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[54] **ELECTRODE FOR ELECTROANALYTIC STUDIES**

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[52] **U.S. Cl.** .... **204/195 R;** 204/280
[51] **Int. Cl.** **G01n 27/30**
[58] **Field of Search** .... 204/280, 195 R, 1 T

[56] **References Cited**

UNITED STATES PATENTS

1,453,602	5/1923	Price	204/195 R X
2,215,213	9/1940	Ellis	204/280 X

OTHER PUBLICATIONS

F. C. Cowlard et al., J. Materials Science, Vol. 2, pp. 507–512, (1967).

H. E. Zittel et al., Analytical Chem., Vol. 37, No. 2, pp. 200–203, (1965).

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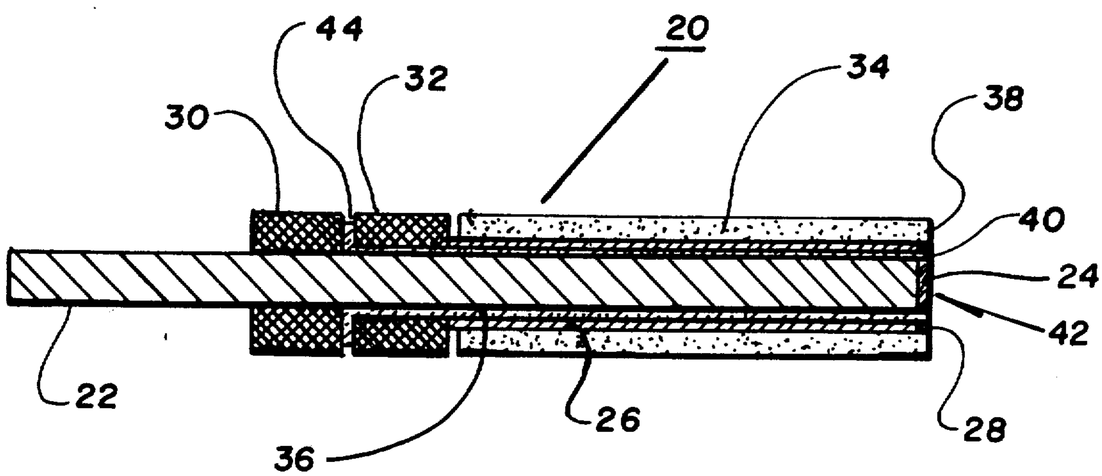
[57] **ABSTRACT**

An electrode construction for electroanalysis of fluids comprises a first contact and a second contact closely spaced therefrom, and conductive members electrically engaging the first and second contacts respectively for establishing conductive paths thereto. Arrangements are provided for electrically isolating the first and second contacts from one another and the conductive members from one another, and for sealing the contacts and the conductive members against the entry of fluid so that fluid is prevented from contacting the conductive members and any non-contact surfaces of the first and second contacts. In a modification of the invention the first contact is fabricated from one of the group consisting of glassy carbon and the second contact is made from platinum, gold silver, palladium, other noble metals and glassy-carbon. In another modification of the invention, particularly wherein the electrode is arranged for rotation during the electroanalysis, desirably both of the contacts are made from glassy-carbon. In another modification, the contacts are made from glassy-carbon and platinum respectively.

