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Davis et al.

[54] **GAS PHASE PHOTOACOUSTIC DETECTOR FOR INFRARED SPECTROSCOPY**

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[73] Assignee: **The United States of America as represented by the Secretary of the Army,** Washington, D.C.

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[51] **Int. Cl.**[4] **G01N 21/35**

[52] **U.S. Cl.** **250/343**

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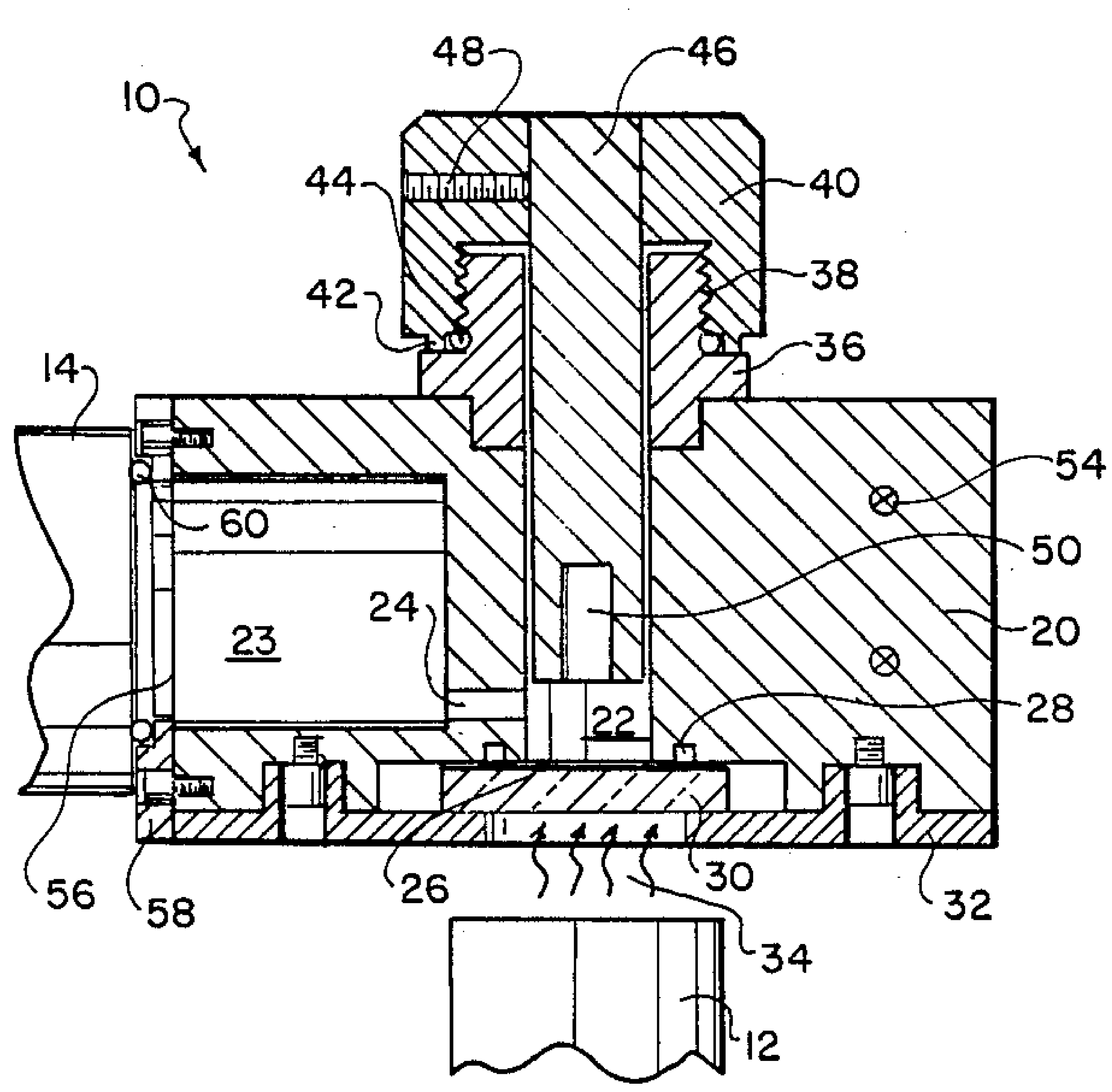
[57] **ABSTRACT**

A photoacoustic detector includes an evaporation space for receiving an organic vapor. The space is bounded by a window which is transparent to infrared radiation. A spectrometer irradiates the space with infrared radiation through the window to heat the vapor and acoustically modulate it at a frequency corresponding to the frequency of the infrared radiation. The acoustic modulations are picked up by a microphone which produces a signal which is amplified and used to form a characteristic spectrum. In this way gases or liquid in the space between the infrared source and the window can be detected by examining changes in the spectrum.

