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(71) Applicant *(for all designated States except US)*: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: DOUMA, Bindert, Sjoerd [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). DWARS, Sicco [NL/GB]; Pool Lane, Ince, Chester, Cheshire CH1 3SH (GB).

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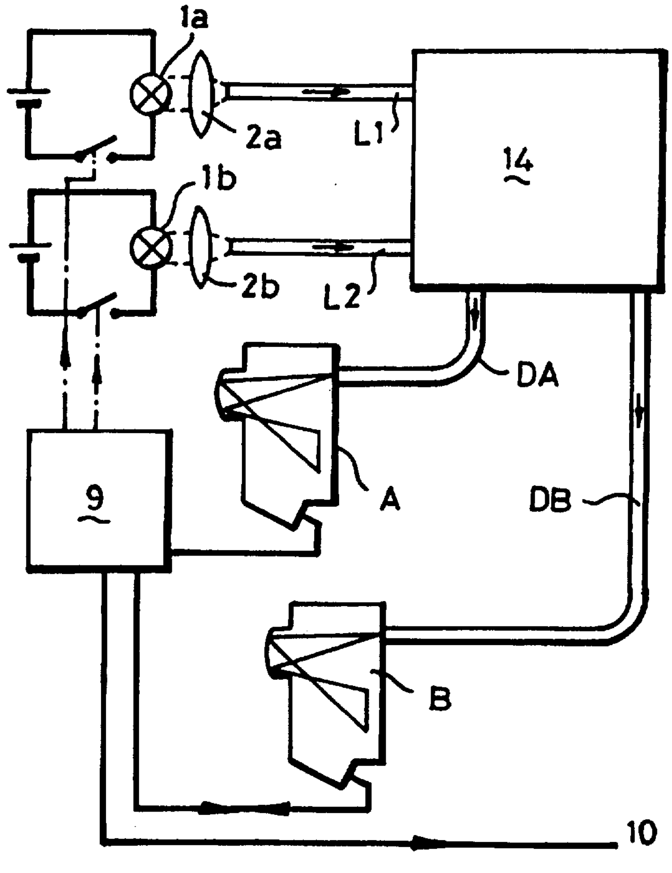
(54) Title: SELF-CORRECTING SPECTROSCOPIC PROCESS ANALYSIS

(57) Abstract

A method for self-correcting spectroscopic analysis of a fluid stream is provided. The method comprises actuating optical source means so as to create at least one optical beam, transmitting optical signals from said at least one optical beam in at least two modes of operation to a first optical detecting means and to a second optical detecting means, and monitoring the electrical signals as detected by each detecting means. In a first mode of operation the optical signals transmitted to the first detecting means pass trough the sample cell and optical signals transmitted to the second detector bypass the sample cell. In a second mode of operation the optical signals transmitted to the first and second detecting means bypass the sample cell.



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SELF-CORRECTING SPECTROSCOPIC PROCESS ANALYSIS

The invention relates to a method and apparatus for self-correcting spectroscopic process analysis, i.e., analysis of a (broadband) spectrum.

Analytical instruments have gained a permanent place in industrial plants such as refineries and the like to determine for example physical parameters of fluids such as liquids or gases found in effluents and in industrial processes. Examples of such instruments include photometric analysers, typically measuring the total intensity of a (single or dual-wave) light source, but -more interestingly- also spectroscopic analysers that if properly interpreted provide a wealth of information.

Conventional instrumentation for the measurement and control of temperature, pressure, flow or level merely allowed the required product supply specifications to be met indirectly, i.e. by adjustment of the above four quantities. In such system the operator's experience was a very important factor. Product quality was checked indirectly by means of a laboratory analysis. However, such a check can only be effective if the time needed for the test results to reach operations is shorter than the relevant time constants of the processes. In actual practice time lags as long as eight hours have been encountered, whereas time constants in relation to such quantities as flash point, composition of top and bottom products, etc. range from ten minutes to one hour. Obviously, when time lags are a multiple of the time constants, process control can scarcely be efficient, if at all possible. Thus, if for no other reason, the use of analytical instruments which as a rule produce results very rapidly is a necessity. Furthermore, analysers make it possible to:

- limit production losses upon start-up or change of feedstock;
- achieve the desired quality;
- operate boilers and furnaces more efficiently;
- prevent public nuisance, such as water- and air-pollution and spread of bad odours;
- detect potential hazards (gas poisoning, explosion risks, etc.).

The environment of spectroscopic process analysers in a plant requires robustness of all the components involved. Attractive components for spectroscopic analysers are optical fibres, which enable the mechanical decoupling of a spectrum analyser from a sampling system. However, against the advantages of using optical fibres there are also some disadvantages. For spectroscopic analysis one of the main disadvantages is the influence of environmental conditions e.g. temperature variations on the spectral transmission of optical fibres. For instance, the spectrometer may receive a signal that is changed for some, but not for other wavelengths.

General configurations of fibre spectroscopic process analysers are known to those skilled in the art and consist of a broadband light source, an optical fibre that guides the light to a sample cell and an optical return fibre to an optical spectrum analyser. These configurations are both applied for Fourier Transform (FT), scanning monochromator, filter wheel, acousto-optic tunable filter and diode array type analysers. Such systems are successfully used in laboratory type analytical instruments where samples of the monitored process or product are brought to the instruments. Current business needs point towards on-line and eventually in-line systems that have a direct interface with the product stream or process. This route sets different requirements on the analytical apparatus and its components with respect to robustness, stability, shock resistivity, fouling, calibration, operating temperatures and sample cell pressures.

It will be appreciated by those skilled in the art that besides sample cell and spectrum analysers, the optical fibres that guide light to and from the sample cell can contribute significantly to overall system performance. Therefore a special type of fibre with low spectral degradation due to ageing, mechanical- and temperature stresses can be applied. Similar problems and solutions are encountered at the light source and the detector ends. This route of upgrading the components of laboratory type instruments to plant floor resistant versions does not fully eliminate the problems mentioned above and finally leads to an expensive, bulky type of process analyser.

