United States Patent

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Division of Ser. No. 453,030, May 4, 1965, Pat. No. 3,508,836

[54] METHOD FOR INFRARED SPECTROSCOPY

2 Claims, 3 Drawing Figs.

[52] **U.S. Cl.** **356/38,** 250/83.3, 250/218, 356/51, 356/244, 356/246, 118/49.1
[51] **Int. Cl.** **G01n 1/00,** G01n 33/28, G01n 1/10
[50] **Field of Search** ..... 356/36—38, 102—104, 96, 244, 246, 51; 250/218, 83.3; 118/49.1

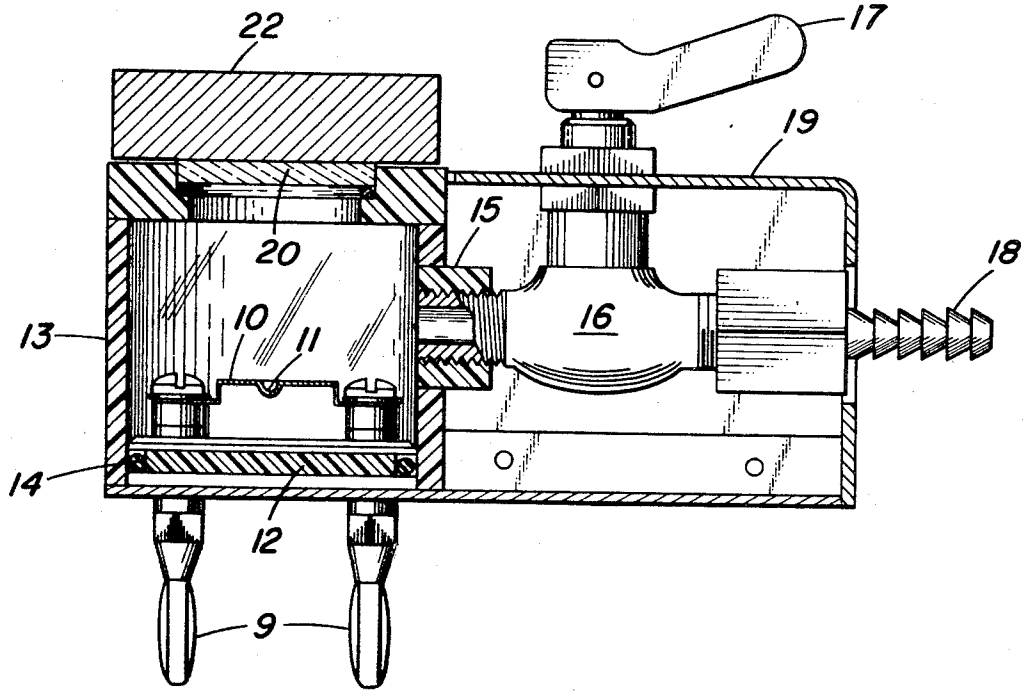
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ABSTRACT: A process and apparatus for obtaining nongaseous pyrolyzate samples of materials for infrared analysis is described. The collecting devices or cells for nongaseous pyrolyzates which at ordinary temperature may be liquid or partially solid are provided with a heat ribbon having a depression to take the pyrolysis sample and a cover with a hermetically sealable opening taking a pyrolyzate plate which may be an attenuated total reflection plate, one side being exposed to the pyrolysis vapors on the inside and the other coolable. The heater is connectable to a power source and the cell to a source of vacuum with a valve which can be shut after pyrolysis is complete to maintain the vacuum.