6 Claims, 6 Drawing Sheets



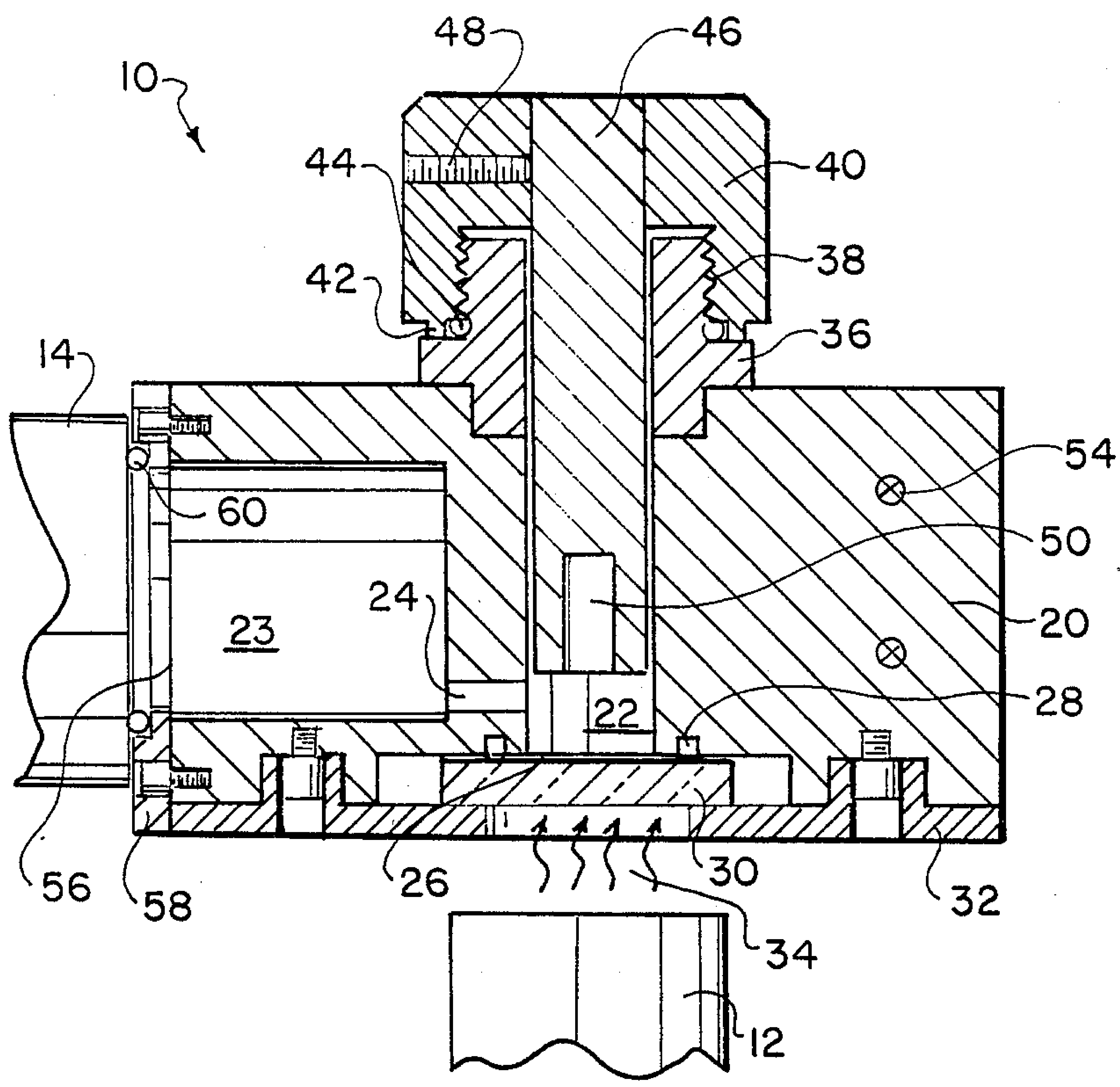

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FIG. 1

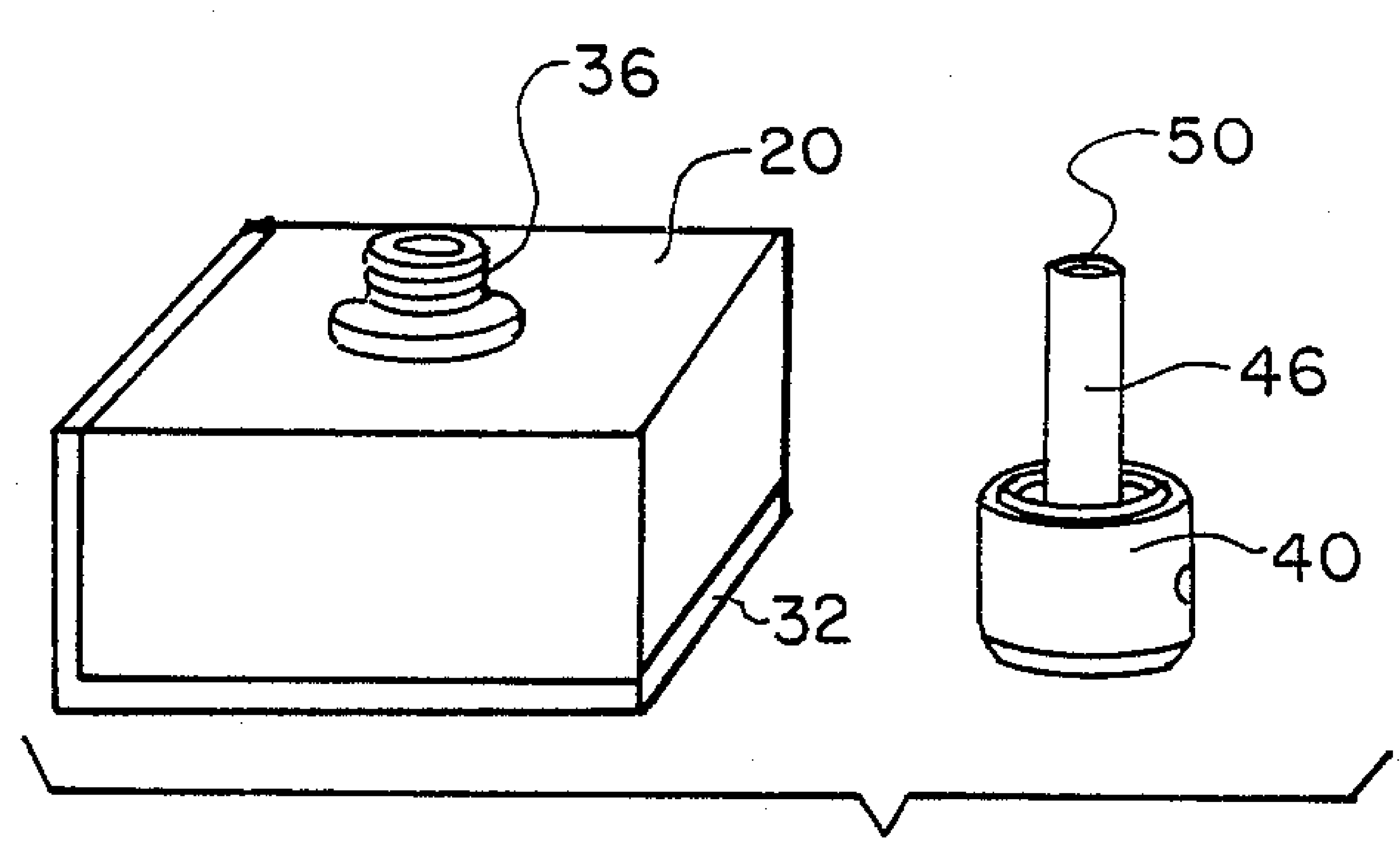
