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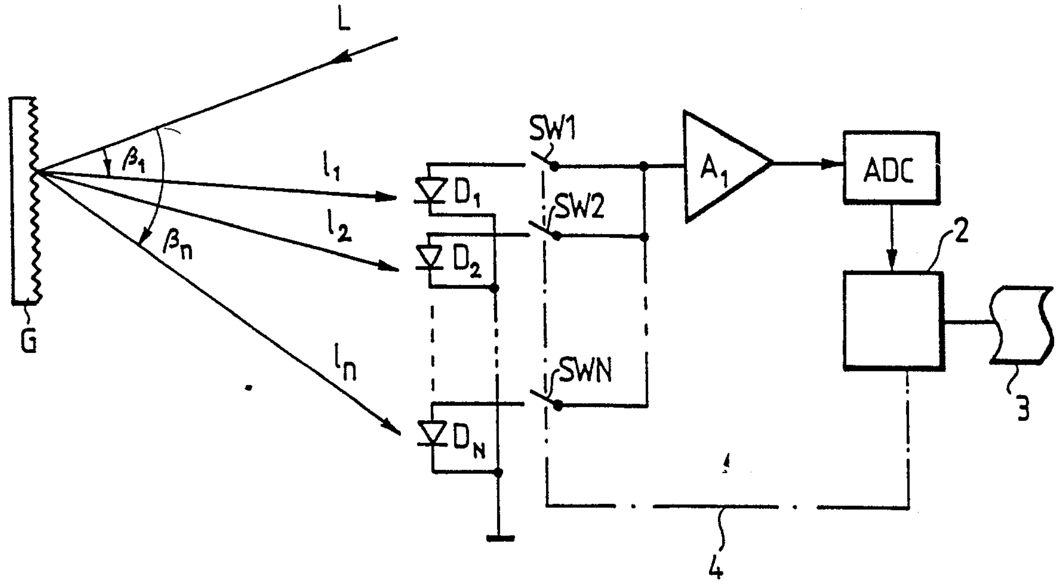
(54) Title: A SPECTROMETRIC METHOD AND A SPECTROMETER



(57) Abstract

The invention relates to a spectrometric method and a spectrometer for analyzing optical radiation. The spectrometer comprises an optical means (G) capable of causing dispersion of an optical beam (L) to be measured when the beam strikes it, and detecting means (D1 ... DN) for detecting the intensity of several discrete wavelengths (l_1 ... l_n) of the dispersed optical beam. According to the invention the detecting means comprises an array of at least N detector elements (D1 ... DN) having outputs connected to connecting means (SW1 ... SWN, A1) to connect the output signals of the detecting means in N different combinations to form N different sum signals during one measuring period, where N is the number of discrete wavelengths to be analyzed.

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A spectrometric method and a spectrometer

The invention relates to a spectrometric method and a spectrometer for analyzing optical radiation by causing dispersion of an optical beam and detecting the intensity of one or more discrete wavelengths of the dispersed optical radiation.

The spectrum of light passed through a material and reflected or scattered from it provides information on the chemical and physical structure of the material. The spectral analysis, starting from the ultraviolet region far into the infrared region of light, is usually carried out by a spectrometer by means of which light is collected from an object, polarized and then dispersed into the spectrum of its wavelength components by means of a prism or grating, for instance. A light intensity detector is thereby subjected to monochromatic radiation the wavelength of which depends on the position of the grating or prism with respect to the incoming beam of light and the detector. By mechanically turning the prism or grating or alternatively by displacing the detector, the intensities of the different wavelength components of light can be measured. The precision mechanism required by this prior art measuring technique makes this kind of spectrometers expensive and large in size, in addition to which they are not particularly well suited for use in industrial environments, where vibration, temperature variations and air impurities prevent reliable operation of the mechanism.

Instead of the above-described spectrometer, an alternative solution is to use the Michelson interferometer and the acousto-optical crystal. Both of them are used widely but the available constructions are expensive and liable to disturbances; on the other hand, they require less space than the mechano-optical construction described above.

