United States Patent [19]

Gough et al.

[11] **3,876,305**

[45] **Apr. 8, 1975**

[54] **DEMOUNTABLE SPUTTERING CATHODE FOR ATOMIC ABSORPTION SPECTROSCOPY**

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[22] Filed: **Aug. 17, 1973**

[21] Appl. No.: **389,088**

[30] **Foreign Application Priority Data**

Aug. 18, 1972 Australia 147/72

[52] **U.S. Cl.** **356/85**

[51] **Int. Cl.** **G01j 3/02**

[58] **Field of Search** 356/85, 96, 97; 204/192, 204/298

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Assistant Examiner—F. L. Evans
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[57] **ABSTRACT**

Techniques and apparatus for measuring the concentration of elements in a solid metal sample by atomic absorption and fluorescence are described. A silica disc with an annular discharge-suppressing gap surrounding the sample area and an O-ring seal are used to locate a surface of the sample for sputtering, and gas passages in the disc allow sputtered atoms to be swept into the body of a vacuum chamber for convenient analysis.

10 Claims, 9 Drawing Figures

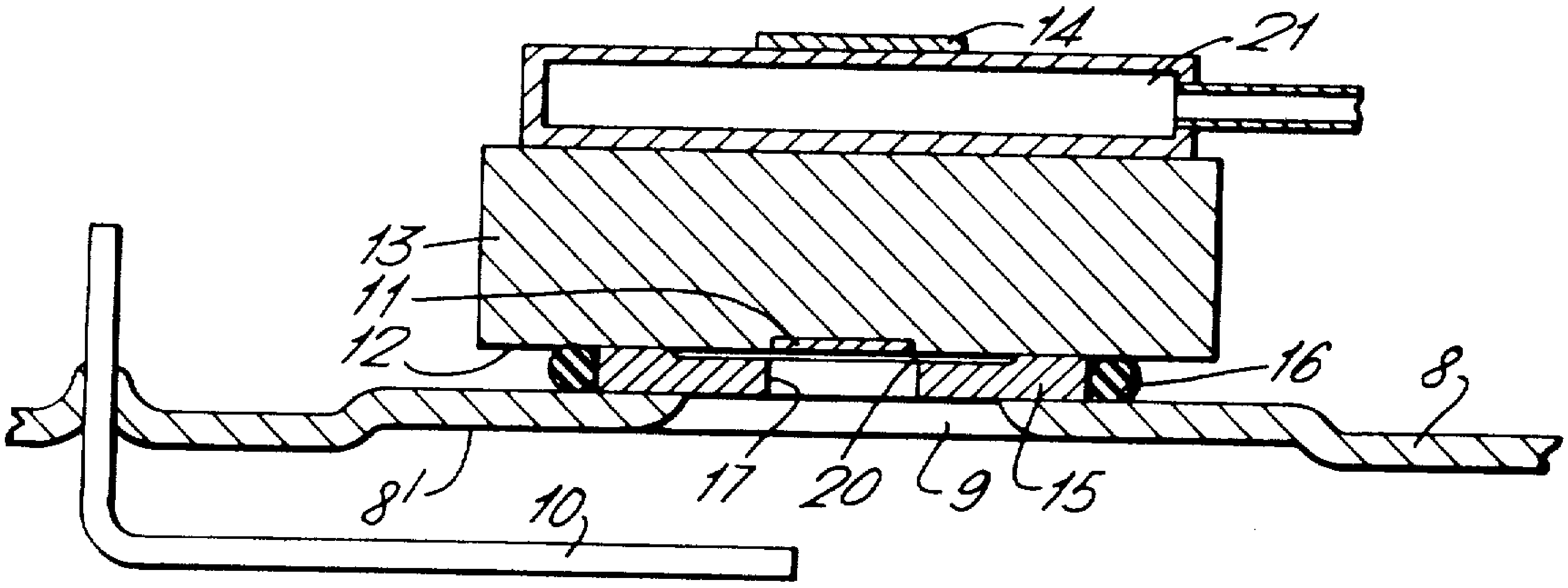


FIG.1.