18 Claims, 3 Drawing Figures



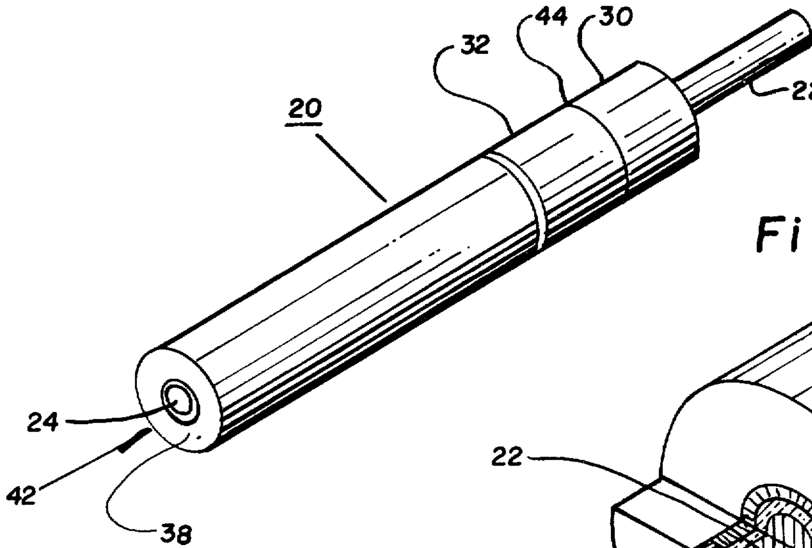


Fig. 1

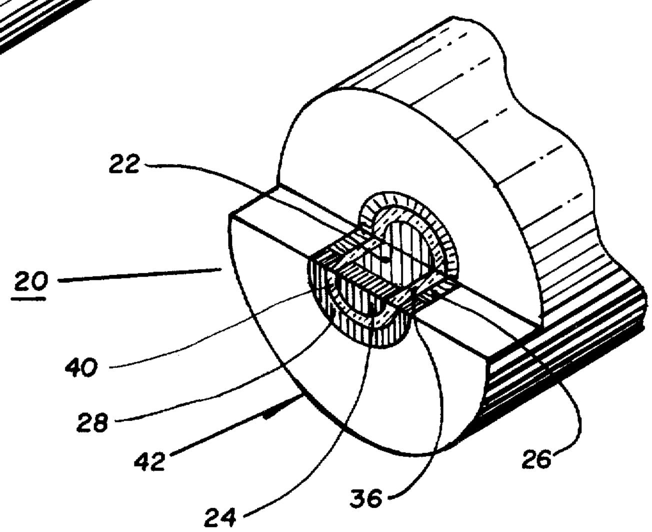


Fig. 2

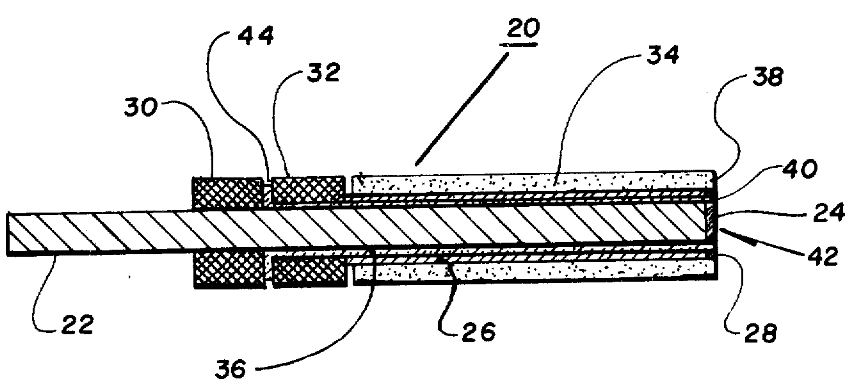


Fig. 3

ELECTRODE FOR ELECTROANALYTIC STUDIES

The present invention relates to electrodes for electroanalytic measurements and designed for rotation more or less rapidly within the medium being measured, and more particularly to an electrode of the character described, which has at least one contact thereof fabricated from glassy-carbon. The invention is particularly directed to an electrode of this type which can be conveniently assembled without the possibility of deterioration caused by leakage corrosion or the like.

Various types of rotating electrodes have been employed in chromatographic analyses for a number of years. Through voltametric studies, various products of chemical reactions that are electroactive, can be identified by their characteristic though minute positive or negative responses.

A number of electrode contact materials have been utilized for construction of rotatable electrodes in the past. These materials have varying ranges of electrical response, which make them more or less desirable in chromatographic applications. A platinum electrode furnishes a fair range of electroresponse, but cannot be used in negative solutions owing to oxide formation. Gold affords a limited negative response but does not have the positive range of platinum. Silver is not normally used in chromatographic studies as its range of response is too narrow. Mercury has an adequate range in negative solutions, but has the additional disadvantage that it is not solid.