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SHEET 1 OF 2

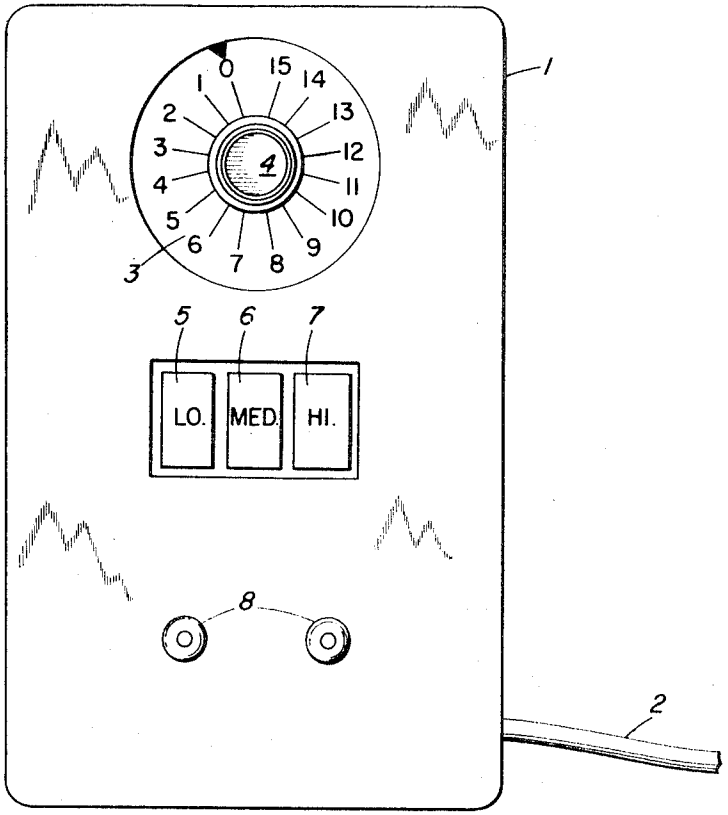


FIG - 1

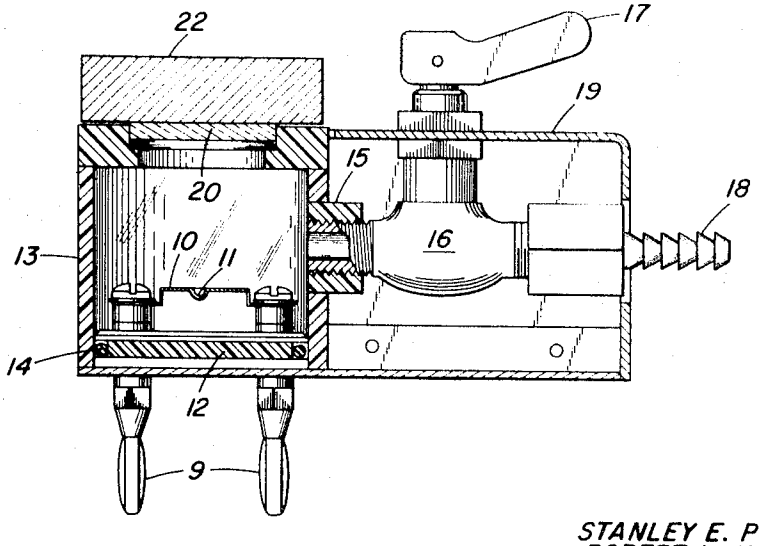


FIG - 2

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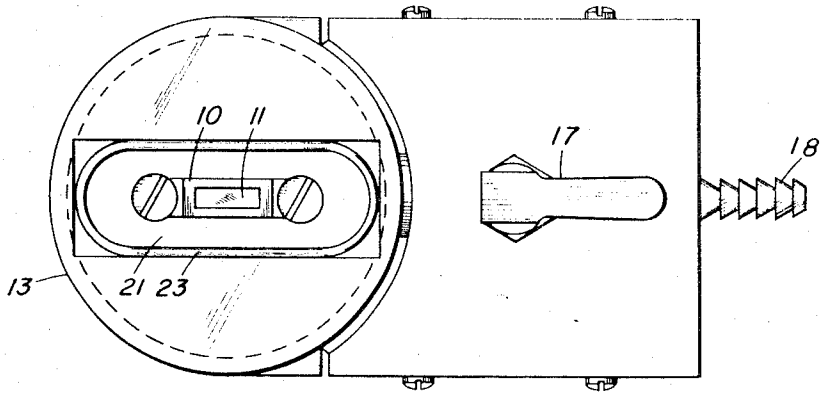


FIG - 3

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METHOD FOR INFRARED SPECTROSCOPY

RELATED APPLICATIONS

This application is a division of our earlier application Ser. No. 453,030, filed May 4, 1965, and now U.S. Pat. No. 3,508,836.

BACKGROUND OF THE INVENTION

In the past it has often been desirable to pyrolyze materials and collecting samples for infrared or other spectral analysis. The problem is most common for infrared analysis and the description in the specification will be in terms of this purpose. However, the instruments are useful for other types of spectral investigation. One of the reasons why pyrolysis of samples is desirable is because many substances such as, for example, rubber with fillers and other polymers do not lend themselves to direct spectral analysis either by transmission or attenuated total reflection including both single and multiple reflection, which in the remainder of this specification will be abbreviated in its customary manner ATR. The materials are often difficult to mount for spectral analysis and the presence of fillers can completely mask the spectral analysis of the organic materials themselves. Accordingly, pyrolysis has been used to decompose the material or depolymerize the polymers and collect the pyrolyzate in liquid form. In general most fillers are not decomposed and, therefore, the resulting spectrum is free from their contribution. In the past this has been effected manually, for example, by placing a small amount of the material in a test tube, heating the material and collecting the pyrolyzate either as gas in the upper part of the test tube or as liquid drops on the walls of the upper part of the test tube.

