Nov. 17, 1964 J. M. ROCHE 3,157,788

ATTENUATED TOTAL REFLECTANCE INFRA RED SAMPLING DEVICE

Filed Nov. 27, 1962

FIG. 1.

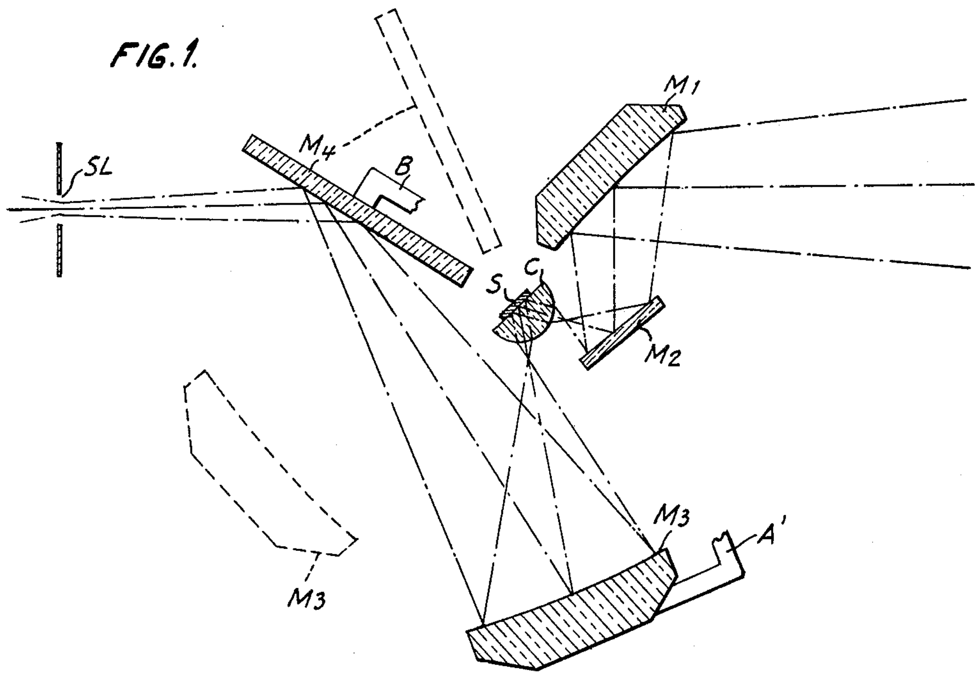
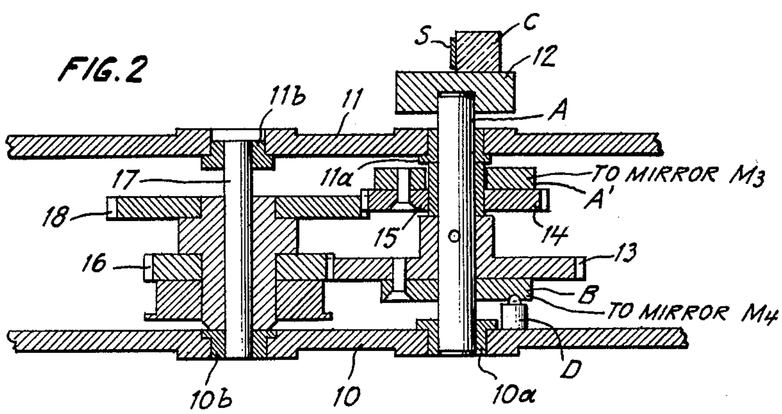


FIG. 2



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3,157,788

Patented Nov. 17, 1964

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3,157,788

ATTENUATED TOTAL REFLECTANCE INFRA RED SAMPLING DEVICE

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Filed Nov. 27, 1962, Ser. No. 240,367
15 Claims. (Cl. 250—83)

This invention relates to an improved accessory for use with an infra-red spectrophotometer, and more particularly, to a compact optical-mechanical arrangement permitting obtaining spectra with a micro-sized sample over a wider range of incident angles than heretofore possible with known techniques and equipment.

Attenuated total reflectance, or ATR as it is frequently called, is based on the fact that when a beam of radiation is totally reflected, as in a hemicylindrical prism, some of the radiation escapes from the reflecting surface (the flat side) and penetrates somewhat into whatever is in contact with the reflecting surface. When a physical sample is placed in contact with the reflecting face, penetration of the sample increases at wave lengths at which the sample absorbs, and this absorption is selective as to wave length. By plotting the energy of the reflected beam with respect to wave length, one obtains an absorption spectum closely resembling that obtained by heretofore known transmission techniques, such, for instance, as shown and described in Patent No. 2,870,343 to Golay, to which reference may be had.