The output of a single beam spectrometer is in first instance the result of the light source, the transmission of the optical fibres (if used), the detector response, and the sample. The output versus wavelength of a spectrometer without any sample is not constant. The various components have different contributions as function of wavelength. By recording the response without a sample, a reference signature is obtained and all subsequent spectra can be referenced against this signature to obtain the actual sample spectrum. Single beam spectrometers can be used in a laboratory environment where such referencing is adequate for taking sample spectra. This approach however, is less attractive in a process environment. There a double beam approach is more appropriate. In the double beam approach one beam guides the light through the sample while the other beam passes through a reference channel. The difference between the two beams provides the sample spectrum. A similar approach has been adopted by Yokogawa Electric Corp. For instance, the InfraSpec NR500 (Bulletin 12Y3A0-06E of 1996) uses an analyser equipped with optical fibres of special configuration which make them hardly susceptible to the influence of environmental conditions such as temperature variations. Besides, the reference channel is connected laterally to the signal channel to compensate for such variations. Unfortunately, this analyser uses fibres that are very expensive. Besides, this approach doesn't fully compensate for minor differences in the fibre channels themselves and for minor differences in environmental conditions between the reference channel and the signal channel.

However, the above described optical configuration can not be used to compensate for spectral changes in all optical fibres.

It is an object of the invention to provide a method for self-correcting spectroscopic process analysis and a robust and low cost on-line spectroscopic process analyser wherein the adverse effect of light source ageing, fouling and fibre degradation on the overall reliability of spectroscopic process analysers is eliminated and wherein in particular the adverse effects on the spectral transmission are referenced out by a specific configuration of the sample cell and optical fibres.

The invention therefore provides a method of self-correcting spectroscopic analysis of a fluid stream, the method comprising

a) actuating optical source means so as to create at least one optical beam, transmitting optical signals from said at least one optical beam in at least two modes of operation to a first optical detecting means and to a second optical detecting means, and monitoring the optical signals as detected by each detecting means, said modes of operation comprising:

b) a first mode of operation wherein the optical signals transmitted to the first detecting means pass through a sample cell containing fluid from said fluid stream, and optical signals transmitted to the second detector bypass the sample cell; and

c) a second mode of operation wherein the optical signals transmitted to the first and second detecting means bypass the sample cell.

In this manner it is achieved that the transmission spectrum of the sample cell is a function of the optical signals as monitored by the detecting means, without being a function of the spectral composition (or variations thereof) of the optical source means or optical transmission means such as optical fibres. More particular, as shown by way of example in the detailed description hereinafter it is achieved that the transmission spectrum of the sample cell (T_{sample}) can be derived from the expression:

$$T_{sample} = D_{A.L1} * D_{B.L2} / D_{B.L1} * D_{A.L2}$$

in which

$D_{A.L1}$ is the optical signal measured at the first detecting means, in the first mode of operation,
$D_{A.L2}$ is the optical signal measured at the first detecting means, in the second mode of operation,
$D_{B.L1}$ is the optical signal measured at the second detecting means, in the first mode of operation,
$D_{B.L2}$ is the optical signal measured at the second detecting means, in the second mode of operation.

Suitably steps b) and c) are carried out cyclically in time.

It is preferred that the optical signals from said at least one optical beam are transmitted to the first and second optical detecting means by dividing the optical beam into at least two sub-beams using optical beam splitting means.

Advantageously said optical source means comprises at least two optical sources which are operated in a manner that in the first mode of operation the optical signals originate from a first optical source and in the second mode of operation the optical signals originate from a second optical source.

The invention also provides a process analyser for self-correcting spectroscopic analysis of a fluid stream, comprising

- optical source means for creating at least one optical beam, means for transmitting optical signals from said at least one optical beam in at least two modes of operation to a first optical detecting means and to a second optical detecting means, and means for monitoring the electrical signals as detected by each detecting means;
- in a first mode of operation, means for passing the optical signals transmitted to the first detecting means through the sample cell and means for bypassing the optical signals transmitted to the second detector, the sample cell; and
- in a second mode of operation, means for bypassing the optical signals transmitted to the first and second detecting means, the sample cell.

The invention is based upon the idea that during the sequence of optical measurements the influence, if any, of the optical sources, optical fibres and fibre connectors and sensitivity fluctuations in detectors on the obtained signals is already taken into account. Also in photometric analysers these problems have been encountered and indeed some solutions are provided, for instance by Li Jianshu et al, "On-line Concentration Measurement System With Optical Fibers" in SPIE Vol. 1230

International Conference on Optoelectronic Science and Engineering '90, pp 559-561; and by Giles et al, "Self-Compensating Technique for Remote Optic Intensity Modulated Transducers" in SPIE Vol. 522 Fibre Optics'85 (Sira), pp 233-239. The fibre sensor of the former article, however, suffers from intensity interference. The second article merely focuses on a balanced sensor system. Neither its potential to improve on spectroscopic analysers is appreciated, nor does it teach to reference out fluctuations in all fibres, all fibre connectors, and diode array spectrometers with respect to sensitivity.

The invention can e.g. be applied in on-line measurement of physical parameters of fluids such as polyol (e.g. OH value, PO and EO concentrations).

The invention will now be described by way of example in more detail by reference to the accompanying drawings in which:

Fig. 1 represents schematically a standard arrangement of a spectroscopic process analyser;

Fig. 2 represents schematically an improved standard arrangement of Fig. 1;

Fig. 3 represents schematically the principle of the invention;

Fig. 4 represents schematically an advantageous sample cell to be applied in Fig. 3; and

Fig. 5 represents schematically another advantageous configuration of optical dividing means and sample cell to be applied in the configuration of Fig. 3.

In the Figures like reference numerals relate to like parts of the various arrangements shown.

Referring now to Fig. 1 a classical arrangement of a spectroscopic analyser is shown.

Optical radiation is transmitted from a light source 1 via a lens 2, an optical fibre 3 and a lens 4 to a sample cell 5 and subsequently via a lens 6 an optical fibre 7 to an optical spectrum analyser 8, e.g. a diode array.

The signals obtained are processed in a computer 9 and one or more composition signals 10 are provided in any suitable manner for the purpose.

Such a spectroscopic process analyser must be referenced or calibrated.

