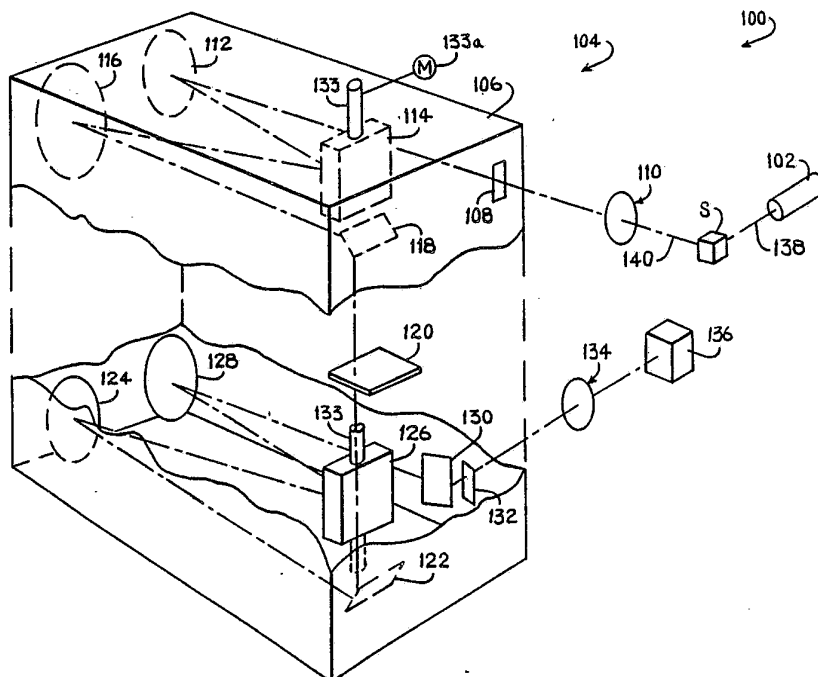


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁴ : G01N 21/65</p>	<p>A1</p>	<p>(11) International Publication Number: WO 89/ 01622 (43) International Publication Date: 23 February 1989 (23.02.89)</p>
<p>(21) International Application Number: PCT/US88/02688 (22) International Filing Date: 8 August 1988 (08.08.88) (31) Priority Application Number: 085,530 (32) Priority Date: 14 August 1987 (14.08.87) (33) Priority Country: US (71) Applicant: D.O.M. ASSOCIATES, INC. [US/US]; Post Office Box 688, Manhattan, KS 66502 (US). (72) Inventors: FATELEY, William, G. ; 1928 Leavenworth, Manhattan, KS 66052 (US). TILOTTA, David, C. ; 1225 Porter Street, Des Moines, IA 50315 (US). (74) Agents: COLLINS, John, M. et al.; Hovey, Williams, Timmons & Collins, 1101 Walnut, Suite 1400, Kansas City, MO 64106 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report</i> <i>With amended claims.</i> Date of publication of the amended claims: 23 March 1989 (23.03.89)</p>

(54) Title: RAMAN SPECTROMETER HAVING HADAMARD ELECTROOPTICAL MASK AND DIODE DETECTOR



(57) Abstract

A Raman spectrometer device is provided which provides useful spectral information in situations where Raman spectroscopy has heretofore been unworkable. The spectrometer (100) makes use of a stationary electrooptical masking device (120) in lieu of conventional slit scanning optics, with the mask (120) being computer controlled to provide a multiplexing function, typically employing Hadamard mathematics. The stationary encoding mask permits use of a relatively inexpensive photodiode detector, as compared with photomultiplier tubes conventionally used in Raman instrumentation. Advantageously, unwanted Rayleigh scattered radiation can be completely eliminated, either by blanking those zones of the mask (120) receiving such radiation, or physically locating the device in such orientation that the Rayleigh scattered radiation does not pass through operative portions of the mask (120).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

AMENDED CLAIMS

[received by the International Bureau on 14 February 1989 (14.02.89)
original claims 1, 2, 5 - 9 cancelled; new claims 10 - 26 added; other claims
unchanged (7 pages)]

1

1. (Cancelled)

2. (Cancelled)

5

3. The spectrophotometer of Claim 15,
said detector being a photodiode detector.

4. The spectrophotometer of Claim 15,
10 said source being operable for generating mono-
chromatic radiation having a wavelength of from
about 0.1 to 2.0 microns.

5. (Cancelled)

15

6. (Cancelled)

7. (Cancelled)

20

8. (Cancelled)

9. (Cancelled)

25

30

35

1 10. An apparatus for detecting Raman
spectra in electromagnetic radiation emanating
from a sample to be analyzed as a result of
directing a beam of monochromatic light from a
5 source thereof into the sample, the radiation
including Raman and Rayleigh scattered radiation,
said apparatus comprising:

 dispersing means for receiving and disper-
 sing said radiation as dispersed rad-
10 iation along a path, said dispersed
radiation including Raman and Rayleigh
scattered radiation;

 a stationary, electro-optical device situ-
 ated for impingement of at least a
15 portion of said dispersed radiation
thereon and including --

 a body presenting a pair of opposed faces,
 zone defining means carried by said body for
 dividing at least one of said faces
20 into a plurality of discrete, electri-
cally alterable zones, and

 zone altering means operably coupled with
 said zone defining means for selective
 alteration of each zone respectively
25 between a relatively transmissive
condition relative to said dispersed
radiation and a relatively opaque
condition relative to said dispersed
radiation;

30 means for preventing passage of Rayleigh
scattered radiation present in said
dispersed radiation through relatively
transmissive ones of said zones during
analysis of the sample and for allowing
35 passage of at least a portion of said

1 Raman scattered radiation present in
said dispersed radiation through trans-
missive ones of said zones during
analysis of the sample;
5 dedispersing means for receiving and dedis-
persing radiation passing through
transmissive ones of said zones; and
detector means for receiving and detecting
dedispersing radiation from said dedis-
10 persing means in order to detect Raman
spectra thereof.