Certain disadvantages have characterized the heretofore known tehcniques used in ATR. Among these may be mentioned:

(1) The sample had to be placed at an oversized and defocused beam position, with a consequent limited range of incident angle;

(2) Usually, poor sample-to-crystal contact occurred, because of the necessity of using a relatively large sample;

(3) Non-uniform (non-collimated) radiation occurred at the sample-crystal surface;

(4) The optical system was usually inefficient;

(5) The range of incident angle control was usually small (40–65°);

(6) The mechanical system usually gave poor reproducibility.

Among the objects of my invention are:

To provide an improved mechanical-optical system for ATR, which permits the use of relatively smaller samples, with consequent reduced difficulties due to poor contact between sample and crystal;

To provide an improved system of the character described, permitting a wider range of incident angle, such as between 25° and 65°, with improved control;

To provide an improved system giving a more nearly uniform radiation at the sample-crystal surface;

To provide a more efficient optical system with constant energy and image quality at all angles of incidence.

To provide better reproducibility of the mechanical system.

Still other objects and advantages of my invention will be apparent from the specification.

The features of novelty which I believe to be characteristic of my invention are set forth with particularity in the appended claims. My invention itself, however, both as to its fundamental principles and as to its particular embodiments, will best be understood by reference to the specification and accompanying drawing, in which

FIG. 1 is an optical schematic diagram of the system of my invention, and

FIG. 2 is a sectional elevation of one form of mechanism employed in my invention.

Referring now more particularly to FIG. 1, stationary

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toroid mirror M1 receives a converging beam of infrared radiation from a primary source, not shown, and reflects it to stationary flat mirror M2 which in turn directs it toward the hemicylinder high index crystal C, where a reduced image of the radiation source is formed at the primary focal length plane of the crystal (in this case, germanium).

All radiation in this plane will then be collimated by the crystal, yielding a small sample size with collimated incident radiation. The image size at the flat back of the crystal, where the sample S is placed (i.e., sample-crystal surface), in this instance is less than 2 x 12 mm.

The reflected radiation beam is then focused at the primary focal length plane of the crystal and diverges, impinging on rotatable toroid mirror M3, which reflects it to rotatable flat mirror M4. The 10° off-axis toroid mirror M3 and flat M4 refocus the image at the proper point and with the proper dimensions (in this instance at the entrance slit SL of the spectrophotometer). This refocusing is done at any angle of incidence between 25° and 65°, and it may be noted here that mechanical limitations prevent further travel (further variation of the angle of incidence).

For precision of operation and reproducibility of results, it is necessary to maintain an optical path of constant length over the permissible variation of the angle of incidence, as the toroid mirror M3 and flat mirror M4 swing about their common center of rotation to positions such as shown in dotted lines. It is also necessary that the angular travel of toroid mirror M3 be exactly twice that of flat mirror M4. One form of mechanism, according to my invention, for accomplishing this will now be described.

Referring now to FIG. 2, showing the mechanical elements of my arrangement, in accordance with this embodiment of my invention, I provide a base plate **10** and a top plate **11** both extending from a support (not shown), providing the frame of the instrument. Shaft A is journalled in bearing bushings **10*a*** and **11*a*** in plates **10** and **11** for rotation, and carries at its projecting upper end a platform **12** on which are secured the crystal C and sample S, so that crystal C and sample S rotate with shaft A. Toroid mirror M3 is mounted on arm A′, the center of rotation for which is shaft A, but arm A′ is not fixed to shaft A and does not rotate therewith.

A second arm, B, which carries flat mirror M4, is secured to shaft A for rotation therewith. Flat mirror M4 carried by arm B is secured to a 99 tooth gear **13** and both are locked to shaft A for rotation therewith.

Toroid mirror M3 is secured to a 70 tooth gear **14** and both are mounted on a bearing **15** on shaft A, to permit them to rotate about shaft A as a center, but they do not rotate with shaft A.

The drive for arm A′, gear **14**, and mirror M3 is obtained from 99 tooth gear **13**, meshing with 70 tooth gear **16** on countershaft **17**, journalled in bushings **10*b*** and **11*b*** in plates **10** and **11**, and driving gear **16**. Countershaft **17**, driven by gear **16**, in turn driven by gear **13**, drives countershaft gear **18**, having 99 teeth, meshing with and driving 70 tooth gear **14**, which rotates mirror M3.

In order to maintain an optical path of constant length over the total variation of the angle of incidence, mirror M3 must rotate exactly 2:1 with the rotation of flat mirror M4. This is obtained in the instance shown by employing a motion step-up ratio from gear **13** to gear **16** equal to $\sqrt{2}$, and a step-up ratio from gear **18** to gear **14** and arm A′ of $\sqrt{2}$, giving a total step-up of 1 to 2 from flat mirror M4 to toroid mirror M3. At the same time, the plane of the mirror surface of mirror M4 must be in the same plane as the axis of rotation i.e., that of shaft A.