Since diode arrays are low cost units, it is a feasible option to install two diode arrays instead of one diode array. Reference is made to Fig. 2 wherein the same reference numerals as applied in Fig. 1 have been used to represent the same parts of the arrangement. Further, one diode array module 8a serves for referencing, while the other 8b is used to measure the spectrum. The basic idea (Fig. 2) is to split a fraction of the light from the optical path 1, 2, 3 and 4 by means of a suitable beam splitter 11 (e.g. 50/50) and a lens 12 before it enters the sample cell 5 and monitor it with the second diode array 8a. The reference light path is represented by 7a, whereas 7b represents the sample light path. This all-solid-state configuration makes the system independent for spectral variations in the light source 1 and the fibre 3 that guides the light from the source 1 to the sample cell 5. However, variations induced in the two return fibres 7a, 7b and in both diode arrays 8a, 8b are not compensated for. The requirements for the light source and its fibre are less stringent in this configuration. If the two diode arrays 8a, 8b are read out simultaneously the light source may even fluctuate in time, both in intensity and in spectral composition without corrupting the determination of the sample absorption spectrum. The sample analysis is split into the following steps:

Initialisation/calibration:

phase -2: lamp off (or blocked); measure the diode arrays dark currents. The dark current is the signal which is left when no light falls on the detector.

phase -1: lamp on (or unblocked); empty the sample cell and measure the single beam reference responses on the diode arrays by first subtracting the phase -2 dark currents and then dividing the responses on the two arrays.

Normal operation:

phase 0: lamp off; measure dark currents

phase 1: lamp on; measure responses on both arrays, subtract the new background, divide them and divide the result by the outcome of phase -1.

The end result is a "pure" transmission spectrum which can be further analysed, e.g. serve as an input to a chemometric model to calculate relevant process parameters. Such further analysis is known to those skilled in the art and will not be described in detail.

A drawback of the above procedure is the need for calibration (say once a day) with a reference fluid in the sample cell. This calibration is required to correct for changes in the spectral transmission of the two diode arrays and their fibres.

A self-referencing dual channel sampling probe in which a mechanical shutter at the sample cell selects either an optical reference path via glass rods or the optical path via the liquid or gas sample volume has been proposed. Similar routes are to move a glass rod in and out of the sample path or to mechanically shorten the sample path by moving the reflector forward. These mechanical solutions allow continuous compensation for spectral alterations in both light sources, optical fibres and the spectrometer. However, a major drawback is the fact that mechanical components (or LCD-shutters) are to be used in or very close to the sample cell, which is, from a reliability point of view, not preferred.

In Fig. 3 according to the invention not only two diode arrays A and B and fibres DA and DB but also two individually switchable light sources 1a and 1b with individual fibres L1 and L2 and lenses 2a, 2b are shown. This leads to a so called "quad fibre configuration" having a "quad fibre sample cell" 14 with four fibres between sample cell and the respective opto-electronic components.

The "quad fibre sample cell" 14 is shown in more detail in Fig. 4 in which DA, DB, L_1 and L_2 correspond to DA, DB, L_1 and L_2 indicated in Fig. 3. The "quad fibre sample cell" 14 includes a sample cell 16 and four optical beam splitters 18, 20, 22, 24. The beam splitters are arranged such that an optical beam transmitted through fibre L1 is split by splitter 18 to form a first sub-beam transmitted to sample 16 and splitter 20, and a second sub-beam transmitted to splitter 24. The first sub-beam is again split at splitter 20 so that part of the first sub-beam is transmitted to fibre DA, and the second sub-beam is again split at splitter 24 so that part of the second sub-beam is transmitted to fibre DB. Furthermore, an optical beam transmitted through fibre L2 is split by splitter 22 to form a third sub-beam transmitted to splitter 20, and a fourth sub-beam transmitted to splitter 24. The third sub-beam is again split at splitter 20 so that part of the first sub-beam is transmitted to fibre DA, and the fourth sub-beam is again split at splitter 24 so that part of the fourth sub-beam is transmitted to fibre DB. The arrows indicate the path of the optical radiation from L_1 and L_2.The system should cyclically pass through the following measuring sequence:

- phase 0 : both lightsources (e.g. lamps) off, dark current responses $D_{A.L0}$ and $D_{B.L0}$
- phase 1 : lamp 1 on, light source 2 off, responses $D_{A.L1}$ and $D_{B.L1}$
- phase 2 : lamp 1 off, light source 2 on, responses $D_{A.L2}$ and $D_{B.L2}$;

in which $D_{x.Ly}$ represents a complete reading of diode array x for activated lamp y, when necessary corrected for wavelength calibrations of the individual diode arrays.

After this sequence, the spectra are corrected for the dark currents and subsequently the actual sample transmission spectrum is calculated by:

$$T_{sample} = D_{A.L1} * D_{B.L2} / D_{B.L1} * D_{A.L2}$$

A detailed analysis of these formulas is as follows: In the quad fibre mode of the invention a sample spectrum is acquired in the following sequence:

phase 0 : both lamps off, dark current responses measured $D_{A.L0}$ and $D_{B.L0}$

phase 1 : lamp 1 on, lamp 2 off, responses measured $D_{A.L1}$ and $D_{B.L1}$

phase 2 : lamp 1 off, lamp 2 on, responses measured $D_{A.L2}$ and $D_{B.L2}$.

After this sequence, the following calculations are performed:

1. Subtract dark currents

$$D_{A.L1} := D_{A.L1} - D_{A.L0} \quad [1]$$

$$D_{B.L1} := D_{B.L1} - D_{B.L0} \quad [2]$$

$$D_{A.L2} := D_{A.L2} - D_{A.L0} \quad [3]$$

$$D_{B.L2} := D_{B.L2} - D_{B.L0} \quad [4]$$

Response $D_{A.L1}$ is the product (per wavelength) of the light source (L_1) multiplied by the spectra of the following optical components: optional filter, fibre connection, fibre L_1 to sample cell, fibre connector L_1, lens, beam splitter 1 (1->2), sample, mirror, sample, beam splitter 1 (2->3), mirror, lens, fibre connector D_A, fibre D_A, grating/monochromator D_A, silicon response on D_A, electronics error in D_A, etc.

