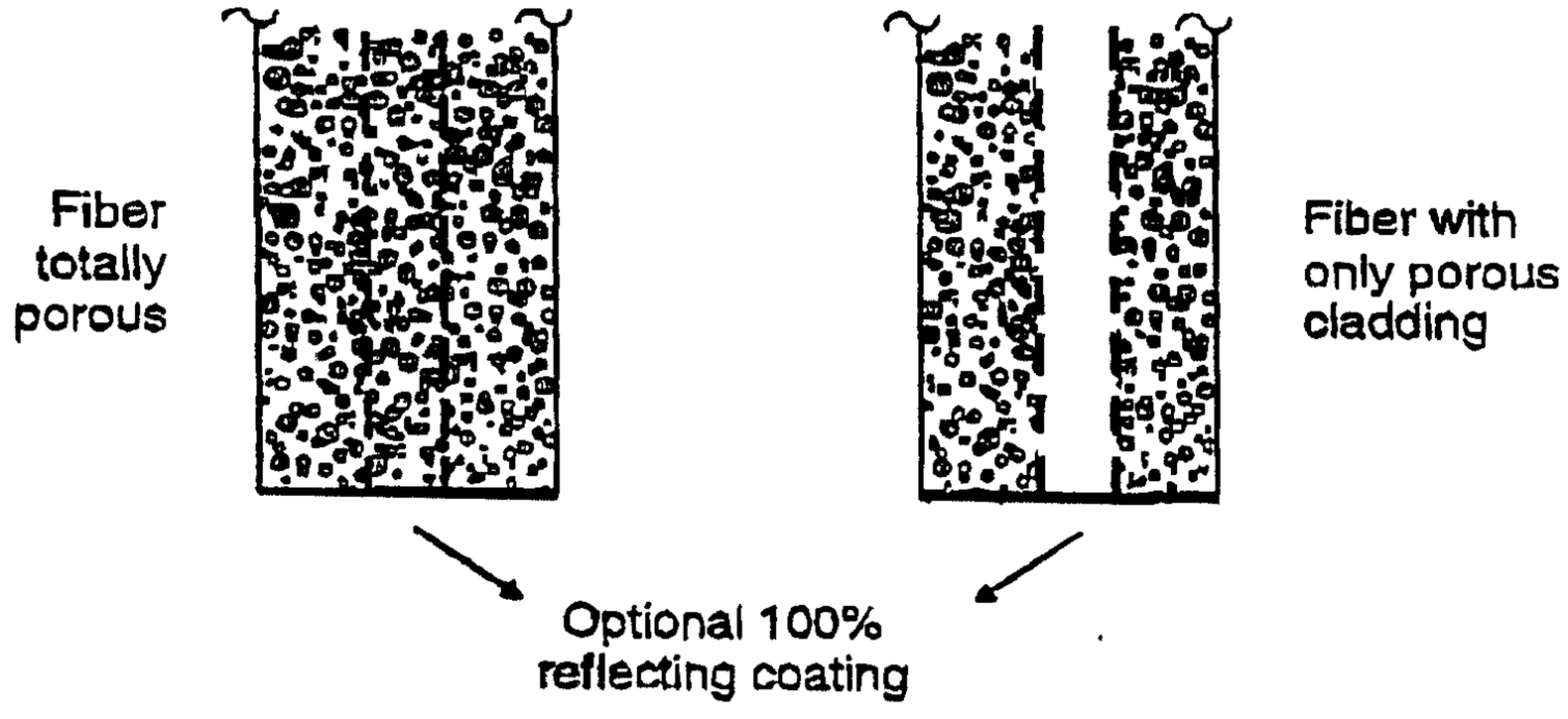

Fiber totally porous
Fiber with only porous cladding
Optional 100% reflecting coating