In the above-described methods, the spectrum of optical radiation is determined by measuring separately the intensity of each discrete wavelength. To improve the signal-to-noise ratio and to increase sensitivity, alternative methods have been developed in which the measuring spectrum to be used is divided into several (N) discrete portions and a mask is disposed between the radiation source and the detector. In accordance with a suitable mathematical transform, usually the Hadamard transform, the mask shields off spectrum portions with N different combinations. The sum of the remaining radiation components is detected and the intensities of individual spectrum portions as well as the final spectrum are calculated by the inverse Hadamard transform from the detection results obtained with the N different combinations. As compared with direct detection, a $\sqrt{N}$-fold improvement is achieved in the signal-to-noise ratio. This kind of multiplexing is also advantageous in that the intensity of the light impinging on the detector is greater than in conventional methods, which further helps to improve the signal-to-noise ratio of the detection.

Previously the mask required by the Hadamard transform has been formed by a mechanically displaceable shield, which is difficult to construct for rapid measurements and for measurements to be performed under difficult conditions. The Hadamard transform and its application in spectrometers are described, e.g., in *Hadamard Transform Optics*, M. Harvit, N.J.A., Sloane, Academic Press, New York, 1979, p. 1-47.

Liquid crystal masks or other electrically controlled masks completely avoiding mechanically moving parts are disclosed in U.S. Patent 4,615,619 and in *Multiplex Advantage in Hadamard Transform Spectrometry Utilizing Solid-State Encoding Masks with Uniform, Bistable Optical Transmission Defects*, D.C. Tilotta *et al.*, Applied Optics, 1 October 1987, Vol. 26, No. 19, p. 4285-4292.

A drawback of the liquid crystal mask is, however, the limited spectral transmittance range (usually a wavelength below 1 µm, poor contrast and slowness particularly at low temperatures).

In a prior art spectrometer used for atmospheric analyses, the light sources themselves are modulated by a Hadamard matrix code instead of a mask. This system is simple as no mechanical devices are used, and no errors due to the mask occur. This kind of spectrometer is described in *Hadamard Transform Active Long Path Absorption Spectrometer*, N. Sugimoto, Applied Optics, 15 March 1986, Vol. 25, No. 6, p. 863-865.

The object of the present invention is to provide a novel spectrometric method and a spectrometer in which the sensitivity and the signal-to-noise ratio can be improved by various mathematical transforms with a construction simpler and more advantageous than previously.

This is achieved by the spectrometric method defined in claim 1 and the spectrometer defined in claim 4.

The present invention applies the Hadamard transform or some other suitable mathematical transform by causing the dispersion of the radiation to be analyzed by a diffraction prism or grating or some other technique in such a way that the wavelength components of the dispersed radiation fall on predetermined N detector elements in a detector array, and each detector element in the array produces an electric signal proportional to the intensity of the radiation which strikes it. In the present invention, the optical multiplexing used in the prior art is replaced with the multiplexing of the outputs of the detector elements by connecting them electrically together in N different combinations to form N sum signals, respectively. These sum signals correspond to an electric signal produced by a single detector from an optical sum signal in optical multiplexing. Each sum signal is sampled and after N sum signals have been measured, the intensities of individual wave lengths are calculated by an inverse algorithm corresponding to the summing operation, and the spectrum of the optical radiation to be analyzed is determined. In this way it is possible to construct an advantageous spectrometer providing high sensitivity, high resolution and wavelength accuracy without any mechanical or electric mask and avoiding the restrictions set by the above-mentioned liquid crystal shields on wavelength, speed and temperature. Being highly integrated, the device can be fitted in a very small space with a low power consumption and without moving parts so that it is suitable for use under difficult conditions and is portable.

As a great number of detectors can be integrated in a small space, the number N of the discrete wavelengths to be detected simultaneously is notably greater than in a conventional mask technique, even several thousands, that is, a greater improvement is achieved in the signal-to-noise ratio when the transform method is used.

The use of the above-mentioned system utilizing a Hadamard modulated light source array, for instance, is not possible when measuring the spectrum of active sources, that is, sources capable of emitting optical radiation, such as flames or molten metal. In such applications the present invention offers a new possibility of rapid and sensitive analyses.

The invention will now be described in greater detail with reference to the attached drawings, wherein

Figure 1 illustrates schematically the basic principle of the spectrometer of the present invention;

Figures 2 and 4 are examples of transform matrices to be used in connection with the invention; and

Figure 3 shows a circuit diagram of a detecting and multiplexing circuitry of the invention.