For simplification a number of these components is combined:

$$D_{A.L1} = L1 * T_{fl1} * 0.5 * T_{sample} * 0.5 * T_{fda} \quad [5]$$

where

$D_{A.L1}$ is the response of the first diode array;

L_1 is the spectral composition of light source lamp L_1;

T_{fl1} is the transmission spectrum for fibre l1, its connectors and lenses;

0.5 is introduced by the beam splitter cubes (assumed here as 50/50 ideal splitters);

T_{sample} is the transmission spectrum per wavelength of the process sample (quadratic if the light passes the sample twice such as in Fig. 4);

T_{fda} is the transmission spectrum for fibre DA and its connectors, lenses, monochromator and photo-electric conversion.

Similarly all four responses can be written as follows (note that equation [5] is repeated):

$$D_{A.L1} = L1 * T_{fl1} * 0.5 * T_{sample} * 0.5 * T_{fda} \quad [5]$$

$$D_{B.L1} = L_1 * T_{fl1} * 0.5 * 0.5 * T_{fdb} \quad [6]$$

$$D_{A.L2} = L_2 * T_{fl2} * 0.5 * 0.5 * T_{fda} \quad [7]$$

$$D_{B.L2} = L_2 * T_{fl2} * 0.5 * 0.5 * T_{fdb} \quad [8]$$

Dividing [5] by [7] and dividing [6] by [8] yields in:

$$\frac{D_{A.L1}}{D_{A.L2}} = \frac{L_1 * T_{fl1} * 0.5 * T_{sample} * 0.5 * T_{fda}}{L_2 * T_{fl2} * 0.5 * 0.5 * T_{fda}} \quad [9]$$

and

$$\frac{D_{B.L1}}{D_{B.L2}} = \frac{L_1 * T_{fl1} * 0.5 * \quad 0.5 * T_{fdb}}{L_2 * T_{fl2} * 0.5 * \quad 0.5 * T_{fdb}} \qquad [10]$$

Which can be simplified to:

$$\frac{D_{A.L1}}{D_{A.L2}} = T_{sample} * \frac{L_1 * T_{fl1}}{L_2 * T_{fl2}} \qquad [11]$$

$$\frac{D_{B.L1}}{D_{B.L2}} = \frac{L_1 * T_{fl1}}{L_2 * T_{fl2}} \qquad [12]$$

Substituting [12] in [11] gives:

$$\frac{D_{A.L1}}{D_{A.L2}} = T_{sample} * \frac{D_{B.L1}}{D_{B.L2}} \qquad [13]$$

which results in

$$T_{sample} = D_{A.L1} * D_{B.L2} / D_{B.L1} * D_{A.L2} \qquad [14]$$

In practice, the 50/50 beam splitters will not be ideal, this can result in a correction factor in equation [14] which is constant.

In this configuration the following fluctuations are referenced out:

* Fluctuations in light sources lamp 1 and lamp 2
* Fluctuations in all fibres and all fibre connectors
* Fluctuations in the diode array spectrometers with respect to sensitivity.

However, the system is still sensitive for:

* Fluctuations in wavelength calibration of the diode arrays
* Fouling on the process interface windows.

An alternative advantageous configuration of optical dividing means and sample cell is illustrated in Fig. 5.

In this arrangement L_1, L_2, D_A and D_B represent the same optical means as in figs. 3 and 4, the sample cell is represented by reference numeral 26, and the beam splitters by numerals 28 and 30. In this practical configuration of the optical components additional corner cubes 32 and 36 are applied. The arrows indicate the optical path.

If -and only if- fouling of process windows or in-process mirrors still causes a disturbance in the transmission spectrum (not on total light transmission), it is an option to apply additional 100% transmission references by either:

1) A movable glass rod that replaces the sample volume or,

2) A moveable mirror/retro-reflector that reduces the sample volume or,

3) Filling the sample cell with a reference fluid.

These three options require mechanical components in or near the sample cell and are therefore less favourable in an industrial process analyser.

4) Flushing the sample cell with a cleaning fluid.

When using diode arrays, the three phases of a quad fibre sample cell measurement can be programmed to follow another at short time intervals. The classical approach with diode arrays is to average a large number of readings at the same optical configuration (reference, dark current and sample). Quad fibre mode systems allow very rapid changes in the all-solid state optical configurations in phase 0, 1 and 2. This allows the calculus to be executed prior to averaging, i.e. first compensate for dark current and reference and then average the transmission spectrum. This route significantly reduces the influence of zero and scale drift at the detector, thereby increasing dynamic ranges and thus the overall performance. Due to this gain in signal to noise ratio with quad fibre configurations, expensive detector cooling can in some cases be left out.

It will be appreciated that the configuration of the invention can be implemented in any suitable manner, e.g.:

* The light sources for a quad fibre mode system can be either a filament, LED(array), tuneable laser, a flash light or a gas-discharge source. Fluctuations in the intensity of the source and in its spectral composition are automatically compensated for.

* The wavelength region is in principle not restricted. Benefits are especially expected in the ultraviolet and (near-)infrared region where optical fibres are more handicapped by degradation. Applicable diode arrays for both UV, VIS and (N)IR are available on the market. Especially the emerging infrared (In)GaAS, PbS and Ge-doped array based systems can benefit from the performance upgraded envisaged with quad fibre spectrometric systems.

* Either a single, or multiple light sources can be used to feed the source fibres. When using a single source, optical switches like mechanical shutters, (LCD) choppers or fibre optic switches are required to feed the source fibres with the required pattern of the three phases.

* At the dual spectrometric detector side, there is a multiplexing option to use one spectrometer in combination with a similar optical path switch as described above. Two synchronised chopped paths can be applied, where the detector path is multiplexed at a higher frequency. Multi-channel diode arrays or CCD chips are well applicable as dual channel spectrometer since only one grating element is required and both spectra are acquired at the same time.

* Quad fibre configurations can be realised in a number of different sample systems e.g. as both slip stream

systems and as transflecting dip-in probes. Attenuated total reflection (ATR) probes can also be incorporated in a quad configuration.