A glassy-carbon-mercury electrode has been proposed heretofore for voltametry. This electrode was fabricated by molding glassy-carbon into an epoxy rod with a central tube to permit a mercury contact. Owing to the use of liquid mercury, however, the prior electrode is difficult to handle, as noted above. Moreover, the glassy-carbon-mercury electrode was not adapted for rotation in the solution being monitored.

The present invention involves the use of a rotatable ring-disc electrode in which at least the disc contact and desirably also the ring contact are formed from glassy-carbon. The ring contact can, however, be manufactured more easily from platinum or other suitable material. Use of my novel electrode in voltammetric stripping, for example, is characterized by a lower limit of detection and a shorter period of deposition prior to stripping. In certain applications, the disc electrode contact is constructed from glassy-carbon and the ring electrode contact from platinum, or vice versa, to advantage. The electrode contact or contacts which are fabricated from glassy-carbon desirably are thicker than contacts made from conventional materials owing to the fragility of glassy-carbon. In other applications one of the contacts is advantageously made from glassy-carbon and the other contact, from one of the group consisting of platinum, gold, silver, palladium, other noble metals, and glassy-carbon.

We have also found that our novel, rotatable electrode is capable of detecting extremely minute traces of mercury and platinum for example. The electrode of the invention provides a wider spectrum of electrode response and is capable of detecting a broader category of materials. For certain materials, the electrode of the invention is unexpectedly of the order of one hundred times more sensitive than comparable analytic procedures. This is especially advantageous in the electroanalysis of sparingly soluble compounds or elements.

The use of glassy-carbon in a rotating type electrode for electroanalysis offers a number of unexpected advantages. When the electrode is rotated more or less rapidly, the solution or medium being analyzed is subject to a stirring action for more uniform electroresponse. Initially, a plating voltage is briefly applied to the central or disc contact so that a minute plating of one or more solutes from the solution takes place on the central, or glassy-carbon electrode. The use of glassy-carbon for one or both contacts in this fashion facilitates the plating operation and at the same time affords a wider electroresponse. For this application the contacts also can be made from glassy-carbon and platinum, respectively.

The voltage applied to the electrode contacts is then reversed which deplates the plated materials from the glassy-carbon central contact. This deplating operation is unexpectedly facilitated by use of the glassy-carbon material for the central or disc contact. As the deplated ions leave the disc contact the centrifugal action at the face of the rotating electrode facilitates migration of deplated ions from the central contact to the ring contact which closely encircles the central contact. As the solution flows past the ring contact by the centrifugal flows generated by rotation of the electrode, the ions released from the central contact are collected and a proportionate electroresponse is obtained by the electrode and read on external metering circuitry. Use of glassy-carbon material for the ring contact unexpectedly facilitates gathering of the outwardly flowing ions, and further, an extended range of electroresponse is obtained. Thus, the electrode of the invention affords unexpected advantages when glassy-carbon is employed for the central contact and additional, unexpected advantages when glassy-carbon is employed for both the disc and the ring contacts of the electrode.

Other unexpected advantages of the invention stem from the internal structure of the electrode and are quite independent of the particular contact materials. The electrode construction, as elaborated upon hereinafter in detail, provides unexpectedly a reliable electrical isolation and a virtual hermetic sealing of the metallic components of the electrode against leakage from the solution in which the electrode is rotated.

I overcome the disadvantages of the prior art and accomplish these desirable results by providing an electrode construction for electroananysis of fluids, said construction comprising a first contact and a second contact closely spaced therefrom, conductive members electrically engaging said first and said second contacts respectively for establishing conductive paths thereto, means for electrically isolating said first and said second contacts from one another and said conductive members from one another, and means for sealing said contacts and said conductive members against the entry of said fluid so that said fluid is prevented from contacting said conductive members and non-contact surfaces of said first and said second contacts, at least one of said contacts being fabricated from glassy-carbon.