Reproducibility of incident angle is easily effected by using detent positions on one of the rotating arms, for example, on arm B, as shown by detent D engaging appropriate depressions on the lower side of arm B.

The following points may be noted. Stationary toroid mirror **M1** is mounted 45° off the axis; rotatable toroid mirror **M3** is mounted 10°20′ off the axis; hemicylinder C rotates one to one with flat mirror **M4**, and one to two with toroid **M3**. Rotation of crystal C about its optical axis permits selection of the angle of incidence, within the mechanical limits of the apparatus.

From the foregoing it will be seen that my invention provides the following advantages over the heretofore known methods and apparatus:

(*a*) Good sample-to-crystal contact due to small image size;

(*b*) Collimated radiation in one plane at the sample-crystal surface;

(*c*) High reproducibility of incident angle;

(*d*) Effective optical system using the crystal configuration for pupil image correction in addition to collimating the incident radiation.

(*e*) Wider range of incident angle (25°–65°) with constant energy and image quality at all angles of incidence.

The foregoing design is made intentionally compatible with the limited sample space of present production infrared instruments, but it will be understood that other construction designs are possible where production requires or permits.

It may be noted that the error introduced by using the 99–70 tooth ratio as a close approximation to $\sqrt{2}$ is of the order of 0.01%.

While I have shown and described what are for certain purposes the preferred forms of my invention, and the best mode presently known to me of carrying it out, it should be understood that modifications and changes may be made without departing from the spirit and scope of my invention.

I claim:

1. In an infrared spectrophotometer, in combination, means for focusing a beam of radiation at the primary focal length plane of a hemicylindrical high refractive index crystal to reflect partially at the plane surface of said crystal, a swingable toroid mirror for receiving the reflected beam and directing it along a path, a swingable plane mirror in said path, both said last named mirrors being mounted for rotation about the same axis.

2. The combination claimed in claim 1 in which the angular rotation speeds of said swingable toroid mirror and said swingable plane mirror are in the ratio of 2:1.

3. An accessory for infrared spectrophotometers, comprising, in combination, means for focusing a beam of infrared radiation at the primary focal length plane of a hemicylindrical high index crystal, to produce partial reflection from the flat face of said crystal, and means comprising a pair of mirrors in tandem for receiving the reflected beam and focusing it, said mirrors being coupled together for rotation about the same axis.

4. The combination claimed in claim 3 in which said mirrors are rotated at a speed ratio of 2:1.

5. The combination claimed in claim 3 in which said coupling means includes a shaft, a pair of gears on said shaft, one of said gears being fixed for rotation with said shaft and the other free for rotation about said shaft, and gearing coupling said gears for rotating said free gear at twice the speed of said fixed gear.

6. An accessory for infrared spectrophotometers comprising, in combination, means for supporting a hemicylindrical high index crystal for rotation, means for focusing a beam of infrared radiation at the primary focal length plane of said crystal, means for receiving the partially reflected beam from said crystal and focusing it at the entrance slit, means for varying the angle of incidence of said beam on said crystal, and means for maintaining constant the length of the path of said beam as the angle of incidence is varied.

7. The combination claimed in claim 6, in which said last mentioned means comprises a toroid and a flat mirror for receiving and focusing the beam from said crystal, both said mirrors being mounted for rotation about the same center.

8. The combination claimed in claim 7, in which the angular velocity of rotation of said toroid mirror is twice that of said flat mirror.

9. The combination claimed in claim 7 in which said toroid and flat mirrors are geared together to move in a predetermined angular speed ratio.

10. The combination claimed in claim 7, in which the plane of the flat mirror surface extended contains the axis about which said mirror rotates.

11. In infrared spectrophotometer apparatus, in combination, a hemicylindrical high index crystal for carrying a sample to be examined, means for focusing a beam of infrared radiation at the primary focal length plane of said crystal, means for rotating said crystal about its optical axis to permit selection of the angle of incidence, means for focusing the partially reflected beam from said crystal, and means for maintaining the length of the path of the reflected beam constant with rotation of said crystal.

12. The combination claimed in claim 11 in which said last mentioned means includes a toroid mirror receiving the reflected beam, and a flat mirror receiving the beam from said toroid mirror, and means for rotating both said mirrors in a predetermined ratio with the rotation of said crystal.

13. The combination claimed in claim 12 in which said flat mirror rotates 1:1 with said crystal, and said toroid mirror rotates 2:1 with said crystal.

14. The combination claimed in claim 13 in which the axis about which said flat mirror is rotated is the same as that about which said crystal is rotated.

15. The combination claimed in claim 11 with detent mechanism engaging said crystal rotating means, to provide easy reproducibility of angles of incidence.

No references cited.