* Quad fibre configuration can easily be assembled as (low cost) integrated optics, similar to solid state electrical microchip systems. This can open the route to multiple sample point systems in e.g. segmented analytical gauges. With integrated optics, low cost telecom fibre (<100 μm core) becomes an applicable alternative to fibre bundles or large core single fibres applied nowadays in spectroscopic analysers.

* Fibre optic splitters or bifurcated fibres are an alternative for the beam splitters used in the explanation of the quad fibre method.

* Multi sample cell systems, two lamps per sample cell, only two diode array detectors for all sample cells, but still 100% solid-state.

* The optical fibres are flexible light paths. Without optical fibres but with four light paths, the same benefits are obtained. It is anticipated that, in view of the size reduction of spectrometer modules, a small integrated unit (similar to smart transmitters) might do without optical fibres. In that case the quad method can be realised with an open path configuration. Future developments could even result in a micro machined waveguide component enabling the quad method.

CLAIMS

1. A method of self-correcting spectroscopic analysis of a fluid stream, the method comprising
a) actuating optical source means so as to create at least one optical beam, transmitting optical signals from said at least one optical beam in at least two modes of operation to a first optical detecting means and to a second optical detecting means, and monitoring the electrical signals as detected by each detecting means, said modes of operation comprising:
b) a first mode of operation wherein the optical signals transmitted to the first detecting means pass through the sample cell and optical signals transmitted to the second detector bypass the sample cell; and
c) a second mode of operation wherein the optical signals transmitted to the first and second detecting means bypass the sample cell.
2. The method of claim 1, wherein steps b) and c) are carried out cyclically in time.
3. The method of claim 1 or 2, wherein the optical signals from said at least one optical beam are transmitted to the first and second optical detecting means by dividing the optical beam into at least two sub-beams using optical beam splitting means.
4. The method of any of claims 1-3, wherein said optical source means comprises at least two optical sources which are operated in a manner that in the first mode of operation the optical signals originate from a first optical source and in the second mode of operation the optical signals originate from a second optical source.
5. The method of claim 4, wherein the first optical source transmits optical signals to the first detecting

means via, in sequential order, a first optical beam splitter, the sample cell and a second optical beam splitter, and to the second detecting means via, in sequential order, the first optical beam splitter and a third optical beam splitter.

6. The method of claim 5, wherein the second optical source transmits optical signals to the first detecting means via, in sequential order, a fourth optical beam splitter and the second optical beam splitter, and to the second detecting means via, in sequential order, the fourth optical beam splitter and the third optical beam splitter.

7. A process analyser for self-correcting spectroscopic analysis of a fluid stream, comprising

- optical source means for creating at least one optical beam, means for transmitting optical signals from said at least one optical beam in at least two modes of operation to a first optical detecting means and to a second optical detecting means, and means for monitoring the electrical signals as detected by each detecting means;
- in a first mode of operation, means for passing the optical signals transmitted to the first detecting means through the sample cell and means for bypassing the optical signals transmitted to the second detector, the sample cell; and
- in a second mode of operation, means for bypassing the optical signals transmitted to the first and second detecting means, the sample cell.

8. The process analyser of claim 7, comprising optical beam splitting means for dividing said at least one optical beam so as to transmit the optical signals to the first and second optical detecting means.

9. The process analyser of claim 7 or 8, wherein said optical source means comprises at least two optical

sources, a first optical source transmitting optical signals to the first detecting means via, in sequential order, a first optical beam splitter, the sample cell and a second optical beam splitter, and to the second detecting means via, in sequential order, the first optical beam splitter and a third optical beam splitter.

10. The process analyser of claim 9, wherein a second optical source transmits optical signals to the first detecting means via, in sequential order, a fourth optical beam splitter and the second optical beam splitter, and to the second detecting means via, in sequential order, the fourth optical beam splitter and the third optical beam splitter.

11. The process analyser of any of claims 7-10, wherein the optical beam splitting means is a single optical crystal.

12. The process analyser of any of claims 7-10, wherein the optical beam splitting means is a combination of optical components such as a corner cube and beam splitting elements.