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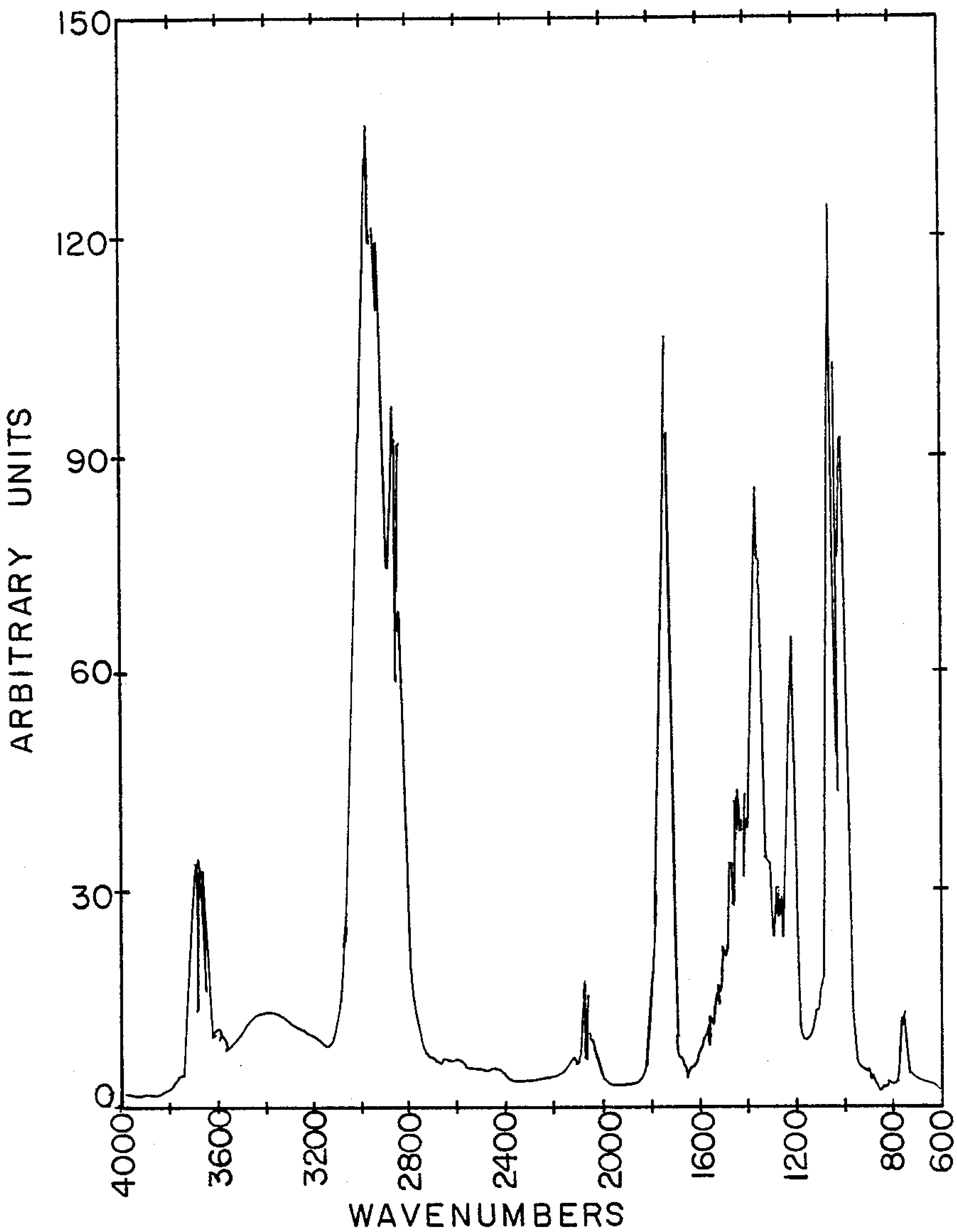
FIG. 2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WAVENUMBERS