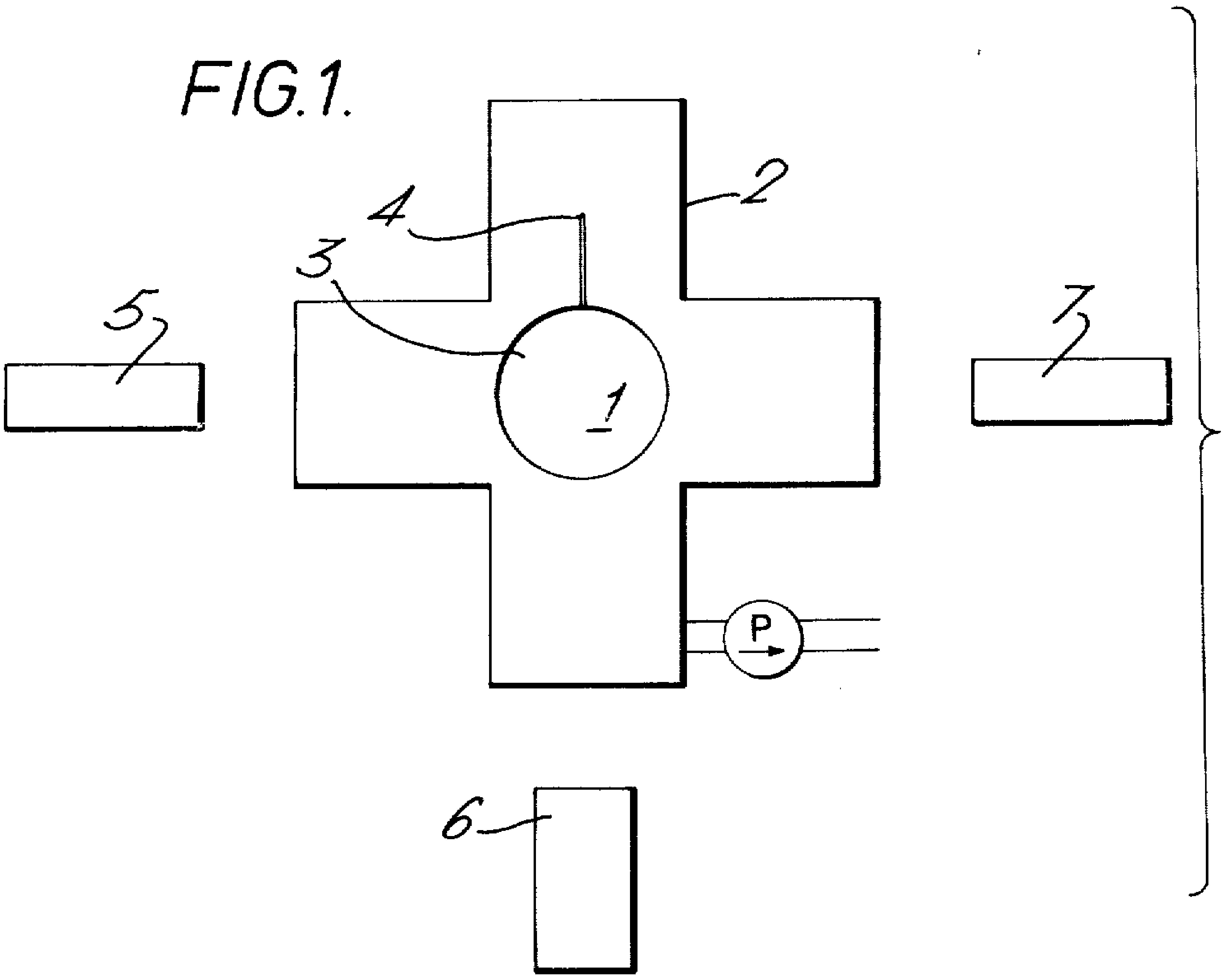
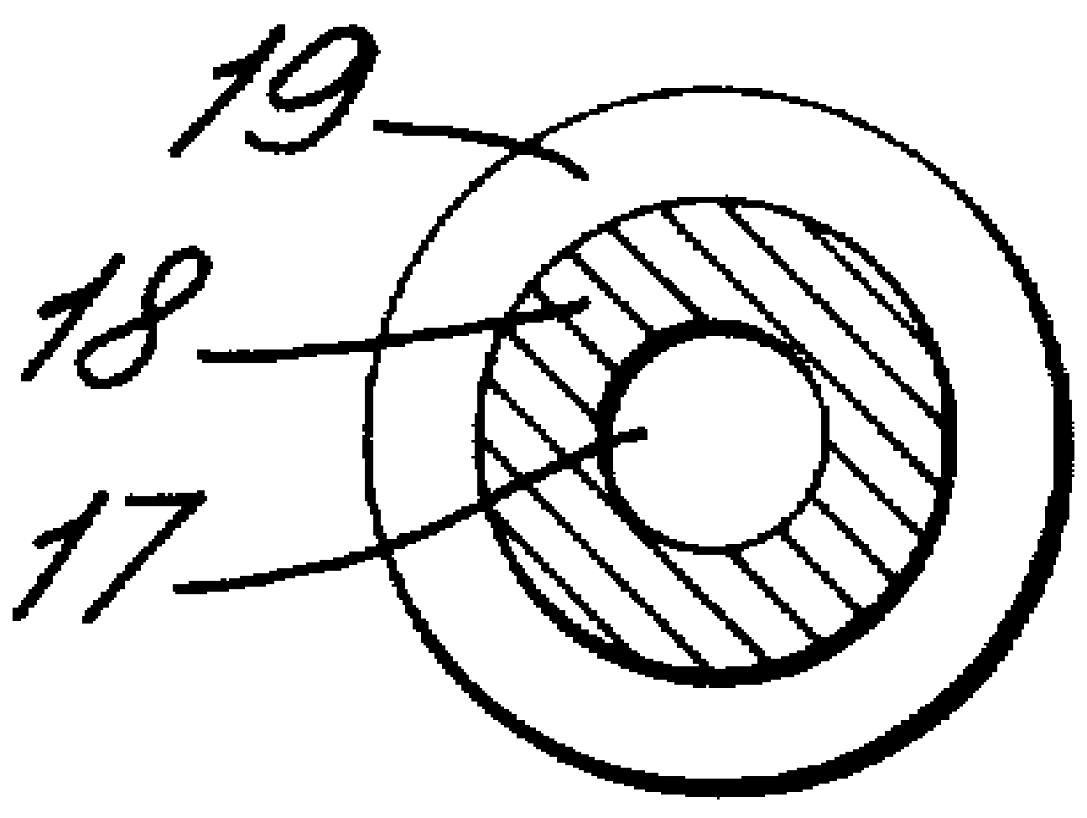


FIG.3.



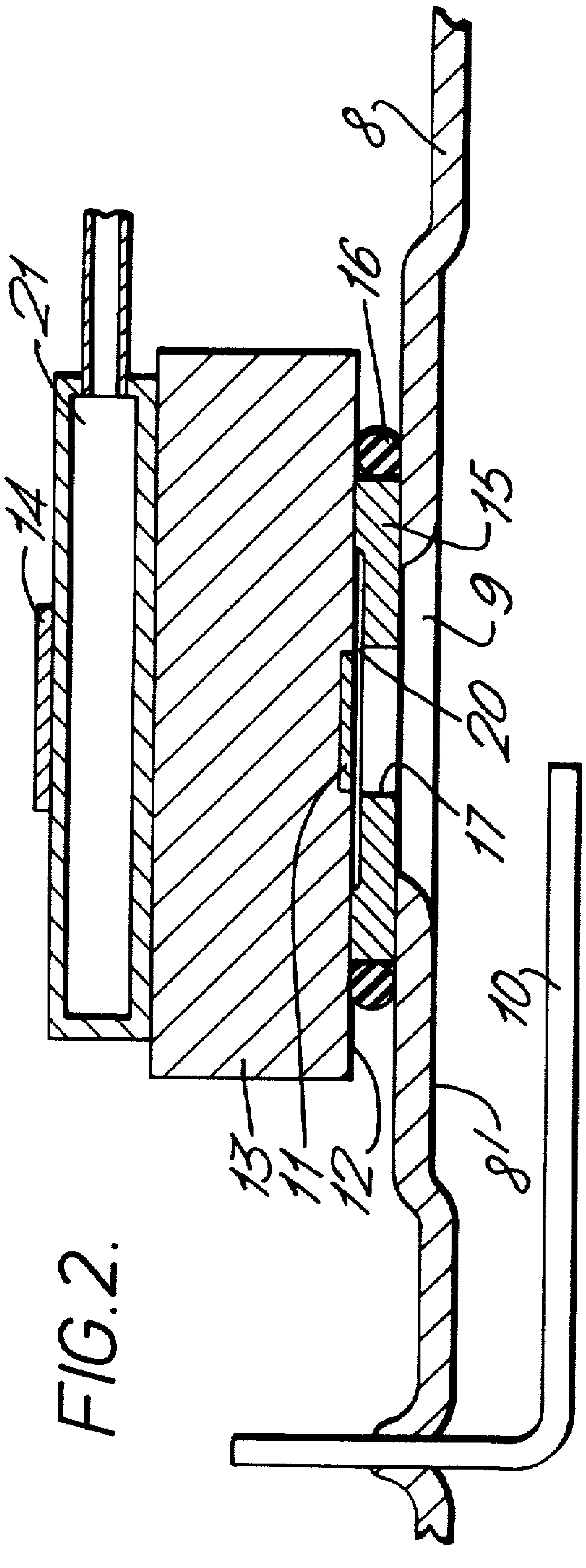


FIG.2.