11. The apparatus as set forth in
Claim 10, further including a laser as said
15 source of said monochromatic light beam and means
for directing said beam into the sample.

12. The apparatus as set forth in
Claim 10, said masking device including a liquid
20 crystal masking device.

13. The apparatus as set forth in
Claim 10, said zone altering means including --
means for successively and sequentially
25 changing over time in a predetermined
fashion the patterns of said zones
altered relatively transmissive and
opaque during analysis of the sample,
and
30 means operably connected with said detector
means for successively receiving and
analyzing detected radiation informa-
tion from said detector means during
each of said patterns in order to
35 provide a spectral analysis.

1 14. The apparatus as set forth in
Claim 10, said preventing means including means
for selectively adjusting said path of said
dispersed radiation in order to prevent impinge-
5 ment of said Rayleigh scattered radiation on
transmissive ones of said zones.

10 15. The apparatus as set forth in
Claim 10, said Rayleigh scattered radiation
present in said dispersed radiation impinging on
certain ones of said zones, said preventing means
including means for altering said certain ones of
said zones to said relatively opaque condition
thereby preventing passage of said Rayleigh
15 scattered radiation through relatively trans-
missive ones of said zones.

20 16. The apparatus as set forth in
Claim 10, said zone altering means including a
microcomputer.

25 17. The apparatus as set forth in
Claim 10, said detector means including a
photodiode.

30

35

1 18. In a method of detecting Ramam
spectra including the steps of directing a beam
of monochromatic light into a sample to be
analyzed, and collecting electromagnetic radi-
5 ation emanating from the sample as a result of
the beam, the radiation including Raman and
Rayleigh scattered radiation, the improvement
which comprises the steps of:

 dispersing the radiation emanating from the
10 sample as dispersed radiation along a
path, said dispersed radiation includ-
ing Raman and Rayleigh scattered
radiation;

 providing and positioning a stationary
15 electro-optical masking device for
impingement of at least a portion of
said dispersed radiation thereon
wherein said masking device includes --
a body presenting a pair of opposed faces,
20 zone-defining means carried by said body for
dividing at least one of said faces
into a plurality of discrete, electri-
cally alterable zones, and zone-alter-
ing means operably coupled with said
25 zone-defining means for selective
alteration of each zone respectively
between a relatively transmissive
condition relative to said dispersed
radiation and a relatively opaque
30 condition relative to said dispersed
radiation;

 preventing passage of Rayleigh scattered
radiation present in said dispersed
radiation through relatively trans-
35 missive ones of said zones during

1 analysis of the sample and allowing
passage of at least a portion of said
Raman scattered radiation present in
said dispersed radiation through rela-
5 tively transmissive ones of said zones
during analysis of the sample;
dedispersing radiation passing through
relatively transmissive ones of said
zones by use of a dedispersing device;
10 and
detecting the dedispersed radiation from
said dedispersing device in order to
detect Raman spectra thereof.

15 19. The improvement as set forth in
Claim 18, further including the step of providing
a laser as the source of the beam of monochro-
matic radiation and directing the beam into the
sample.

20 20. The improvement as set forth in
Claim 18, further including the step of detecting
the dedispersed radiation with a photodiode.

25 21. The improvement as set forth in
claim 18, said monochromatic radiation having a
wavelength of from about 0.1 to 2.0 microns.

30 22. The improvement as set forth in
Claim 18, said masking device including a liquid
crystal masking device.

35

1 23. The improvement as set forth in
Claim 18, further including the steps of:

 successively and sequentially changing over
 time in a predetermined fashion the
5 patterns of said zones altered rela-
 tively transmissive and opaque during
 analysis of the sample, and

 successively receiving and analyzing
 detected radiation information from
10 said detector means during each of said
 patterns in order to provide a spectral
 analysis.

 24. The improvement as set forth in
15 Claim 18, said preventing step including the step
 of selectively adjusting said path of said dis-
 persed radiation in order to prevent impingement
 of said Rayleigh scattered radiation on trans-
 missive ones of said zones.

20 25. The improvement as set forth in
 Claim 18, said Rayleigh scattered radiation
 present in said dispersed radiation impinging on
 certain ones of said zones, said preventing step
25 including the step of altering said certain ones
 of said zones to said relatively opaque condition
 thereby preventing passage of said Rayleigh
 scattered radiation through relatively trans-
 missive ones of said zones.

30 26. The improvement as set forth in
 Claim 18, said zone altering means including a
 microcomputer.

35