FIG. 3

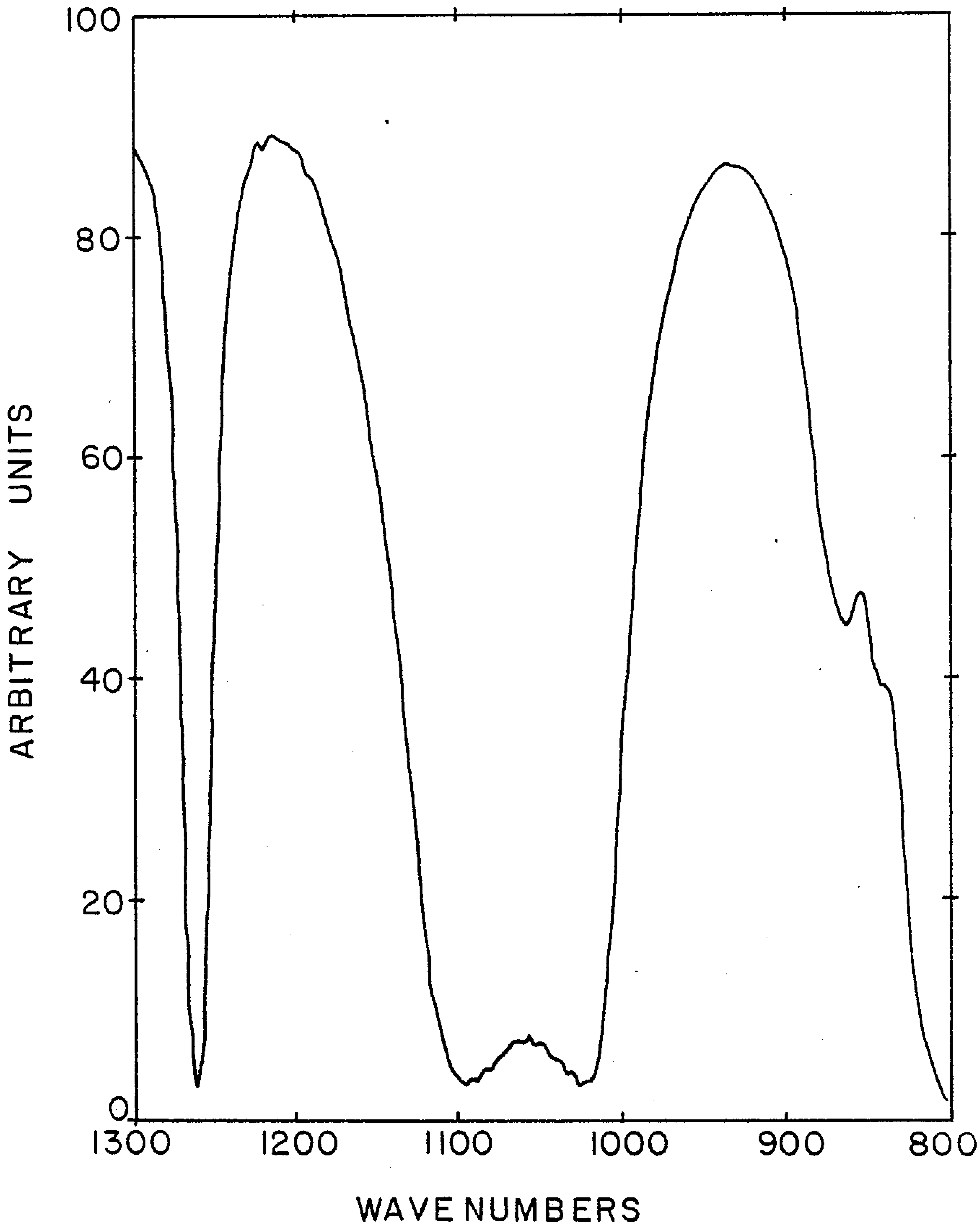
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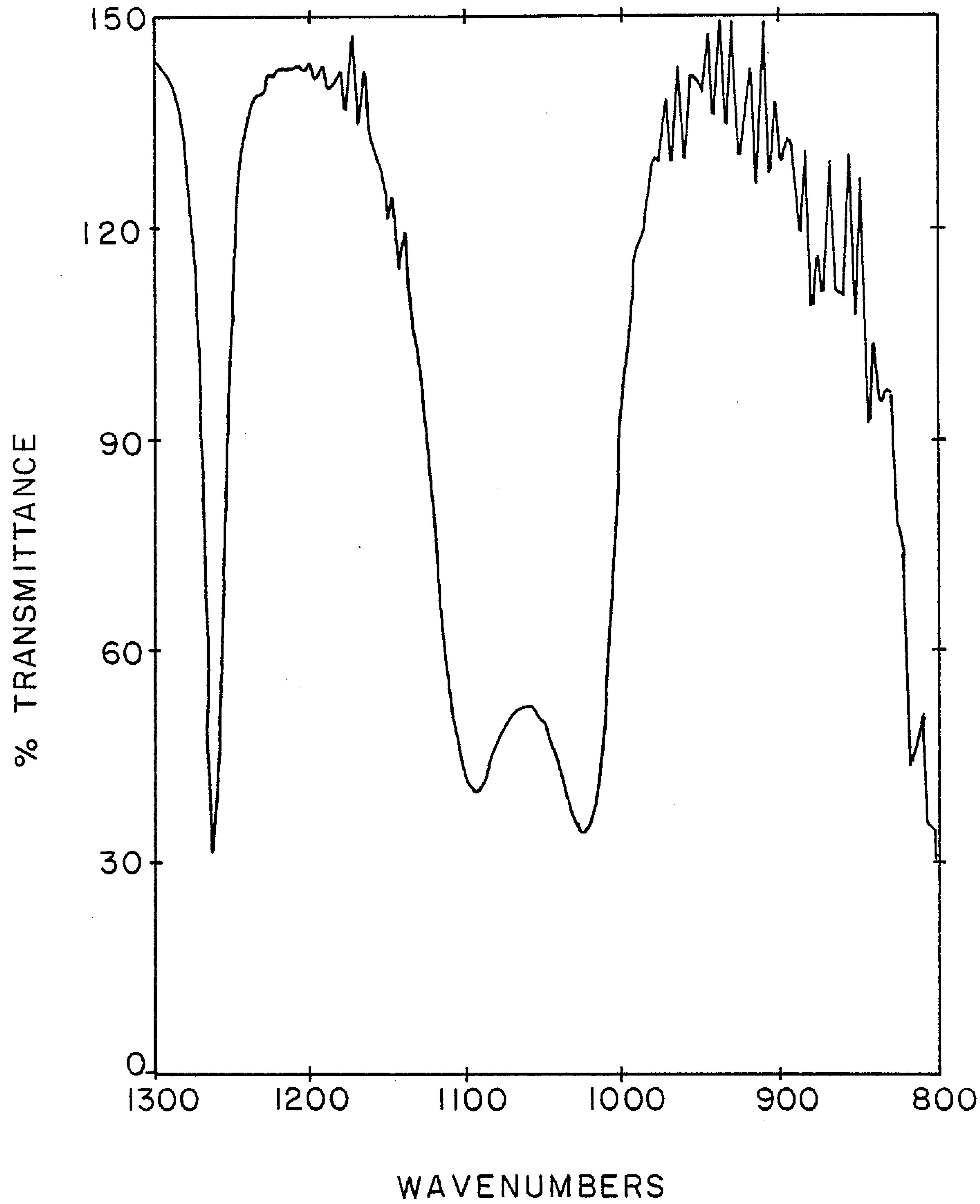
FIG. 4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% TRANSMITTANCE
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1200
1100
1000
900
800
WAVENUMBERS