Figure 3

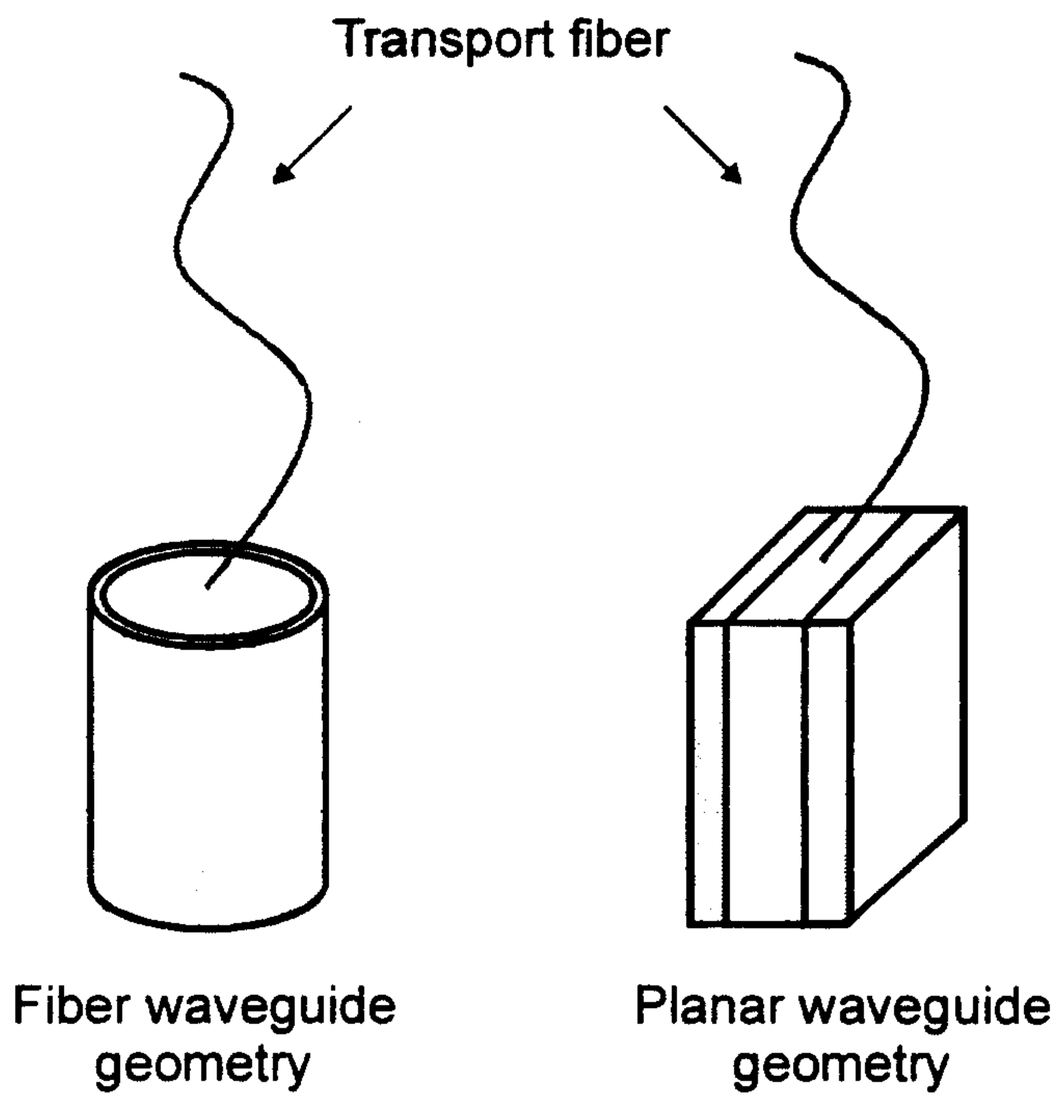

Transport fiber
Fiber waveguide geometry
Planar waveguide geometry

Figure 4