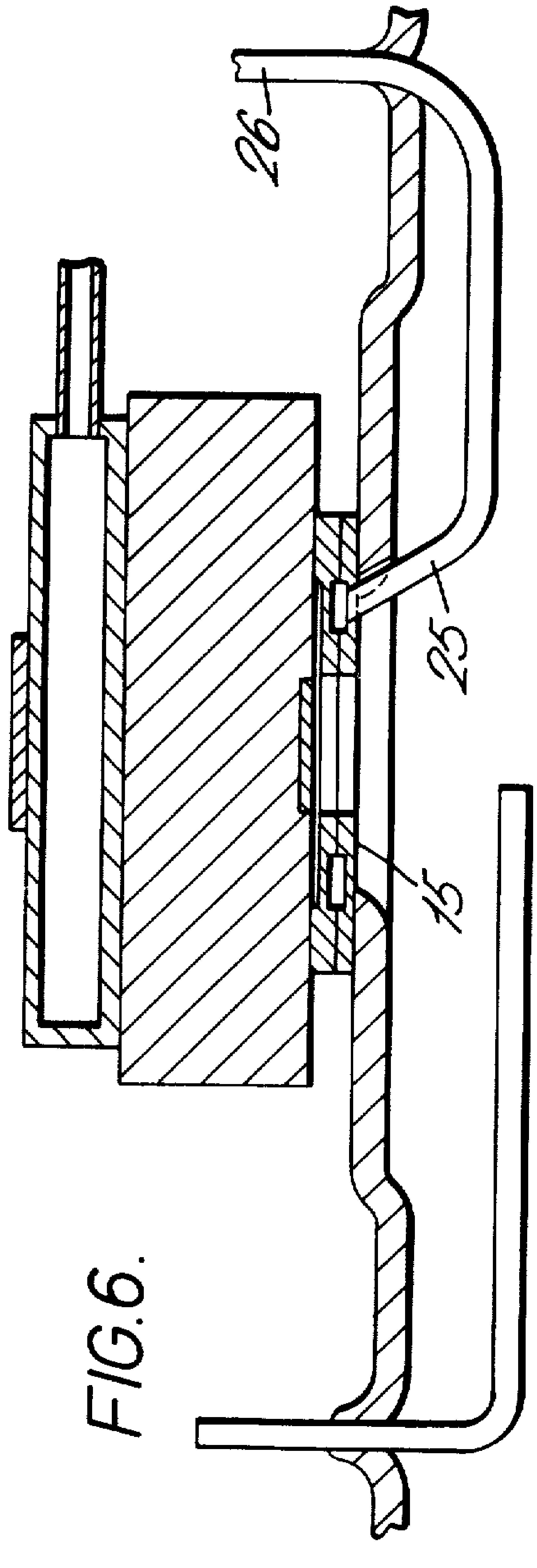


FIG.6.