13. The method substantially as described hereinbefore with reference to the drawings.

14. The process analyser substantially as described hereinbefore with reference to the drawings.

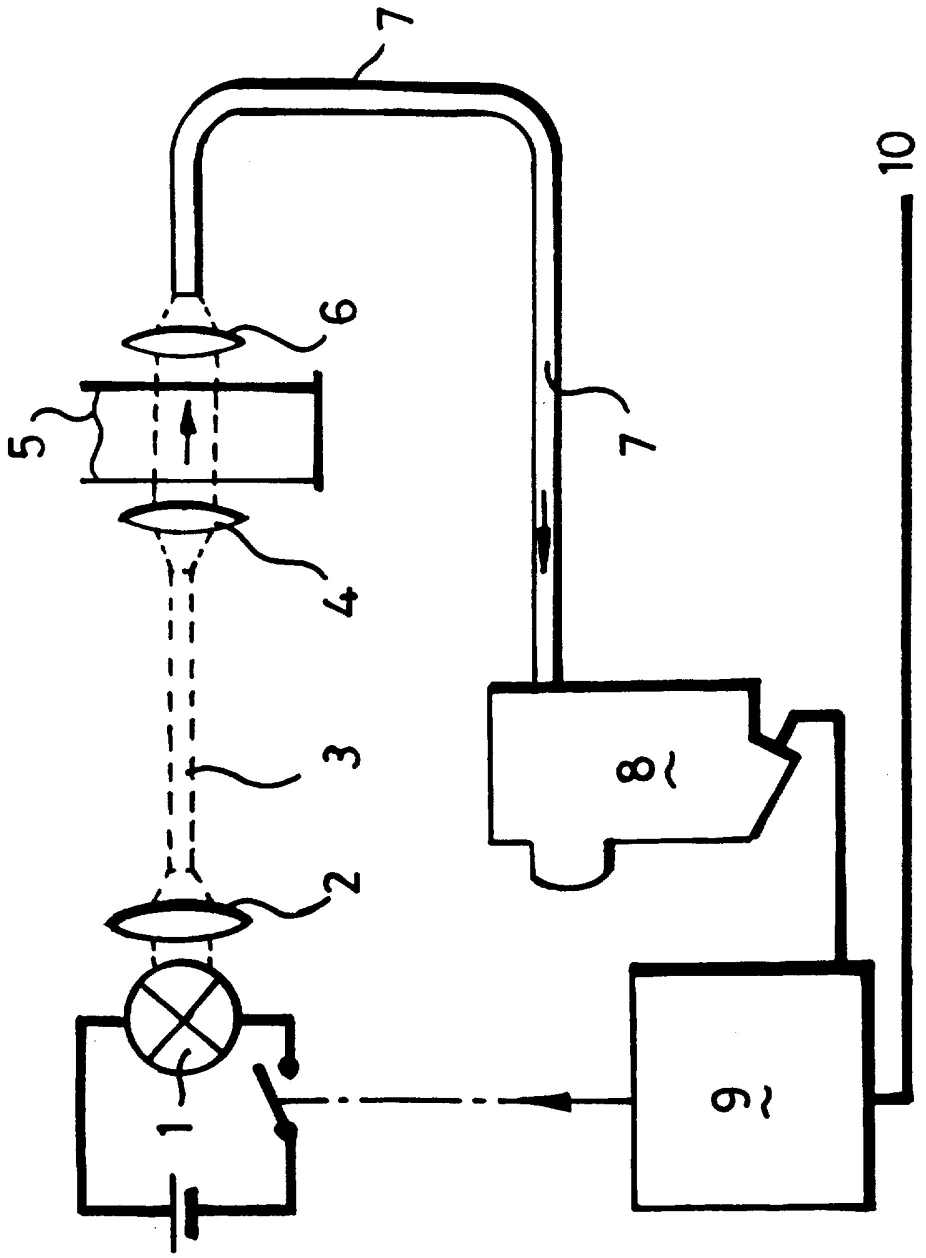

FIG.1

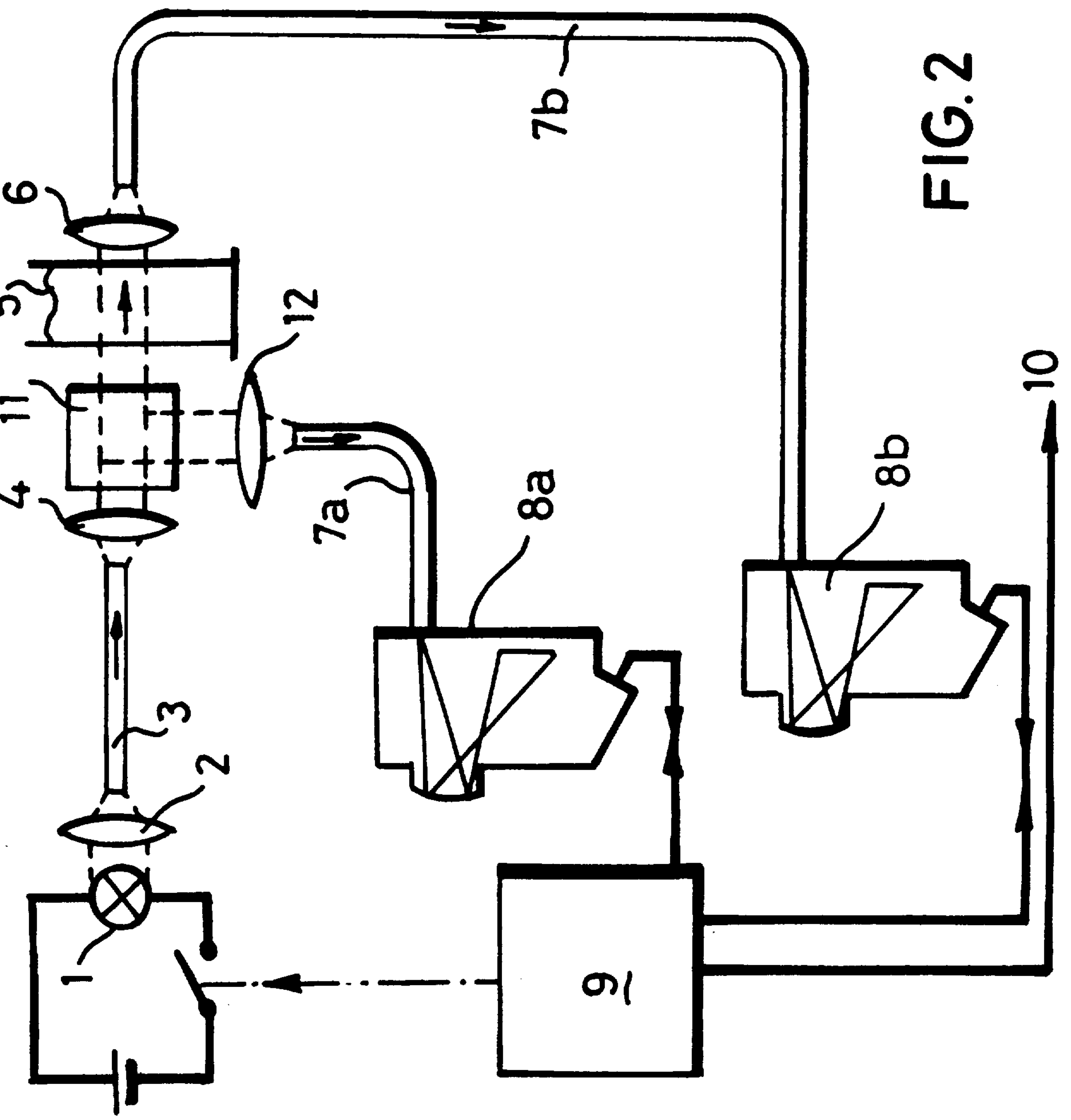

FIG.2

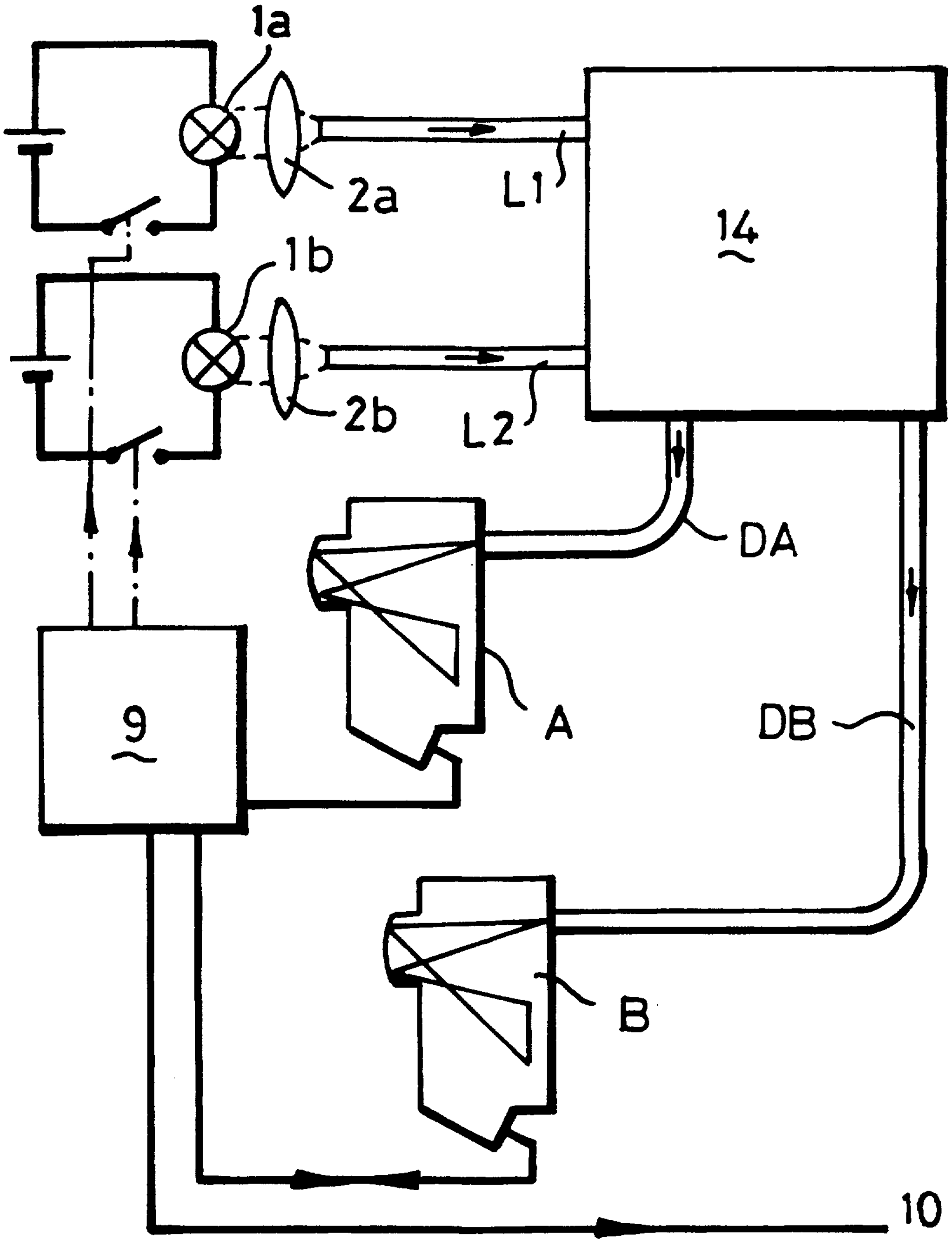

FIG.3

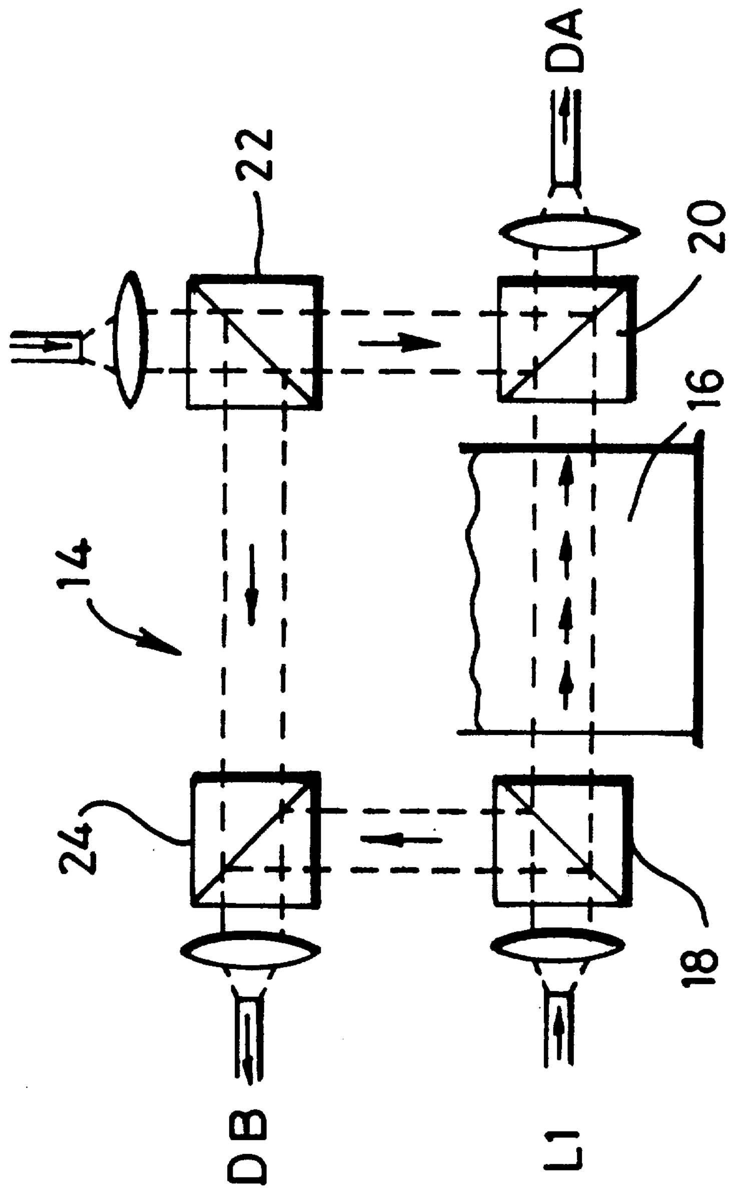

FIG. 4

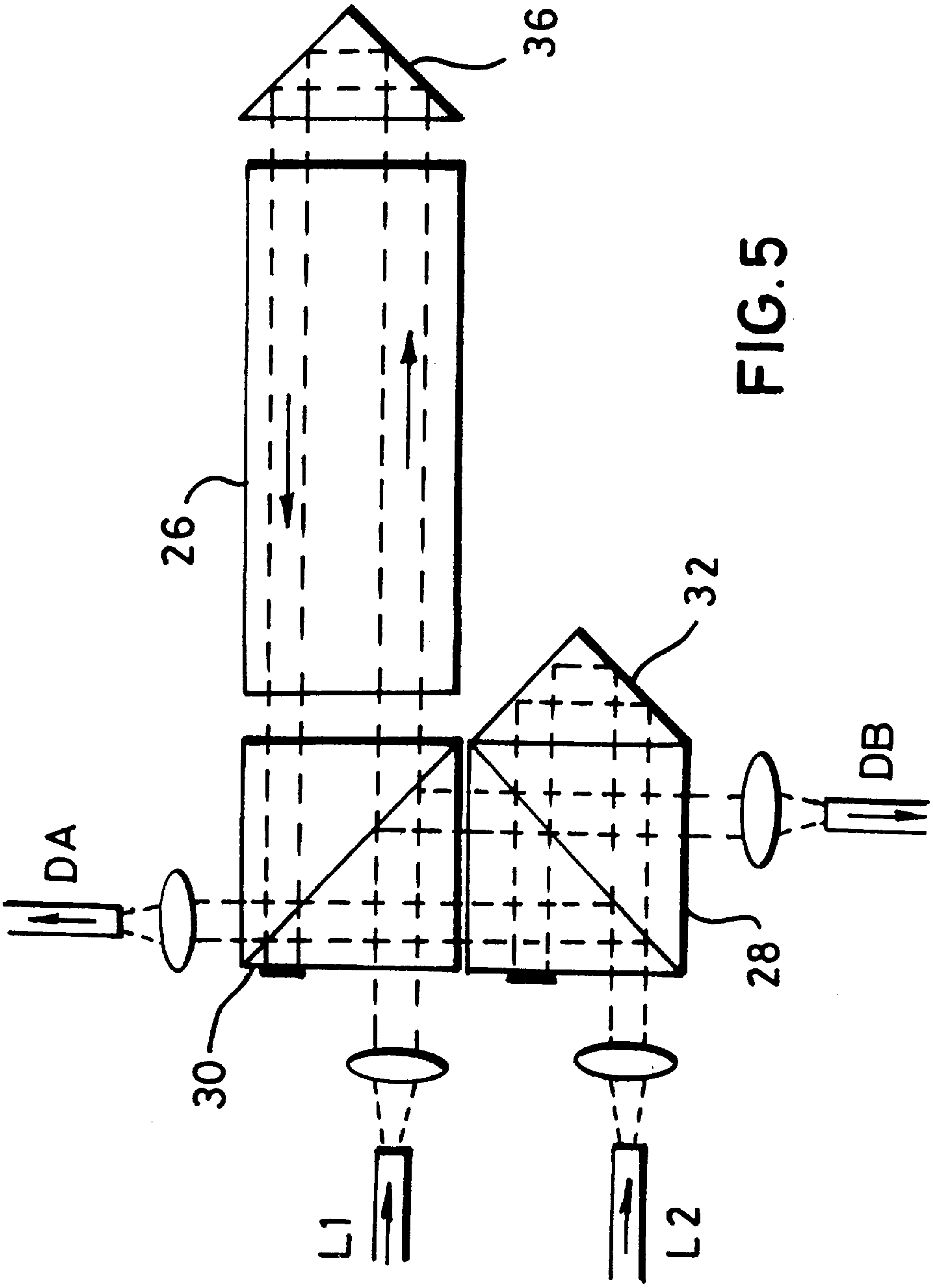

FIG.5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/00645

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N21/27

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)
IPC 6 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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 629 589 A (GLEIXNER) 21 December 1971 see column 3, line 34 - column 4, line 14	1-4,7,8
A	see figure 1 ---	5,6,9,10