A number of problems have arisen in the manual pyrolysis of which several illustrative ones will be mentioned. Often the materials during pyrolysis are reactive with atmospheric gases, particularly oxygen, and it is extremely difficult or impractical to exclude the presence of such an atmosphere. Another problem is that the pyrolyzate has to be on a particular type of plate for ATR spectral analysis and when ordinary infrared analysis is used, the materials of a test tube may present problems of lack of transparency for the infrared which cuts out portions of the spectrum which are sometimes of importance. Often the sample derived from a pyrolysis in a test tube is also insufficient in volume for transfer to an ATR plate or crystal.

SUMMARY OF THE INVENTION

The present invention solves the problem of producing automatically nongaseous samples of the products of pyrolysis in a form suitable for spectral analytic investigation. Essentially the present invention provides a device with a suitable heating element which can be plugged into a power supply and on which heating element a small amount of the material to be pyrolyzed is placed. The heating element is surrounded by a chamber or container having a portion, usually the top portion, provided with a removable element on which liquid pyrolyzates can be collected. The chamber is provided with a connection to a source of diminished pressure such as a vacuum pump or aspirator and with a valve which can be open to exhaust or partially exhaust air from the chamber and then maintain the low pressure by closing the valve. The chamber is then plugged in with the power supply and the heating element heated for a predetermined period and at a predetermined temperature resulting in pyrolysis of the sample and collection of the nongaseous pyrolyzate.

The collecting element may be a disc of suitable material having the correct radiation transmission which is strongly cooled and on which the pyrolyzate collects in drops. The element is then removed, if necessary, provided with a cover in a manner similar to the cover glass of a microscope slide, and is then examined spectrally, either by a spectrophotometer or by ATR. In the latter case, of course, the element must be in the form of a suitably shaped ATR crystal.

Although some kind of a power supply is needed into which the cells can be plugged, the particular design of power supply forms no part of the present invention so long as it can furnish electric power for the heating element of the proper voltage and for the proper time. In the specific description of a particular instrument below, the power supply is provided with a conventional timer which turns off the power supply after the predetermined time period and with switches for selecting several different voltages for the heating element, for example, three different voltages. The design of switches and timer are completely conventional and so the present invention is not to be considered as limited to any particular type of power supply although the devices of the present invention require some power supply for operation.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plan view of the top of a typical power supply;

FIG. 2 is a vertical section through a liquid pyrolyzate collector for spectrophotometric use; and

FIG. 3 is a plan view of a modified liquid pyrolyzate collector for collecting the pyrolyzate on a normal ATR crystal or plate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIG. 1, the power supply is in a box 1 provided with electric wires 2, a conventional settable timer 3, a starting switch 4, three voltage selecting switches 5, 6 and 7 and two jacks 8. As the elements in the power supply box are completely conventional they are not shown. When the starting switch 4 is depressed after one of the switches 5, 6 or 7 has been actuated for a voltage selection, the selected voltage appears on jacks 8 until the timer 3 has moved through its set time interval at which time, as is normal with timers, the starting switch is thrown back into its original open position.

As has been stated, the exact design of the power supply forms no part of the present invention. However, typical values for the power supply are three voltages which, with a standard resistance heating element, produce 450° C., 900° C., or 1350° C. This choice of temperatures is suitable for most pyrolysis but, of course, where a different temperature is needed in some special case, a modified power supply is provided with a suitable voltage output.

Turning to FIG. 2 which illustrates a liquid pyrolyzate collector, the collector has two pins 9 which plug into the jacks 8. These pins pass through a suitable insulating base 12 and connect to the ends of a ribbon heating element 10 provided with a small depression 11 to receive a sample of the material to be pyrolyzed. The heating element is in a chamber 13 sealed from the insulating base 12 by a suitable gasket 14 in the form of an O-ring. The top of the collecting chamber is provided with a flanged opening in which a disc 20 of suitable transparent material is mounted. For infrared use this may be a suitable salt disc. The chamber is on a common base 28 on which there is mounted a cover 19 which communicates with the chamber 13 through the channel 15. This cover which forms a second chamber is provided with a suitable vacuum valve 16 actuated by a handle 17 and provided with a serrated connecting end 18 projecting beyond the cover 19. The serrated projecting channel is suitable for attachment to elastic tubing from a source of diminished pressure (not shown). Of course, if the source utilizes a hose with a different coupling the element 18 must be provided with the proper design of coupling. These features are conventional and, therefore, only the rubber hose form is shown by way of illustration.