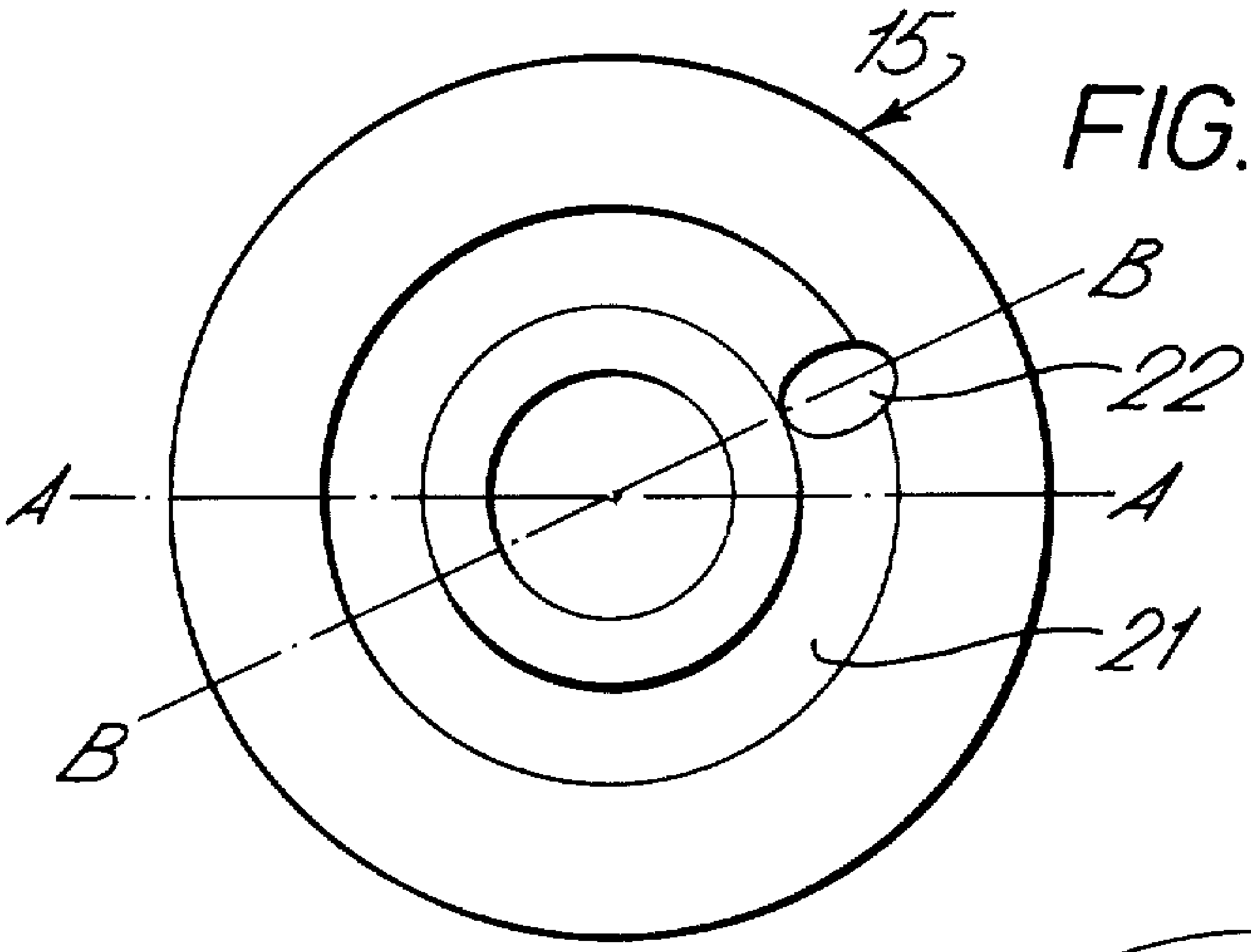
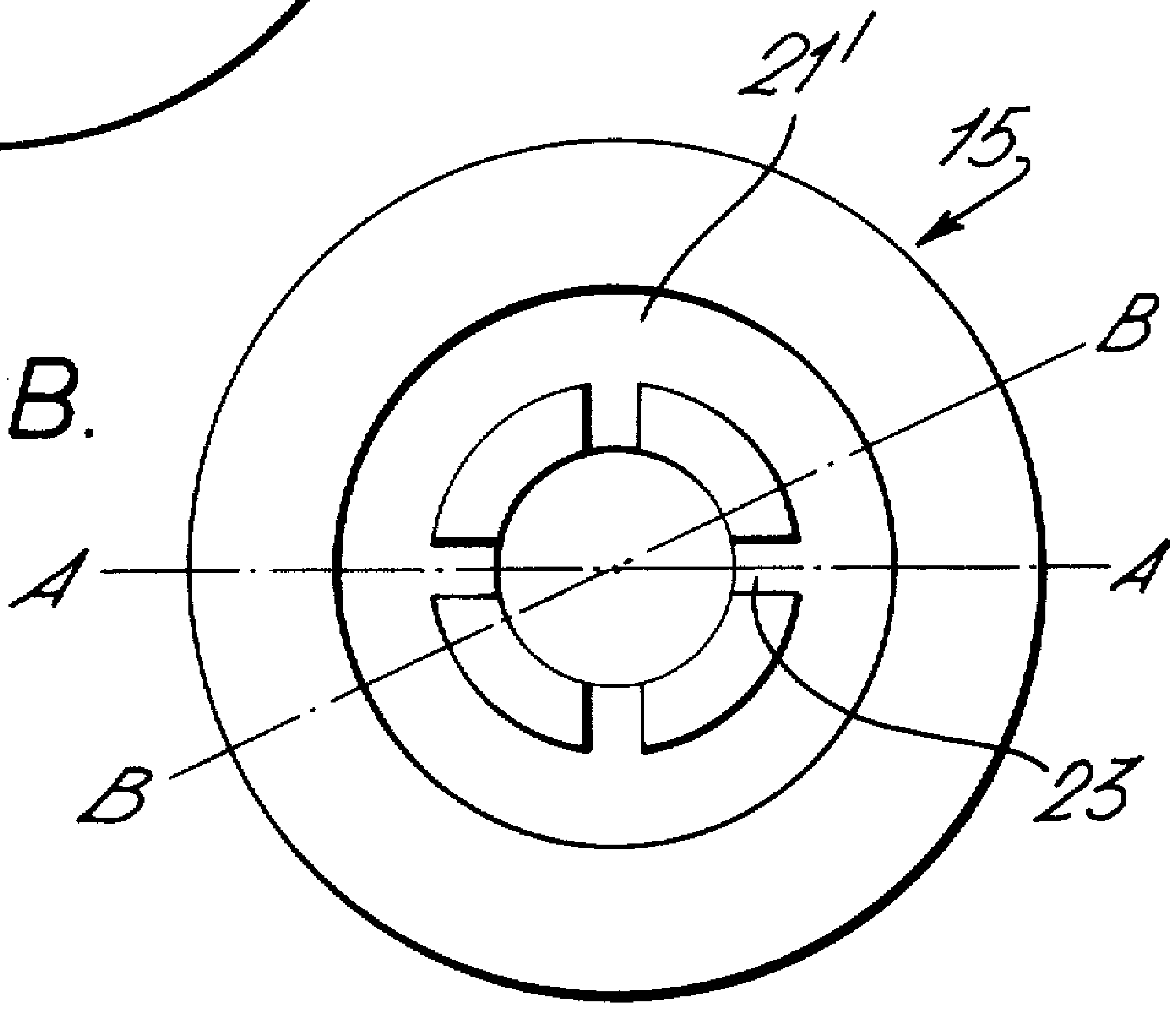


FIG.4A.

FIG.4B.