Figure 1 illustrating the general operation of the spectrometer of the invention will now be referred to. A beam of light to be analyzed impinges on an optical means, in this particular case a grating G which refracts different wavelengths into different refracting angles $ß_1 \ldots ß_n$, thus causing the dispersion of the beam of light L to be analyzed into different wavelength components, of which each N wavelength component $l_1 \ldots l_n$ strikes a detector element $D_1 \ldots D_N$ assigned to it in an array of detector elements positioned in the refraction plane of the beam of light. Each detector element produces an output signal proportional to the intensity of the wavelength component which has struck it. A controllable switching means SW1 ... SWN is connected selectively to the output of each detector element D1 ... DN. By means of the switching means, each output signal can be connected selectively to the input of a common amplifier A1. The switches SW1 ... SWN are controlled in an order determined by an applied mathematical transform, such as the Hadamard transform, one after another into N different combinations of closed and opened switches. These combinations produce N successive sum signals formed by the different output signals in the input of the amplifier A1 and amplified in its output. Digital samples are extracted from the output signal of the amplifier A1 by means of an analog-to-digital converter ADC. The digital samples are applied to a computer 2 which calculates, by the inverse Hadamard transform from the N sum signals obtained with the different switch combinations, the intensity of each discrete wavelength l_1 ...l_n to be analyzed and therethrough the spectrum of the optical radiation to be analyzed and displays it as such graphically or numerically or directly as a calibrated material concentration or in some other suitable manner by means of a printer 3, for instance. As it is in fact the computer 2 that determines which way of transform and transform matrix is used as well as the positions of the switches SW1 ... SWN, the connection between the computer 2 and the switches is indicated with a broken line 4.

In the preferred embodiment of the invention, the photodetectors are photodiodes, but they can alternatively be any detectors capable of producing a signal proportional to the intensity or energy of the light impinging on them, such as photoresistors, pyrometric elements, etc. Accordingly, the operation of the detectors may be based on photoelectricity or photoconductivity, and the measurements may utilize combination of signals proportional to the sums of resistances, voltages or currents.

In Figure 1, the reflection grating G causing the dispersion of the optical beam to be analyzed may be replaced with any optical device capable of causing dispersion. In place of reflected refracted light it is thereby possible to measure the intensity of the different wavelengths of refracted light passed through such a device.

In place of the combination of a computer and a measuring circuit described above it may in certain cases be preferable to construct the entire system with its mathematics processor into a fixed logic circuit or to divide the interface between the measuring circuit and the computer in some other way than that described above.

As to the Hadamard matrices and mathematical transform methods, the teachings of the above-mentioned references and articles can in this respect be directly applied in the present invention.

The example of Figure 2 shows a cyclic Simplex matrix suited for use in the above-described connection. Each position in a horizontal row of the matrix corresponds to one switching means, whereby the positions indicated "1" signify a closed switch and the positions indicated "0" signify an open switch. This kind of Simplex matrix control is easily realizable by a shift register provided with a parallel output. The computer controlling the measuring operation applies the first row of the matrix in series form to the shift register. Thereafter the code passes cyclically through the shift register in such a way that the last bit emerging from the shift register is returned to the beginning of the shift register. The signal-to-noise ratio obtained by this kind of Simplex matrix is $\sqrt{N}$ times better as compared with individual measurements carried out by N detectors.

Figure 3 shows the circuit according to the preferred embodiment of the invention to realize the system of Figure 1. In the figure, the computer 2 controlling the measuring applies the Hadamard matrix one row at a time through a parallel bus 34 in e.g. binary form to a decoder 31 which again converts the applied data into the original matrix row, in which the state of each position appears as the "0" or "1" state of the corresponding output of the decoder 31. Each output in the decoder 31 is connected to one input in a corresponding AND gate 32 when a trigger signal TRIG is applied to another input in the gate 32. The output of each gate 32 is applied to a corresponding memory element 33 having both an inverting and a noninverting output. A reset signal RESET is applied to the reset input of each memory element 33. The noninverting input of each memory element 33 controls a corresponding switch transistor Q11 ... Q1N connected between the cathode of the corresponding detector diode D1 and the noninverting input of the amplifier A1. Similarly the inverting output of each memory element 33 is connected to a corresponding switch transistor Q21 ... Q2N connected between the cathode of the corresponding detector diode D1 ... DN and the inverting input of the amplifier A1. The anodes of the detector diodes D1 ... DN are connected to a low potential, such as earth.