FIG. 5

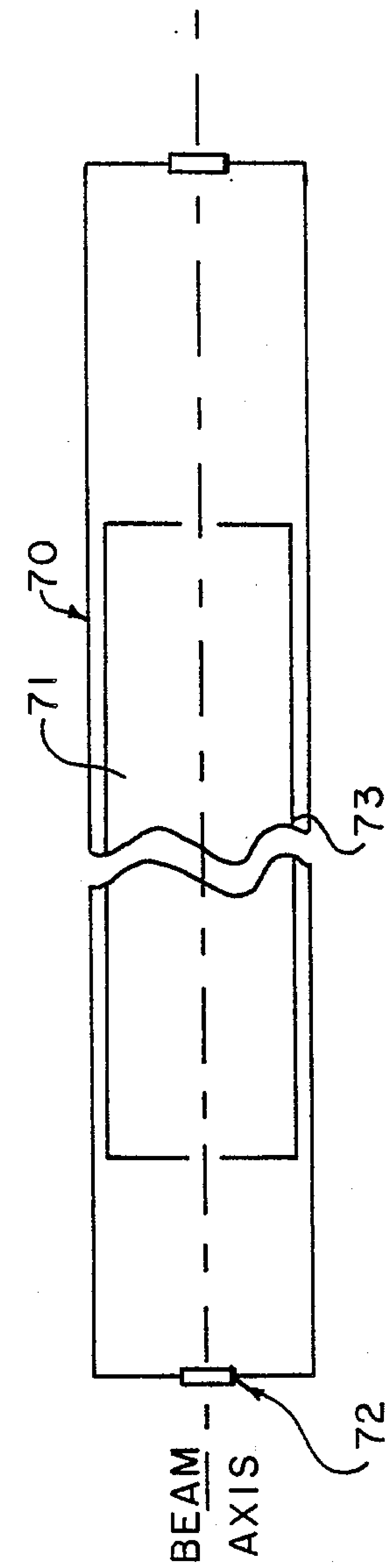


FIG. 6

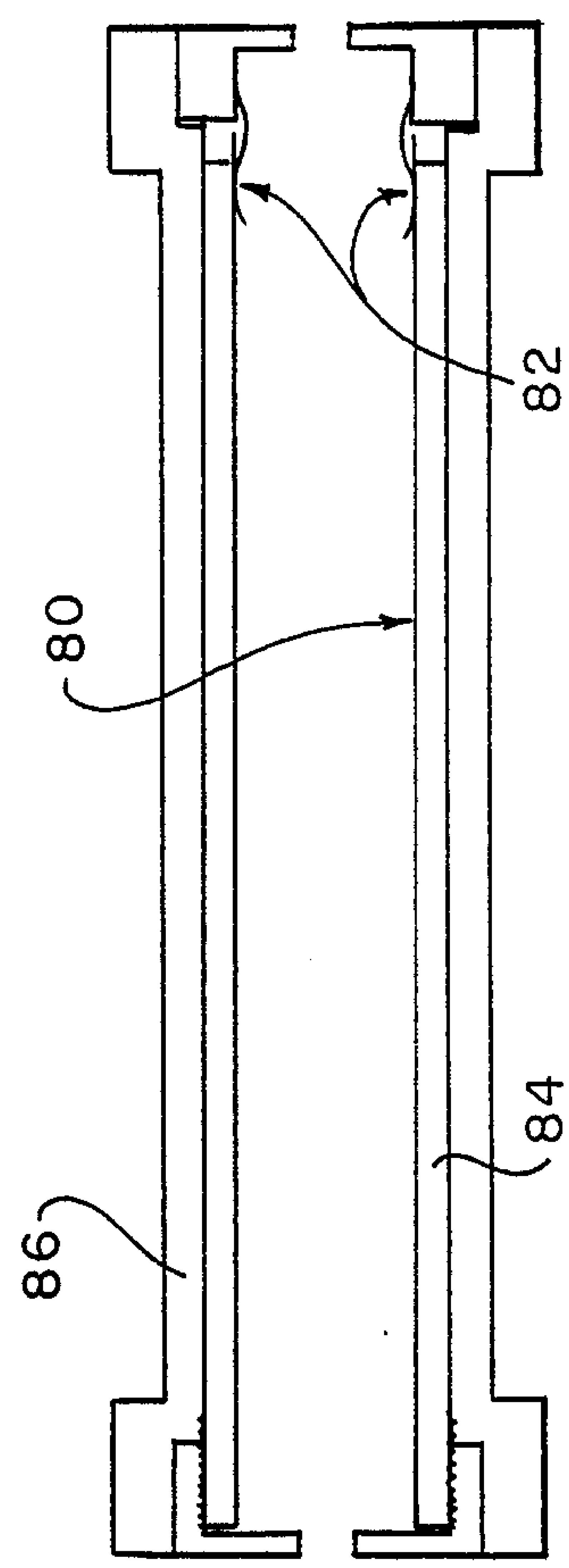
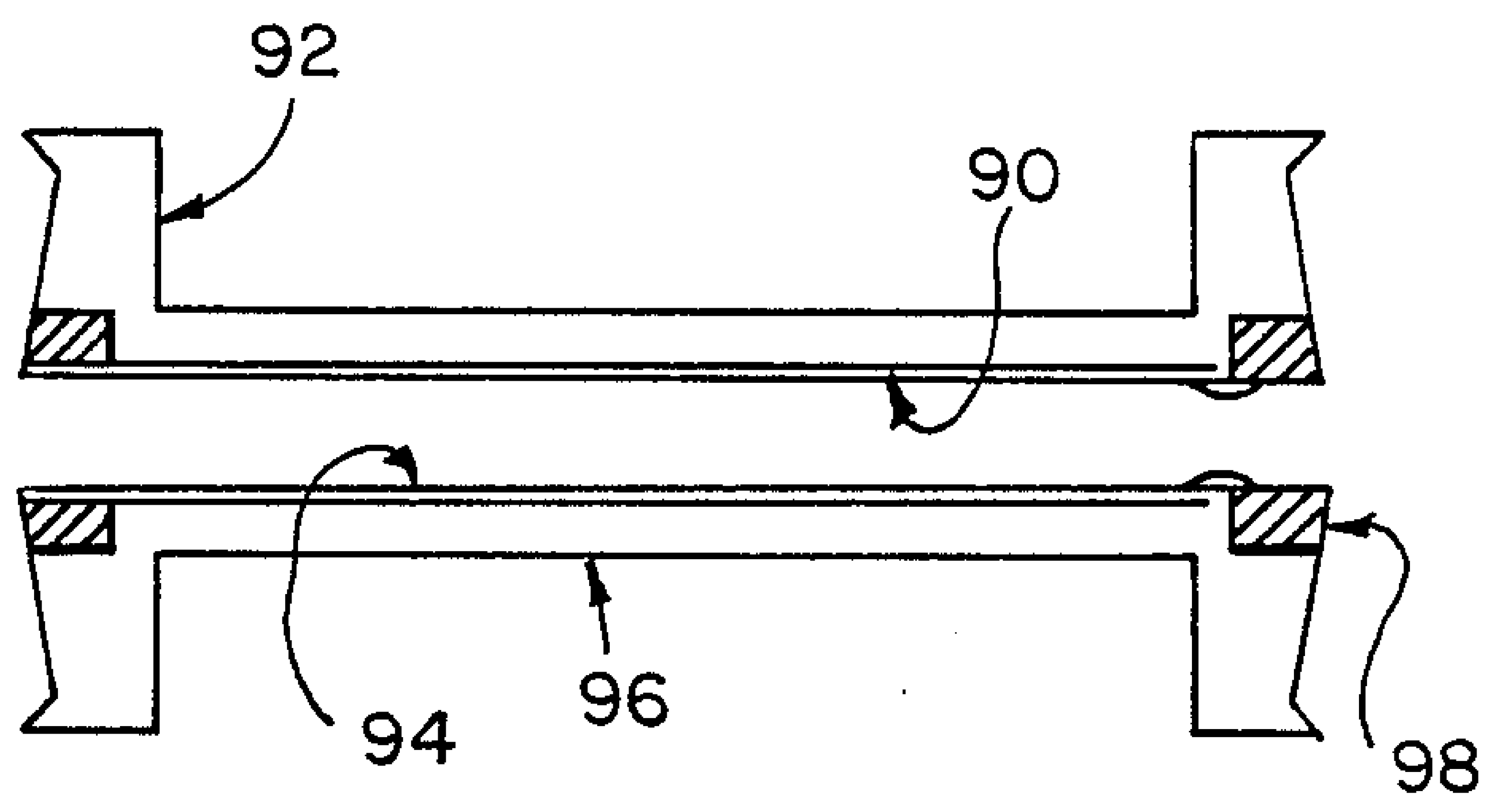