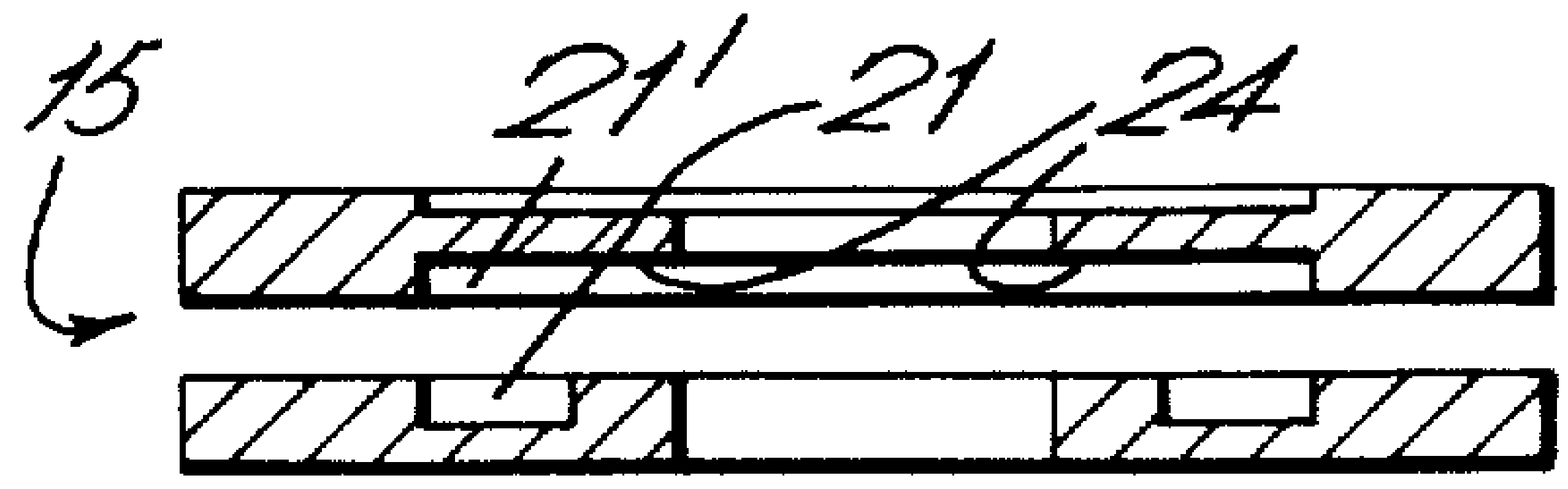


FIG.5A.

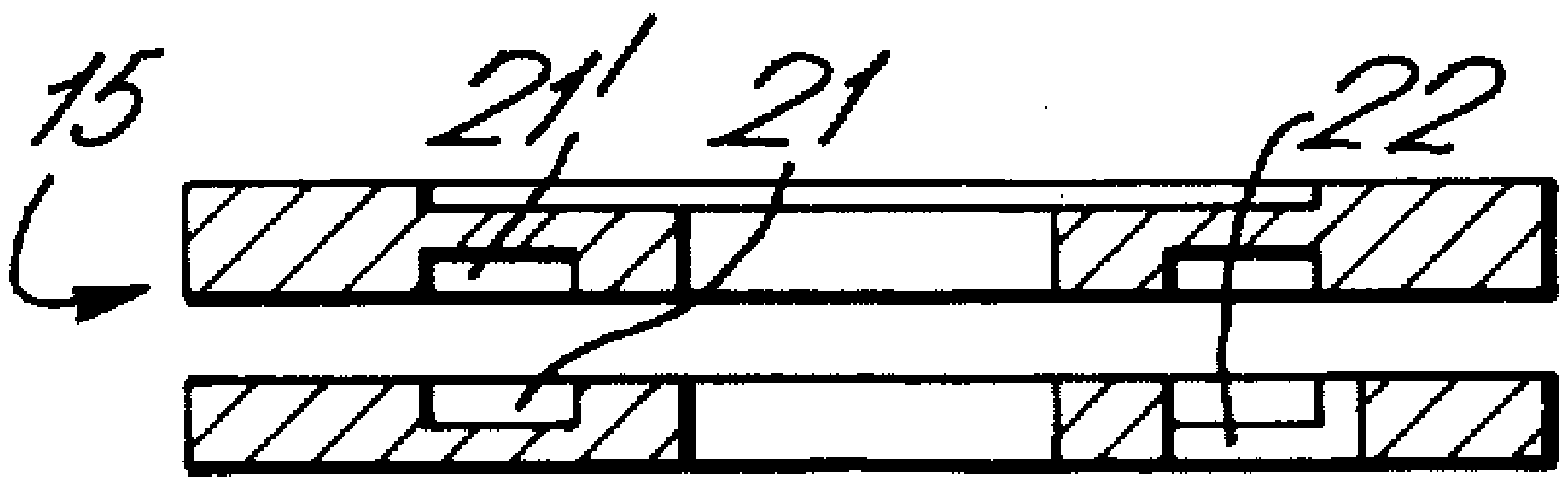
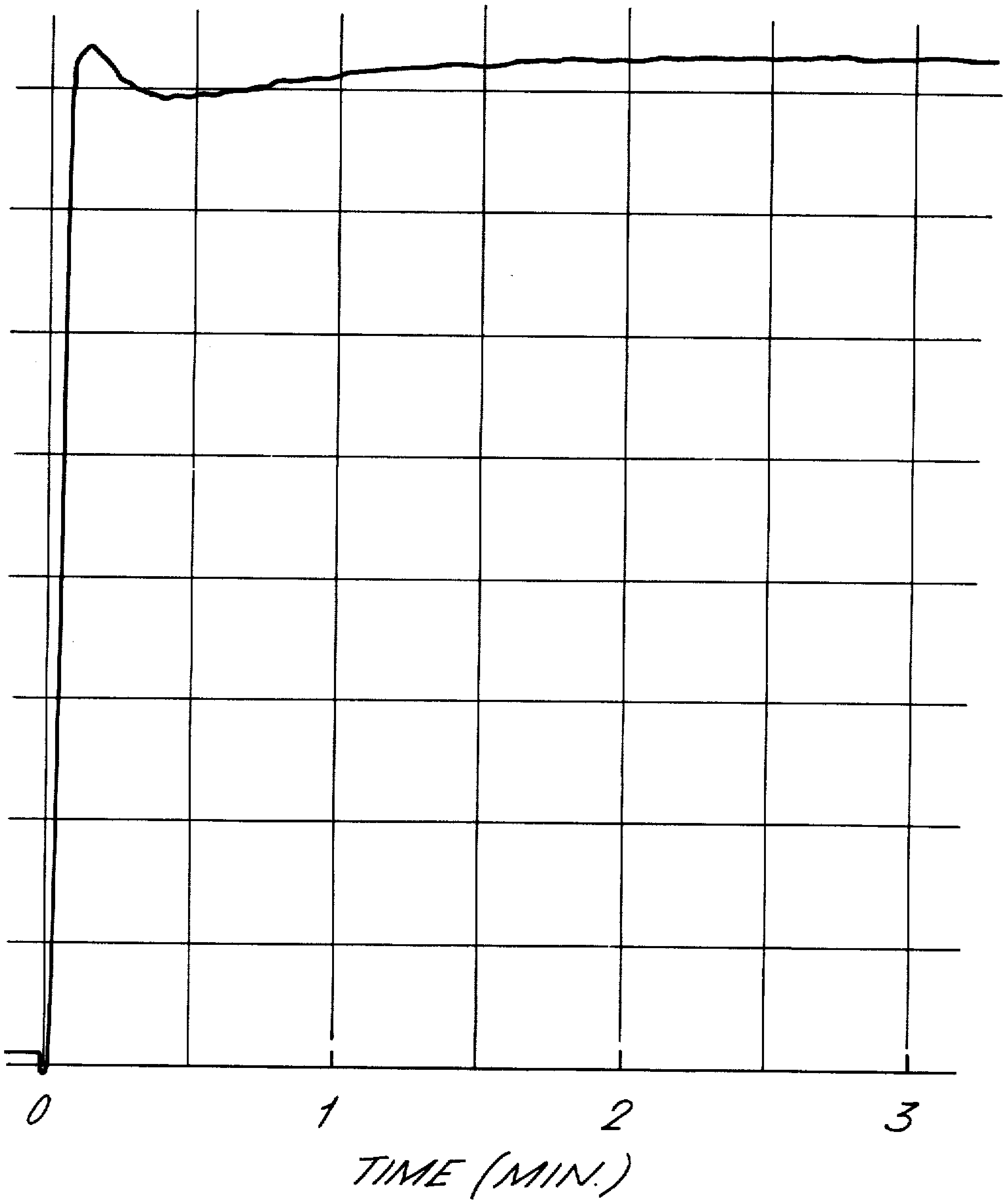