The output signals of the decoder 31 set the memory elements 33 through the AND gates 32 to a "0" or "1" state in accordance with the first matrix row of the Hadamard transform when the trigger signal TRIG is in the state "1". The outputs of the memory elements 33 control the corresponding switch transistor pairs Q11 ... QN and Q21 ... Q2N in such way that the photo diode D1 ... DN corresponding to the memory element 33 is connected to the noninverting input of the differential amplifier when the noninverting output of the memory element is 1, and equivalently, to the inverting input of the amplifier A1 when the inverting output of the memory element 33 is in the state "1". A charging voltage V_{load} is simultaneously applied to the inputs of the amplifier A1 through the transistors Q3 and Q4, respectively, and thus also to the cathodes of the photodiodes D1 ... DN, whereby the junction capacitances of the diodes are charged in the reverse direction. When the control signal LOAD-CMD of the transistors Q3 and Q4 is removed, the charging voltage V_{load} is removed and the diodes remain connected to the inputs of the amplifier A1 in accordance with the respective matrix row. The load of each diode D1 ... DN is discharged by a leakage current proportional to the intensity of light striking the diode, whereby a voltage proportional to the difference between the total intensities of light entering the diode groups connected to the inputs of the differential amplifier A1 is obtained from the output of the differential amplifier A1 after a selected measuring period. This voltage is sampled, and the sample is digitized and stored in the memory of the computer 2. The memory elements 33 are then reset to zero by the signal RESET and a new Hadamard matrix row is applied through the decoder 31 to the memory elements 33, whereafter the above-mentioned charging and measuring operations are removed. The same is repeated until all N horizontal rows of the Hadamard matrix are gone through and the corresponding measuring data are stored in the memory of the computer. The intensities of individual wavelength regions are then determined by the inverse Hadamard transform and the results are shown in suitable form. This measuring method, in which two detector assemblies are compared with each other, provides a $\sqrt{N}$-fold improvement in the signal-to-noise ratio as compared with separate measurings carried out by N elements. In the preferred embodiment of the invention, 1024 elements are used, so the obtained improvement is 32-fold.

Figure 5 shows an 8-row matrix H_8 suited for the above-mentioned connection. In the matrix, the elements indicated "1" signify diodes to be connected to the noninverting input of the amplifier A1, and the elements indicated "-1" signify diodes to be connected to the inverting input. In the output of the decoder 31 the state "0" corresponds to the element "-1" of the matrix H_8.

It is also possible to use Hadamard-coded radiation sources or detectors of varying construction either separately or in synchronization with each other. In the latter case an improvement in the signal-to-noise ratio is obtained under noise conditions if scattered random radiation of high intensity occurs in proximity to the detector in the same wavelength region in addition to a weak signal coming from a long distance, and this random radiation is able to pass through the measuring optics to the detector by scattering from the impurity particles of the surroundings. This may happen, e.g., in industrial establishments when measuring air pollutants.

The figures and the description related to them are only intended to illustrate the present invention. In its details the present invention may vary within the scope of the attached claims.

Claims:

1. A spectrometric method of analyzing optical radiation, comprising the steps of causing dispersion of an optical beam to be analyzed and detecting the intensity of one or more discrete wavelengths of the dispersed optical radiation, characterized in that the method further comprises producing an electric signal proportional to said intensity separately for each wavelength to be analyzed; combining said signals in N different combinations to form N different sum signals during one measuring period, where N is the number of discrete wavelengths to be analyzed; and determining the intensities of the different wavelengths by means of said N sum signals.

2. A method according to claim 1, characterized in that two signal groups are formed for each sum signal from said signals proportional to the intensity, the difference between the total intensities of the two signal groups forming said sum signal.

3. A method according to claim 1 or 2, characterized in that said signals proportional to the intensity are combined on the Hadamard transform principle.