A block 22 of material preferably at a very low temperature, for example, a metal block which has been cooled in liquid nitrogen or a thermoelectric cooler is placed on the disc 20 cooling it down to the desired low temperature. Before the disc 20 has been mounted a sample of the material to be pyrolyzed is placed in depression 11. After plugging in the collector in the jacks 8 of the power supply, the switch 4 is closed and the element 10 is heated up to the temperature selected by the particular switch 5, 6 or 7 which is depressed and for

the time during which the timer is set to operate. Typically the latter may be about 10 seconds and a typical dimension of the disc **20** is a circular disc of 25 mm, diameter. The small sample of material in the depression **11** is pyrolyzed and the condensable vapors are condensed on the cold disc **20**. Before the operation is started, the lever **17** is thrown to the open position and the atmosphere in the chamber **13** is reduced to the desired subatmospheric pressure whereupon the valve **16** is closed.

After collection of the liquid pyrolyzate on the cold disc **20** the disc is removed and, if desired, a cover plate of suitable transparent material placed over the pyrolyzate droplets. The disc then can be examined by placing in the holder of a conventional infrared spectrophotometer. Typical models of such spectrophotometers have holders which take a 25 mm, disc which is the reason for the choice of device size as described above. The liquid film of pyrolyzate between the cover and the disc is then examined spectroscopically and in the case of a recording spectrophotometer, a record of the infrared absorption spectrum produced.

When the sample was of a polystyrene plastic with a filler the spectrum shows no interference by reason of the fillers. For such a plastic the temperature of 900° C., for 6 seconds is suitable.

Successive pyrolyzate samples can be obtained by cleaning off the heater **10** and inserting a new collector disc without unplugging the collector from the power supply. However, in many cases it is more convenient to have a number of collector chambers available so that a number of samples can be examined quickly and in such a case the cells can be unplugged and disconnected from the source of lowered pressure.

FIG. **3** illustrates in plan view a cell of the same general design as FIG. **2** but provided with an elongated opening **21** with a gasket **23** to take a typical ATR plate. The same elements bear the same reference numerals as in FIG. **2**. When the collecting cell with mounted ATR plate is operated either at room temperature or cooled as described above, a liquid pyrolyzate example is obtained which is then spectrally analyzed by ATR. As only a thin film of the liquid is needed for such an examination the ATR modification presents advantages where the absorption bands of the liquid film do not have to be at all critical in thickness. This is sometimes of advantage with certain materials.

A typical example of operation of the collector of FIG. **3** involves the pyrolysis of an epoxy resin. In this case the temperature of 900° C. is used but the time is advantageously set for 10 seconds. An excellent ATR analysis is obtained which would be impossible by ordinary ATR means since too hard and rough a surface is presented by the unpyrolyzed resin. In the chamber referred to above there is a small amount of water vapor produced by the pyrolysis of the epoxy resin and the ATR infrared spectrum, therefore, showed absorption bands for water vapor. As the position of these absorption bands is well known they do not create any confusion in the interpretation of the spectrum produced.

We claim:

1. A process of infrared spectral analysis of nongaseous phase pyrolyzates comprising, in combination,

a. heating at subatmospheric pressure a substance capable of pyrolysis to form vapors condensable to the nongaseous phase and relatively nonvolatile at room temperature, the heating being to a temperature sufficiently high to pyrolyze the material at the subatmospheric pressure to produce pyrolysis vapors,

b. exposing one side of an infrared transmitting plate to the pyrolysis vapors, and maintaining the other side of the plate out of contact with the pyrolysis vapors,

c. cooling said other side of the plate to a temperature at which condensable pyrolysis vapors condense to the nongaseous stage, whereby a layer of the nongaseous pyrolyzate is formed on said one side of the plate, and

d. analyzing the pyrolyzate layer on the plate by infrared spectral analysis.

2. A process according to claim **1** in which the plate is an ATR substrate and wherein the step of analyzing comprises analysis by attenuated total techniques.