FIG. 7

FIG. 8



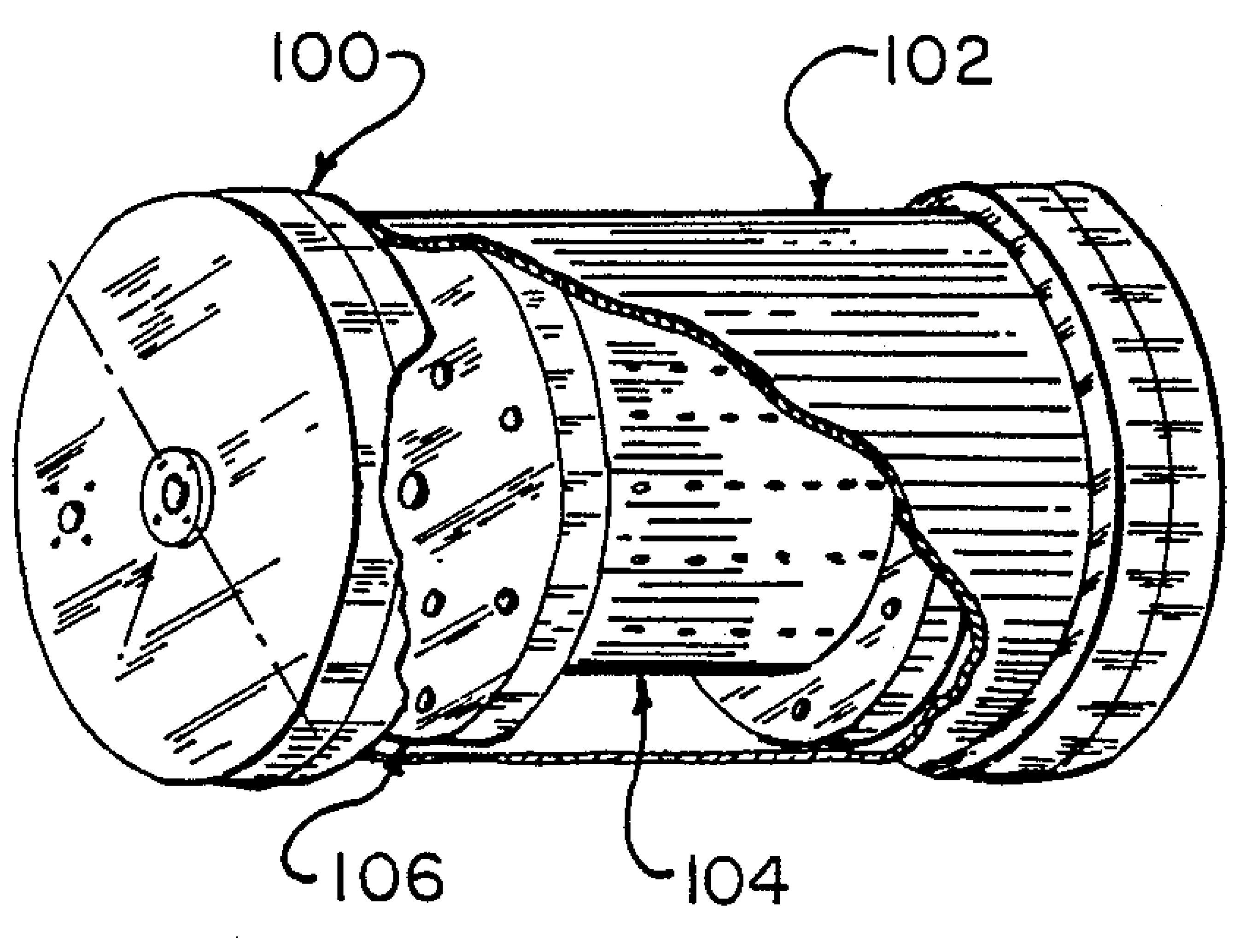


FIG. 9

GAS PHASE PHOTOACOUSTIC DETECTOR FOR INFRARED SPECTROSCOPY

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured, used and licensed by or for the Government for Governmental purposes without the payment to us of any royalties thereon.

FIELD AND BACKGROUND OF THE INVENTION

One of the major problems of interest in defending against chemical warfare is the detection of chemical agent contamination of the atmosphere. This problem has existed since chemical warfare was first used.

To this end the U.S. Army has developed a portable Fourier Transform Infrared Spectrometer which monitors the 8 to 12 micron region of the infrared spectrum. The spectrometer is designated the XM 21. The XM 21 currently uses a narrow band mercury cadmium telluride (MCT) detector. This MCT detector has a number of problems associated with its use in the XM 21. Among these problems are that the detector must operate at 77° K. using liquid nitrogen provided by a Stirling cooler. The Stirling cooler uses 20–30 watts of power. The MCT response curve also drops off sharply when not on the relatively narrow responsivity peak for the detector. In addition the current mean time between failures of the Stirling cooler is only 500 hours.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a detector which avoids the various drawbacks of the MCT detector.

The present invention comprises a gas phase photoacoustic detector which has been fabricated and tested. Among the various advantages of the inventive photoacoustic (PAS) detector are the fact that it operates at ambient or near ambient temperatures. This eliminates the need for the Stirling cooler or any other refrigeration or cooling equipment.

The PAS detector uses less than one watt of power and has a responsivity curve which is constant across the 8 to 12 micron range. The theoretical detectivity of the PAS detector is approximately 3×10^{12}cm Hz$^{\frac{1}{2}}$W^{-1}. This is compared to the theoretical detectivity of 5×10^{10}cm Hz$^{\frac{1}{2}}$W^{-1} for the MCT detector.