4. A spectrometer comprising an optical means (G) causing dispersion of an optical beam (L) to be measured when the beam strikes it, and detecting means (D1 ... DN) for detecting the intensity of one or more discrete wavelengths ($l_1 \ldots l_n$) of the dispersed optical beam, characterized in that the detecting means comprises an array of at least N detector elements (D1 ... DN) having outputs connected to connecting means (SW1 ... SWN, A1) so as

to connect the output signals of the detector elements in N different combinations to form N different sum signals during one measuring period, where N is the number of discrete wavelengths to the analyzed.

5. A spectrometer according to claim 4, characterized in that the output of each detector element (D1 ...DN) is selectively connectable through a controllable switching means (SW1 ... SWN) to the input of a common amplifier means (A1).

6. A spectrometer according to claim 4, characterized in that the output of each detector element (D1 ... DN) is selectively connectable through a first controllable switching means (Q11 ... QN) to the inverting input of the common amplifier means (A1) and through a second controllable switching means (Q21 ... Q2N) to the non-inverting input of said amplifier means (A1).

7. A spectrometer according to claim 4, 5 or 6, characterized in that said optical means capable of causing dispersion is a diffraction grating or diffraction prism.

8. A spectrometer according to claim 4, 5, 6 or 7, characterized in that the detector element is a photodiode.

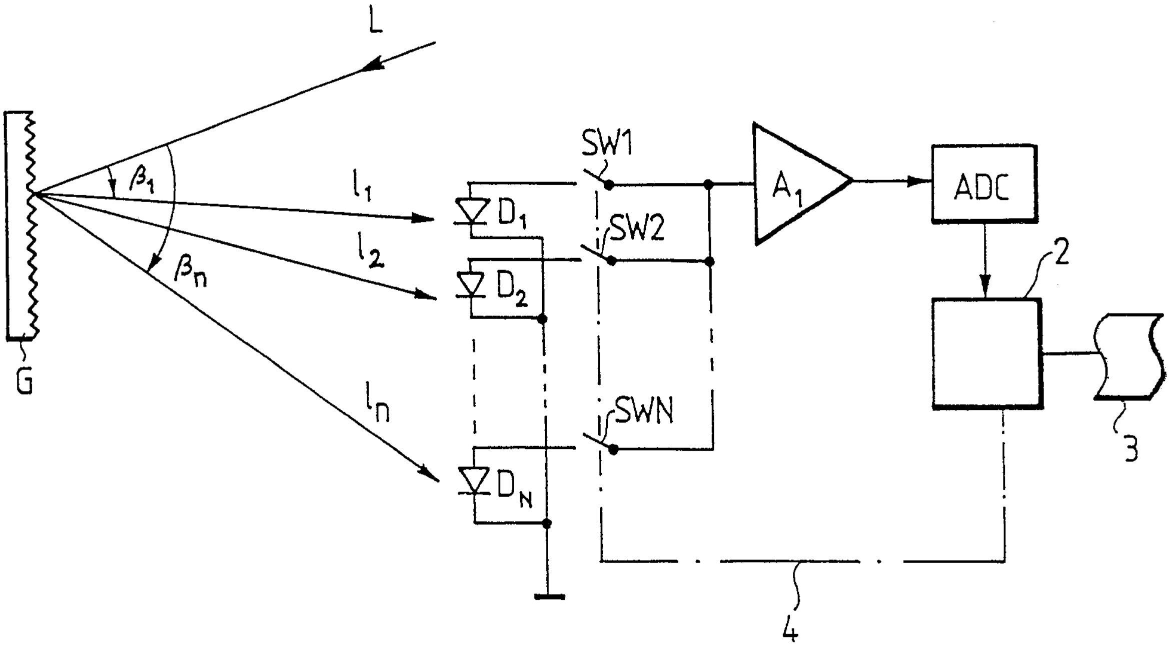

FIG. 1

$$S_7 = \begin{bmatrix} 1 & 1 & 1 & 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 1 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 1 & 1 \\ 0 & 1 & 0 & 0 & 1 & 1 & 1 \\ 1 & 0 & 0 & 1 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 & 1 & 0 & 1 \\ 0 & 1 & 1 & 1 & 0 & 1 & 0 \end{bmatrix}$$