FIG.5B.

FIG. 7.



DEMOUNTABLE SPUTTERING CATHODE FOR ATOMIC ABSORPTION SPECTROSCOPY

BACKGROUND OF THE INVENTION

This invention relates to spectrochemical analysis, and seeks to provide a system which permits a rapid change-over of samples submitted for analysis. Spectrochemical analysis, for the purposes of this specification, should be taken to include atomic absorption analysis, atomic fluorescence analysis, and spectral emission analysis.

In spectrochemical analysis, it is necessary to create an atomic vapour from the sample so that the spectral characteristics determined are those of the atoms alone, and not those of atoms in combination with other atoms — whether of the same element or different. In atomic absorption and fluorescence spectroscopy, high-temperature flames have been used almost exclusively as the means for converting samples into atomic vapour. A disadvantage of this method is that, with solid samples, a preliminary time-consuming step is necessary before the technique can be used, as the sample for flame photometry must be in the form of a solution. Moreover, the results of the tests on the solution must be related back through the dissolution step to give the desired result in the form of an analysis of the original sample.

The flame method also suffers to a greater or lesser extent from other disadvantages, including pressure broadening of absorption lines, quenching of fluorescence radiation, compound formation in the flame, and opacity of the flame gases to vacuum-ultraviolet light.

An alternative to the flame method, cathodic sputtering of the sample atoms to form an atomic vapour, has been known for some time (see, for example, our copending Australian patent application 37,184/68).

When a metal specimen is made the cathode of a d.c. glow discharge, particles of the cathode material are sputtered from the surface by energetic ions accelerated in the high field of the cathode fall. These particles, which consist largely of single ground-state neutral atoms are ejected from the cathode with large initial energies, of the order of 10eV for the ion energies available in a glow discharge. The sputtered atoms subsequently lose this energy by elastic collisions with gas atoms as they diffuse out from the cathode to sinks in various parts of the vessel. During transit, the sputtered atoms pass through the negative-glow region of the discharge where they may become excited or ionized by electron impact or by collisions with metastable atoms.

At pressures in the range 1–10 torr, the sputtered atoms rapidly come to thermal equilibrium with the gas, and sputtering and diffusion rates are such that relatively large steady-state concentrations accumulate in the region around the cathode. At the same time, the negative glow is relatively well confined, and the anode glow and positive column can be virtually eliminated by positioning the anode at the edge of the negative glow. Thus large concentrations of relatively emission-free sputtered vapours, in thermal equilibrium with the gas, are available in the region just beyond the negative glow.

When an alloy is vapourized thermally, the depletion of the higher vapour-pressure elements at the surface is rapidly compensated for by diffusion of atoms from the bulk, and net fractional distillation of these elements occurs. For cathodic sputtering, however, the temperature of the alloy is usually too low to permit diffusion of atoms from the bulk, and a thin layer depleted in the faster-sputtering elements rapidly forms near the surface. Once equilibrium is established, this depleted layer apparently compensates for the faster sputtering rates of the depleted elements, and the composition of the sputtered material is then approximately the same as that of the original alloy.

While this sputtering technique offers many advantages in certain situations over flame photometry, it has not as yet gained wide acceptance for routine analysis. One of the prime difficulties has been the time necessary to change from one sample to the next, mainly because of the contamination introduced into the chamber during the change-over, and the relatively large amount of contamination which must be removed from the sample body if it is placed wholly inside the vacuum chamber. The time consumed in the actual change-over of sample bodies has also given rise to significant delays.

BRIEF SUMMARY OF THE INVENTION

The invention provides a method and apparatus whereby samples for spectrochemical analysis by sputtering may be interchanged rapidly. The invention avoids the contamination difficulties associated with the introduction of the whole sample into the vacuum chamber by allowing the bulk of the sample, if it is a solid block, to remain outside the chamber. The sample may be in the form of a solid piece of metal, for example a disc of about 4 cm diameter, or may be formed on the surface of a similar solid block of holding material. In either case, the block will be referred to herein as a "sample body," and the area on the surface from which sample atoms are sputtered will be referred to as the "sample area." The sample area, and a small part of the surrounding surface, are the only portions of the sample body subjected to the vacuum; the remainder being left in contact with the surrounding air.

The term vacuum as used in this specification is intended to cover a partial vacuum, and pressures inside the vacuum chamber are typically of the order of 1–10 torr.

To allow the sample area to be included within the vacuum system, the vacuum chamber is provided with an aperture in one of its walls. The sample area can then form the cathode of a sputtering discharge between itself and an anode located inside the vacuum chamber.

However, it is not practicable for routine spectrochemical analysis merely to place each sample in vacuum tight relation outside an aperture in a vacuum chamber and establish a sputtering discharge to form sample atomic vapours. Material sputtered from the samples will accumulate on all surfaces close to the discharge and interfere with operations by forming additional cathode areas on the walls. These areas will be in electrically conductive relation with the cathode, being at some point continuous therewith, so that the discharge may switch to them as cathodes. Interference may be produced because the material then sputtered may be left over from previous samples, and even if the samples are the same, the relative distribution of atoms in the atomic vapour may be quite different to that in the samples because there is no compensation for different sputtering rates; and furthermore, different current densities characteristic of a new discharge path may result in different discharge conditions. Even more extreme interference can result with a heavy build-up of sputtered material on the walls because eventually a conductive path can form between the anode and cathode, short-circuiting the discharge.