Y	US 4 687 337 A (STEWART) 18 August 1987 see column 1, line 10 - line 15 see column 6, line 43 - line 59 see column 7, line 23 - line 37 see column 9, line 22 - line 37 see column 10, line 26 - line 51 see column 11, line 4 - line 17 see column 13, line 42 - column 14, line 24; figures 1,4 --- -/--	1-4,7,8

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"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

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"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
9 May 1997	16.05.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Thomas, R.M.

- 3

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 477 328 A (TOKUMARU) 19 December 1995 see abstract see column 7, line 23 - line 38 see column 7, line 61 - column 8, line 57 see column 11, line 19 - line 64 see column 13, line 7 - line 17 see figures 4,11 ---	1-4,7,8
A	US 4 076 425 A (SALTZ) 28 February 1978 see column 1, paragraph 1 see column 3, line 44 - line 56 see column 4, line 55 - column 5, line 4 see column 5, line 21 - line 26 see column 7, line 48 - line 50 see column 7, line 58 - line 65 see figure 1 ---	1-3,7,8
A	US 4 329 048 A (CAPITINI) 11 May 1982 see column 1, line 5 - line 8 see column 5, line 29 - line 54 see column 6, line 17 - line 23 see column 6, line 46 - line 52 see figures 1,2 ---	1,7
A	US 3 872 315 A (BOLL) 18 March 1975 see abstract see column 1, last paragraph - column 2, line 33 see column 3, line 53 - line 56; figure 1 -----	1-4,7,8

3

INTERNATIONAL SEARCH REPORT

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In ional Application No
PCT/EP 97/00645

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