FIG. 2

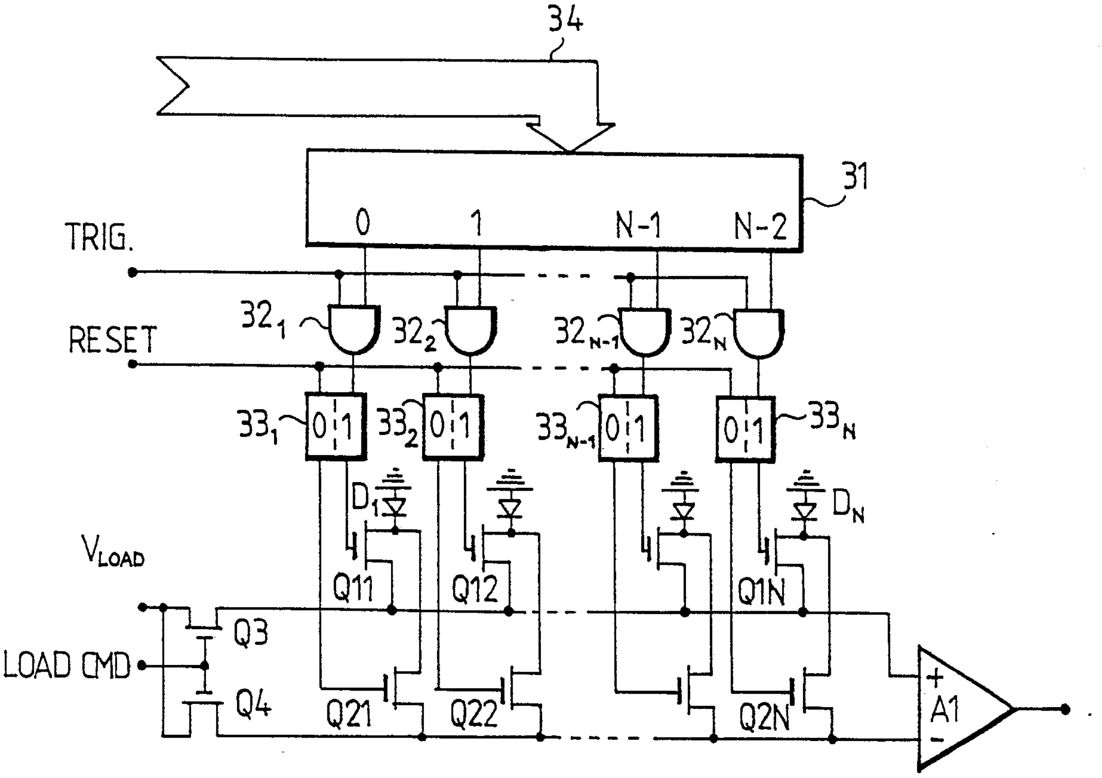

FIG. 3

$$
\begin{bmatrix}
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\
1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \\
1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \\
1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\
1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 \\
1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \\
1 & -1 & -1 & 1 & -1 & 1 & 1 & -1
\end{bmatrix}
$$

FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 90/00202

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: G 01 J 3/30, 3/18, G 01 N 21/27

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	G 01 J; G 01 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US, A, 4318615 (H. SAGUSA ET AL) 9 March 1982, see column 10, line 13 - line 17; abstract; claims 1-9	1-2,4-8
Y		3
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X	US, A, 4557601 (T. KUROISHI ET AL) 10 December 1985, see the figures 4-7 and related text	1-2,4-8
Y		3
	--	
Y	US, A, 4007989 (E. WAJDA) 15 February 1977, see abstract	3
	--	
Y	Patent Abstracts of Japan, Vol 7, No 146, P206, abstract of JP 58- 58423, publ 1983-04-07 TOKYO SHIBAURA DENKI K.K.	1-2,4-8
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IV. CERTIFICATION

Date of the Actual Completion of the International Search 6th December 1990	Date of Mailing of this International Search Report 1990 -12- 1 1
International Searching Authority SWEDISH PATENT OFFICE	Signature of Authorized Officer UDO HINZ

Form PCT/ISA/210 (second sheet) (January 1985)

International Application No. PCT/FI 90/00202

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	Derwent's abstract No. A86 81C C/04, SU 661 263, publ. week 8004 --	1-2,4-8
L	US, A, 4242695 (H. OUCHI ET AL) 30 December 1980, cited in US,A, 4557615 -- --------	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 90/00202

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 90-11-01
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		JP-C- 1313409	86-04-28
		JP-A- 52042782	77-04-02
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