Accordingly, in one aspect the invention comprises apparatus for providing an atomic vapour for spectrochemical analysis from a sample area on the surface of a sample body, the sample area in use forming the cathode of a sputtering discharge, comprising a vacuum chamber having an apertured wall, an anode lying inside the chamber, and apertured sample locating means around the wall aperture comprising an outer annular portion adapted in use to abut the surface of the sample body and an inner annular portion electrically insulated from said outer portion and said anode adapted in use to lie opposite the surface of the sample body but spaced therefrom a short distance to form an annular gap surrounding the sample area, the gapwidth being large enough to electrically isolate the opposed surfaces thereof but smaller than the width of the cathode dark space for the sputtering discharge.

For the purposes of this specification the inner and outer annular portions should be understood as being electrically insulated from each other if one or both are made from electrically insulating material, including the case where they are formed integrally from electrically insulating material.

Preferably also, the vacuum chamber is purged with clean inert gas while maintaining the vacuum level appropriate to the glow discharge so that impurity atoms are swept from the volume.

In a particularly advantageous form, the invention provides gas passages within the disc so that purge gas is directed into the area of the discharge in such a way that atoms sputtered from the sample area are carried away from the discharge region towards the body of the vacuum chamber to facilitate spectrochemical analysis.

In a preferred form, in which a resilient vacuum sealing member is located between the surface of the sample body and a wall of the chamber, the external sides of the outer annular portion also retain the sealing member in place and prevent it from being drawn towards the aperture under the influence of the vacuum. In a particularly preferred embodiment, the sample locating means is in the form of a separate flat disc with a central aperture and an inwardly stepped inner annular portion on one face.

Preferred features of the method and apparatus according to the invention will become apparent from the following description of a particular embodiment of the invention, in which:

FIG. 1 is a diagrammatic representation of apparatus for spectrochemical analysis according to the invention;

FIG. 2 shows a cross-section of a sample holding arrangement of the invention;

FIG. 3 shows in plan view a disc used in the sample holding arrangement; and

FIGS. 4A and 4B show exploded plan views of a disc according to a further embodiment of the invention;

FIGS. 5A and 5B show section views through the disc shown in FIGS. 4A and 4B;

FIG. 6 shows a section view of a further sample holding arrangement according to the invention;

FIG. 7 shows a typical warm-up trace of fluorescence radiation intensity obtained from a surface with no prior sputtering treatment.

Turning briefly to FIG. **1**, the sample body **1** is located against an aperture (not shown) in vacuum chamber **2.** The sample body is electrically conductive and is connected to a negative supply voltage line **3,** and a discharge is struck between it and an anode inside the chamber connected to positive voltage line **4.** A spectral lamp **5,** operated to emit a pulsed high-intensity spectral line characteristic of the element being estimated, is located so that it illuminates the atomic vapour created inside chamber **2.** If fluorescence radiation is being examined, a photodetector **6** is arranged to receive light emitted by the sample vapour in a direction at right angles to the incident radiation. If atomic absorption is being examined, a photodetector of monochromator **7** is arranged in line with the incident radiation. In either case, lenses may be arranged to focus incoming and outgoing light relative to the vacuum chamber, light baffles may be used to minimize the interference due to stray light reflections, and filters may be interposed in the light paths to select appropriate regions of the spectrum.

The detectors **6** and/or **7** are preferably arranged in synchromous demodulation circuits, so that light pulses originating from lamp **5** are selectively detected. A fuller description of circuit and optical arrangements may be found in our Australian patent specification No. 163,586 in relation to atomic absorption and in the specification of the aforementioned Australian patent application No. 37,184/68 in relation to fluorescence.

In FIG. **2**, a preferred sample holding means of the invention is shown in more detail. Portions of the wall of the chamber **2** of FIG. **1** are shown at **8,8'**, with an aperture at **9.** Anode **10** is located inside the chamber at a point about 1 cm below the cathode formed by sample area **11**, the distance of 1 cm corresponding roughly to the edge of the negative glow in order to eliminate as far as possible background interference from an anode glow and positive column. The discharge causes sputtering of sample atoms from the cathode to form an atomic vapour, and the preferred location at which this vapour is examined spectroscopically is about 2 cm below the cathode, thus minimizing the contribution of the negative glow to interfering background radiation.

The sample area **11** is located on the surface **12** of the sample body **13.** Surface **12** is preferably ground flat and is pressed against the wall **8,8'** by a retaining member **14** assisted by outside air pressure when the chamber 2 is evacuated. Interposed between the sample body and chamber wall is a sample locating means **15** and a resilient sealing member **16.**

Sample locating means **15,** shown in plan view in FIG. **3,** in one embodiment, takes the form of a solid disc of insulating, heat-resisting material such as quartz, with a central aperture **17.** In use, this aperture is aligned with aperture **9** in wall **8,8'** of the vacuum chamber. The disc is relatively flat on the side which is placed against wall **8,8'** of the chamber, and on its other side has two annular portions, the inner portion **18** being stepped inwardly relative to the outer portion **19.**

The ratio of the thickness of the disc to that of sealing member **16,** preferably an O-ring, is set so that when the sample body is forced against the disc, the O-ring is sufficiently compressed to form a vacuum-tight seal between the surface **12** and the wall **8,8'**.

The annular gap **20**, formed between the surface **12** and the inner annular portion **18**, is approximately 0.2 mm wide, and extends approximately 5 mm parallel to surface **12**.

The sample body **13** may be cooled to predetermined temperature by means of a water jacket **21**, and gas, preferably argon may be passed through chamber **2** via gas inlet and outlet connections (not shown). The gas connections are preferably arranged on opposite sides of the chamber relative to the sample area so that a flow of pure argon across the cathode surface may be maintained to sweep impurity molecules away from the viewing area.

In a further embodiment, disc **15** instead of being solid may be provided with internal gas flow passages to direct gas into the area of the discharge in such a way that sputtered atoms are swept into the body of the vacuum chamber **2** to facilitate spectrochemical analysis. FIGS. **4** – **6** of the accompanying drawings depict such an arrangement.

In FIGS. **4A** and **4B** a disc **15** having internal gas passages is shown in two halves prior to assembly.