The mean time between failures of the photoacoustic detector is greater than six months.

The photodetector of the present invention comprises a high sensitivity Bruel and Kjaer Model 4129 microphone, a Bruel and Kjaer Model 2642 microphone preamplifier, a Bruel and Kjaer Model 2810 microphone power supply and the photoacoustic cell of the present invention. The microphone, preamplifier and power supply are all commercially available from the Bruel and Kjaer Company.

Accordingly a further object of the present invention is to provide a gas phase photoacoustic detector for infrared spectroscopy which comprises a housing defining an evaporation space, an acoustic modulation space and a passage extending between the evaporation and the modulation spaces, the housing having a port therein communicating with the evaporation space, an infrared radiation passing window providing a port for passing infrared radiation into the evaporation space, a receptacle for receiving a measured quantity of organic liquid, said receptacle being engaged with said housing for sealing the receptacle in the evaporation space so that the organic liquid evaporates into the evaporation space, the evaporating liquid passing through the passage and filling the modulation space, and means for attaching a microphone to the housing for exposing the microphone to the acoustic modulation space whereby infrared radiation passed through the window excites the evaporated liquid in the modulation space to produce an acoustic signal at the same modulation frequency as the incident infrared radiation, the acoustic modulation being picked up by the microohone to form a spectrum which is characteristic of the infrared radiation passing to and through the window.

A further object of the invention is to use a gas phase photoacoustic detector in combination with an infrared spectrometer to produce a characteristic absorption curve that can be used in detecting the presence of a chemical in the area surrounding the housing.

A still further object of the invention is to provide a photoacoustic detector which is simple in design, rugged in construction and economical to manufacture.

The various features of novelty which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this disclosure. For a better understanding of the invention, its operating advantages and specific objects attained by its uses, reference is made to the accompanying drawings and descriptive matter in which a preferred embodiment of the invention is illustrated.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. **1** is a side sectional view of a gas phase photoacoustic detector in accordance with the present invention;

FIG. **2** is an exploded perspective view of the detector of FIG. **1** showing an organic liquid receptacle shaft to be filled with an organic liquid and to be engaged with a housing of the detector;

FIG. **3** is a curve showing a single beam spectrum of a mixture of acetone and methanol vapors generated by a Fourier transform infrared spectroscope used with the photoacoustic detector of the present invention;

FIG. **4** is a curve representing an infrared transmission spectrum of a chemical to be detected using a conventional MCT detector;

FIG. **5** is a graph showing the infrared transmission spectrum for the same compound as in FIG. **4** but using the photoacoustic transducer of the present invention;

FIG. **6** is a schematic side sectional view of a resonant acoustical spectrophone which can be used in accordance with the present invention;

FIG. **7** is a schematic side sectional view showing components of a cylindrical microphone which can be used in the spectrophone of FIG. **6** and in accordance with the present invention;

FIG. **8** is a schematic side sectional view of a double open ended organ pipe type of resonant microphone which can be used in the spectrophone of FIG. **6** and in accordance with the invention; and

FIG. **9** is a perspective view, with portions cut away, of a radial mode spectrophone which can be used in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawings in particular, the invention embodied in FIG. **1** comprises a gas phase photoacoustic detector generally designated **10** for use with an infrared spectrometer, such as a Fourier transform spectrometer shown partially and schematically at **12**. The present invention is also used in conjunction with a highly sensitive microphone shown partially and schematically at **14**.

The detector **10** includes a housing **20** having an evaporation space **22** and an acoustic modulation space **23**. A passage **24** extends between and communicates the spaces **22** and **23**.

Housing **20** has an irradiation port **26** which is surrounded by an O-ring **28** and which is covered by a zinc selenide (ZnSe) window **30**. Window **30** is held against O-ring **28** by a bottom cover **32** in order to seal space **22** from the ambient. Infrared light **34** which is modulated by the Fourier transform spectrometer **12** enters space **22** through the ZnSe window **30**. The zinc selenide is transparent to infrared radiation. The window can be replaced by any other transparent material which is suitably transparent to infrared radiation.

Housing **20** and bottom plate **32** are advantageously made of aluminum.

A shaft screw **36** is fixedly connected into an upper opening of housing **20** which communicates with space **22**. Screw **36** is advantageously made of brass and has threads **38** onto which internal threads of a cap **40** are threaded. Cap **40** has a lower flange **42** which confines an O-ring **44** between cap **40** and screw **36**. A receptacle **46** is fixed to cap **40**, for example, by a set screw **48**. The junction between receptacle **46** and cap **40** is hermetically sealed so that with cap **40** screwed on to screw **36**, shaft **46** extends into space **22** and closes space **22** with respect to the ambient.

Receptacle **46** is advantageously in the form of an internal shaft made of stainless steel and having a blind bore **50** of a selected volume.

As shown in FIG. **2**, cap **40** can act as a support for shaft **46** with its blind bore or receptacle space **50** in an upward position. In this position, receptacle space **50** can be filled with an organic liquid. Housing **20** can advantageously be heated, for example by a heatig coil shown schematically at **54**, so as to evaporate the organic liquid in space **22**. For sufficiently volatile organic liquids, little or no heating may be necessary.

Once evaporated, the vapors move through passage **24** and fill space **23**. Spaces **22**, **23** and passage **24** are thus filled with vapors.

Housing **20** also has a port **56**, which opens into modulation space **32** and is surrounded by an opening in a front plate **58**. An O-ring **60** surrounds the opening and can be engaged against the sound-receiving end of a microphone **14**. In this way the microphone **14** is in an ideal position for picking up any acoustic signals from space **23**.

According to the present invention, with housing **20** heated and a measure of organic liquid being deposited into and sealed within evaporation space **22** by cap **40** and shaft **46**, infrared radiation entering through window **30** will be absorbed by the vapor and converted into heat. The conversion to heat is modulated at the same frequency as the infrared light **34**. This periodic or modulated heating causes pressure fluctuations at the modulation frequency in the spaces **22** and **23**. The pressure fluctuations are then detected by the microphone **14**. The microphone **14** includes a preamplifier and power supply to produce an amplified output signal which is input into signal processing hardware and software (of conventional design) used by the spectrometer.

The sealed volume of the space **23** can also contain a carrier gas such as helium, nitrogen or air.