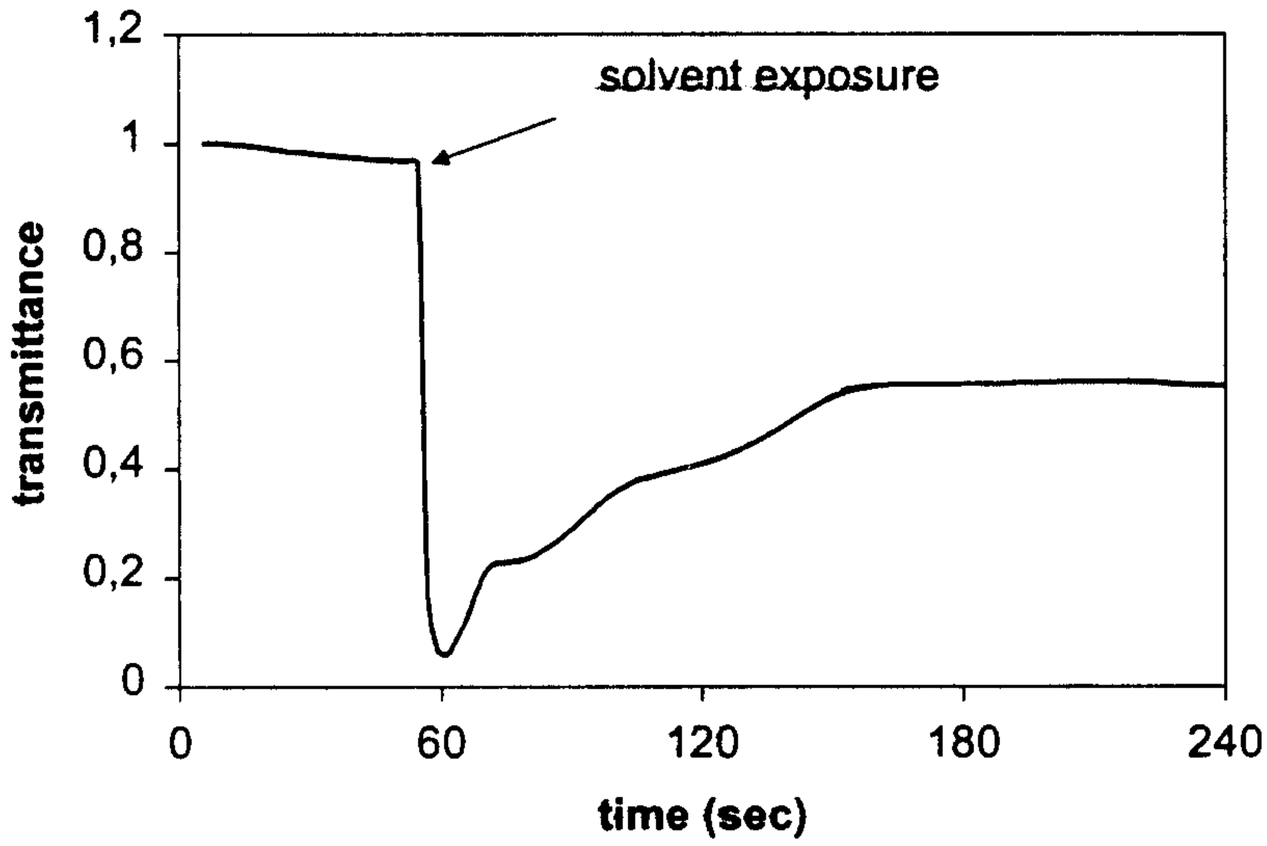
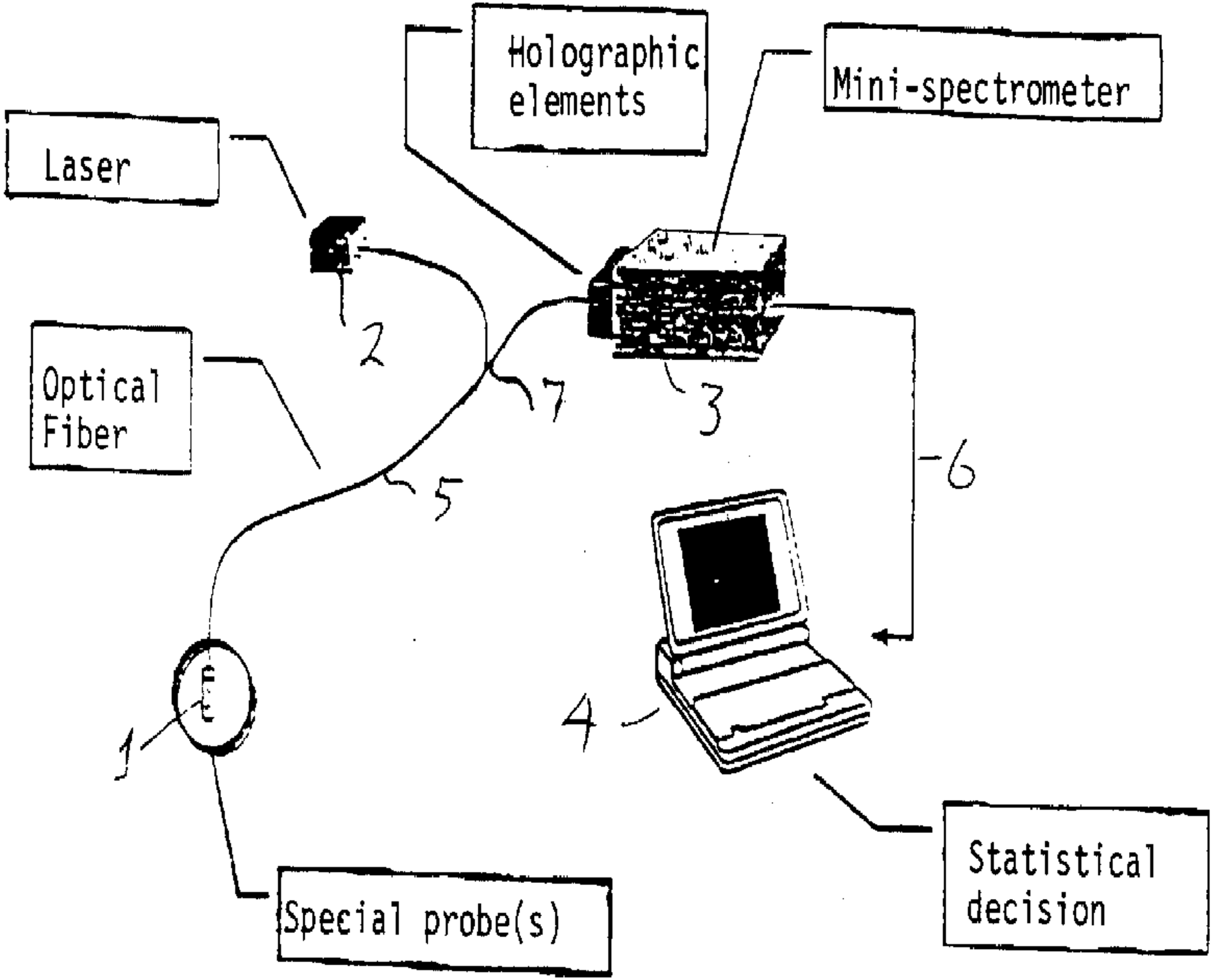

solvent exposure
transmittance
1,2
1
0,8
0,6
0,4
0,2
0
0
60
120
180
240
time (sec)

Figure 5


Holographic elements
Mini-spectrometer
Laser
Optical Fiber
Special probe(s)
Statistical decision
1
2
3
4
5
6
7