FIG. **5A** represents a cross-section through the halves of disc **15** shown in FIGS. **4A** and **4B** along the lines AA, with the halves arranged in opposing relation. FIG. **5B** is a similar view along lines BB in FIGS. **4A** and **4B**. In FIG. **4A**, a circular groove of rectangular cross-section is shown on the upper face of the lower half of the disc, and in FIG. **4B** a corresponding groove **21'** can be seen on the lower face of the upper half of the disc. As shown in FIG. **5B** in particular, grooves **21** and **21'** when aligned opposite each other form a gas circulation passage within the composite disc **15**. A gas inlet port **22** can be seen in FIGS. **4A** and **5B** leading into gas circulation passages **21,21'**. Returning to FIG. **4B**, four additional grooves **23** may be seen leading from the gas circulation passage **21,21'** to the central aperture **17**. In use, the disc **15** is arranged as shown in FIG. **6** with a gas inlet tube **25** inserted partially into hole **22** so that argon, at a suitably low flow rate is directed into the region of the sputtering discharge through gas outlet ducts **24** (shown in FIG. **5A**). It has been found unnecessary in practice for a leak free connection to be made between gas inlet tube **25** and inlet port **22**, as adequate sweeping of atoms, and molecules, out of the discharge region has been attained with quite loose connections. The argon, preferably in a purified form, passes from the discharge region to a vacuum pump, shown schematically in FIG. **1**, which is kept running while the sputtering discharge is operating.

In an alternative construction, the gas circulation passage **21,21'** may be connected to a series of ducts leading into the region of the annular gap **20** shown in FIG. **2**, so that gas then passes out from this region, through aperture **17** in sample locating means **15** and into the body of the vacuum chamber **2**, and thence to the vacuum pump.

In operation, the chamber is brought up to atmospheric pressure with dry argon before being opened, and a fresh sample is placed on the disc **15** over the aperture **9**. The chamber is pumped down to a vacuum of approximately 5 microns over about 1 minute to clear as much contamination from the sample and chamber as possible. The pressure of argon is then let up to about 5 torr, and a steady flow of argon of about 0.2 litre per minute is maintained below the sample. The sputtering discharge is then started and allowed a certain time, usually a minute or so, to further remove surface contaminants and settle to a steady condition before reliable readings may be taken. FIG. **4** shows a typical warm-up trace of the intensity of fluorescence radiation emitted from an atomic vapour derived from the surface which had received no prior sputtering treatment. As can be seen, the signal reaches a peak value after only about 5 seconds, and then approaches a final equilibrium value after 1 minute or so.

Repeated use of the system provided by the invention without discernible interference caused by sputtered layers has been found possible. The annular gap **20** has been found to contain the discharge to the aperture **17** without any fringing into the gap, and material sputtered on the disc and wall surfaces outside the annular gap has not become electrically connected to the cathode.

It will be apparent that many modifications can be made to the embodiment of the invention described herein, and it is to be understood that the invention is not limited to the details of the construction illustrated, but includes all variations falling within its spirit and scope.

The claims defining the invention are as follows:

1. Apparatus for providing an atomic vapour for spectrochemical analysis from a sample area on the surface of a sample body, the sample area in use forming the cathode of a sputtering discharge, comprising a vacuum chamber having an apertured wall, an anode lying inside the chamber and below the wall aperture, and apertured sample locating means lying outside the chamber around the wall aperture and comprising an outer annular portion adapted in use to abut the surface of the sample body and an inner annular portion electrically insulated from the outer portion and the anode, adapted in use to lie opposite the surface of the sample body but spaced therefrom a short distance to form an annular gap surrounding the sample area, the gapwidth being large enough to electrically isolate the opposed surfaces thereof but smaller than the width of the cathode dark space for the sputtering discharge.

2. Apparatus as claimed in claim **1** in which the gapwidth is about 0.2 millimetre.

3. Apparatus as claimed in claim **1** in which the vacuum chamber includes means whereby a stream of gas may be introduced into the vacuum chamber while vacuum is maintained by a vacuum pump, such that impurity atoms and molecules may be swept out of the chamber while the sputtering discharge is operating.

4. Apparatus as claimed in claim **3** in which the sample locating means is provided with at least one internal gas passage for directing at least part of the stream of gas into the region of the sputtering discharge so that sputtered atoms are thereby carried away from the discharge region towards the body of the vacuum chamber to facilitate spectrochemical analysis.

5. Apparatus as claimed in claim **4** in which the sample locating means has a gas circulation passage into which at least part of the stream of gas may be directed, and at least one gas outlet duct leading into the aperture in the sample locating means.

6. Apparatus as claimed in claim **4** in which the sample locating means has a gas circulation passage into which at least part of the stream of gas may be directed, and at least one outlet duct leading into the annular gap between the sample locating means and the surface of the sample body.

7. Apparatus for spectrochemical analysis of a sample by means of a sputtering discharge comprising in combination;

a vacuum chamber having an apertured wall;

an anode lying inside the chamber and below the wall aperture;

a disc-shaped centrally apertured sample locating means disposed outside and around the wall aperture having a surface facing the sample with an outer annular portion abutting the surface of the sample and an inner annular portion electrically insulated from the outer annular portion and the anode, stepped away from the sample surface a distance large enough to electrically isolate the opposed surfaces of the gap so formed but smaller than the width of the cathode dark space for the sputtering discharge;

a sealing member in the form of an O-ring disposed around the periphery of the sample locating means and between the sample and the vacuum chamber wall so as to effect a vacuum seal therebetween;

means to evacuate the vacuum chamber;

means to initiate and maintain the sputtering discharge between the anode and the sample through the aligned apertures in the wall and the sample locating means;

a spectral lamp providing light containing at least one spectral line characteristic of an element under analysis; and

photodetector means for providing an indication of the degree to which the characteristic spectral line is absorbed by atoms sputtered from the sample by the discharge.

8. Apparatus for spectrochemical analysis of a sample as claimed in claim 7 in which the degree of absorbance is determined by measuring the fluorescent light re-emitted by the sputtered atoms.

9. Apparatus for spectrochemical analysis as claimed in claim 7 including means whereby a stream of gas may be introduced into the vacuum chamber while vacuum is maintained by a vacuum pump such that impurity atoms and molecules may be swept out of the vacuum chamber while the sputtering discharge is operating.

10. Apparatus as claimed in claim 9 in which the sample locating means is provided with at least one internal gas passage for directing at least part of the stream of gas into the region of the sputtering discharge so that sputtered atoms are thereby carried away from the discharge region towards the body of the vacuum chamber to facilitate spectrochemical analysis.

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