A mixture of several other gases which exhibit high extinction coefficients in the 8–12 micrometer range can also be used. These vapors are provided by the liquid supplied to the receptacle space **50** and ultimately discharged into the evaporation space **22**.

Unlike the present invention, conventional photoacoustic cells are used to detect gases, liquids or solids which are present in the photoacoustic cell itself. According to the present invention, absorption of infrared radiation by gases, liquids or solids outside the detector housing **20** can be detected. Actual experiments have demonstrated the utility of the inventive photoacoustic (PAS) detector.

In such an experiment, the receptacle space **50** was filled with methanol and acetone and cap **40** was engaged with and sealed onto the housing **20**. The methanol and acetone vapors were at room temperature and filled the spaces **22–23** and **24** in housing **20**. With infrared irradiation through window **30**, using a Fourier transform spectrometer, the spectrum of FIG. **3** was obtained. Of primary interest is the strong absorption between 1,100 and 900 wavenumbers. This is because phosphoryl containing chemical agents have strong absorptions in this region. These represent a large number of chemicals used in chemical warfare. This strong absorption between 1,100 and 900 wavenumbers can be smoothed and broadened to extend from 800 to 1,300 wavenumbers by adding volatile ethers and esters to the mixture in the housing **20**.

After obtaining the spectrum of the acetone-methanol vapor, a thin film of a chemical agent simulant (SF-96) was spread over the outside of window **30** and the transmission spectrum was recorded using both conventional MCT and the inventive PAS detectors. The spectrum recorded using the MCT detector is shown in FIG. **4** and the spectrum using the inventive PAS detector is shown in FIG. **5**.

The two spectra are the same with the exception of the noise level in the 1,225–1,137 and 975–850 wavenumber regions of the spectra. Again, the noise level in these regions of the PAS spectrum can be reduced by adding other gases, such as volatile ethers and esters, to the PAS evaporation space **22**.

Other designs which are in conformance with the present invention are applicable in building a high sensitivity photoacoustic detector. These designs, which are shown in FIGS. **6–9**, described by Charles Bruce in Research and Development Technical Report ECOM-5802 entitled, "Development of Spectrophones for CW and Pulsed Radiation Sources", include spectrophone and microphone designs of the radial mode spectrophone (FIG. **9**), the double open ended organ pipe resonant microphone (FIG. **8**), and the cylindrical microphone (FIG. **7**). Either the double ended organ pipe resonant microphone or the cylindrical microphone of FIGS. **8** or **7** can be employed in the resonant chamber of a resonant acoustic spectrophone (shown in FIG. **6**) and the radial mode spectrophone (shown in FIG. **9**). Capacitance microphone diaphragms (known in themselves) are used in the microphone.

As shown in FIG. **6**, the resonant acoustical spectrophone comprises an outer cylinder **70** having a space **71** and a window **72**. An infrared light beam passes through window **72** and space **71** on a beam axis. An inner cylinder **73** forms the resonant chamber around space **71**.

The microphones of FIGS. **7** or **8** can be inserted into space **71**. FIG. **7** shows a cylindrical microphone having a microphone diaphragm **80**, which for example can be a capacitance microphone diaphragm. The diaphragm carries printed-on electrodes which can be contacted by nickel-plated brass contact clips **82**. The diaphragm also includes a nickel plated brass or SS cylinder **84** which supports as engaged behind the diaphragm **80**. An outer Teflon carrier cylinder **86** supports the cylinder **84**.

As shown in FIG. **8**, a double open ended organ pipe type resonator includes a cylindrical Mylar diaphragm **90** in the proximity of the inner wall of a cylindrical carrier **92** which, for example, is made of Teflon (a trade name). Diaphragm **90** is pressed outwardly against carrier **92** by a stainless steel tube **94**. Wall **96** of carrier **92** is perforated.

Metallic contact locks **98** are also pressed into opposite ends of carrier **92** for mounting against opposite end walls of chamber **73** in FIG. **6** or and walls of the spectroscope in FIG. **9**.

Turning to FIG. **9**, the spectroscope shown therein comprises a Teflon O-ring **100** and a stainless steel casing **102**. The stainless steel microphone **104** is shown within the casing **102**. Teflon microphone mounts **106** are used to carry microphone **104** in the spectrophone.

While a specific embodiment of the invention has been shown and described in detail to illustrate the application of the principles of the invention, it will be understood that the invention may be embodied otherwise without departing from such principles.

What is claimed is:

1. A gas phase photoacoustic detector for infrared spectroscopy comprising:

a housing defining an evaporation space, a modulation space and a passage extending between the evaporation and modulation spaces, said housing having a first exterior port communicating with the evaporation space and a second exterior port communicating with the modulation space;

a window which is substantially transparent to infrared radiation connected to said housing and covering said first exterior port to seal the evaporation space;

receptacle means for carrying a measured quantity of an evaporatable organic liquid and for depositing the liquid into the evaporation space, said receptacle means being engaged with said housing for sealing the evaporation space closed; and

microphone mounting means engaged over said second exterior port for bringing an acoustic receiving portion of a microphone into acoustic association with the modulation space so that when infrared radiation passes through said window and is absorbed by organic vapors in said evaporation space, pressure fluctuations are formed at a frequency of modulation of the infrared radiation to produce acoustic modulations in the modulation space which can be sensed by a microphone connected to said microphone mounting means to form a characteristic spectrum, the characteristic spectrum being changed by substances outside the window through which the infrared radiation passes.

2. A detector according to claim **1** wherein the evaporation space comprises a bore extending through said housing, said first exterior port being at one end of said bore, said housing having a third exterior port at an opposite end of said bore, a shaft screw fixed to said housing at said third external port, said receptacle means comprising a shaft with a blind bore at one end, a cap connected to said shaft at an opposite end and having threads for engaging said shaft screw with said shaft in the evaporation space.

3. A detector according to claim **2** wherein said modulation space comprises a blind opening extending perpendicularly to said bore which forms the evaporation space, said passage comprising a small diameter opening through said housing extending radially to said evaporation space and axially parallel with said modulation space.

4. A detector according to claim **3** wherein said window is made of zinc selenide.

5. A detector according to claim **1** including a microphone connected to said microphone mounting means, said microphone comprising a cylindrical diaphragm extending around said evaporation space.

6. A detector according to claim **5** wherein said microphone includes a cylindrical carrier carrying said diaphragm and having opposite open ends through which a beam of infrared radiation entering through said window passes.

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