I also desirably provide a similar electrode construction wherein said first contact is a disc-shaped member, and said second contact is a ring-shaped member rounding said disc member.

I also desirably provide a similar electrode construction wherein said first contact is fabricated from glassy-carbon, and said second contact is fabricated from one of the group consisting of platinum, gold, silver, palladium, other noble metals, and glassy-carbon.

I also desirably provide rotatable electrode construction for electroanalyses of a given fluid, said construction comprising a central conductive support terminating in a first contact member, a conductive tube spacedly surrounding at least a portion of the length of said support and terminating in a second contact member disposed adjacent said first contact member but spaced therefrom, a pair of brush members spacedly mounted on said structure and electrically engaging said support and said tube respectively, an electrically isolating sheath member disposed between said tube and its brush and contact members on the one hand and said support and its brush and contact members on the other, said sheath member extending into a gap between said brush members and into a gap between said contact members, and means for electrically isolating the outer surfaces of said tube and the adjacent outer surfaces of its contact.

I also desirably provide a similar electrode construction wherein said sheath member has a flange at one end thereof for extension into the gap between said brush members.

I am aware of a number of references disclosing various types of electrodes for chromatography and related forms of electroanalysis. Such references include 37–2 Analytical Chemistry 200–203 (A Glassy Carbon Electrode for Voltammetry Zittel and Miller), U.S. Pat. Nos. 2,758,079 and 2,621,671 and West German Offenlegungshrift No. 2024008. None of these references, however, discloses the novel features of the invention, as set forth above.

During the foregoing discussion, various objects, features and advantages of the invention have been set forth. These and other objects, features and advantages of the invention together with structural details thereof will be elaborated upon during the forthcoming description of certain presently preferred embodiments of the invention and presently preferred methods of practicing the same.

In the accompanying drawings we have shown certain presently preferred embodiments of the invention and have illustrated certain presently preferred methods of practicing the same wherein:

FIG. **1** is an isometric view of one form of rotatable electrode made in accordance with the invention;

FIG. **2** is an enlarged isometric view of an end portion of the electrode shown in the preceding figure, with portions cut away to show the construction more clearly; and,

FIG. **3** is a longitudinally sectioned view of the electrode shown in FIG. **1.**

With reference now to the drawings in greater detail an exemplary rotatable electrode **20** according to the invention includes a conductive, axial support rod **22** to an end of which is secured an electrode disc or contact **24** fabricated from a suitable contact material, i.e. one of the group consisting of platinum, gold, silver, palladium, other noble metals and glassy-carbon. A tubular conductor **26,** fabricated from brass or other suitable electrically conductive material, is spacedly supported on the support rod **22** but is electrically isolated therefrom. A ring-shaped contact member **28** is secured to the outward end of the conductive tube **26** and thus is juxtaposed to the central or disc contact **24,** but is electrically isolated therefrom, as described below. The ring contact **28** also is fabricated from a suitable contact material, such as one of those mentioned above. In the preferred form of the invention, glassy-carbon is utilized although other materials can be used while taking advantage of other features of the invention described below. In certain applications, the central or disc contact member **24** is fabricated from glassy-carbon and the ring contact from platinum, or other noble metal to advantage. Excellent results have been obtained in most applications, however, when both the central or disc contact **24** and the ring contact **28** of the electrode **20** are fabricated from glassy-carbon. Alternatively, the disc contact **24** can be fabricated from platinum or other noble metal, and the ring contact **28** from glassy-carbon to advantage and in keeping with this feature of the inventive concept. As evident from FIGS **1-3** the contacts **24, 28** are mounted flushly in the face **38** of the electrode **20** to avoid any obstruction to flow of fluid across the electrode face.

In a specific embodiment of the invention the central support rod **22** is fabricated from stainless steel while the conductive tube **26** is formed from brass or copper. The disc and ring contacts **24, 28** are adhered to the support and conductive tube **22,26** respectively by means of an electrically conductive epoxy resin. Other electrically conductive cements or adhesives can be employed, or alternatively, the adjacent surfaces of these components can be nickel plated and soldered, although this last mode of connection is less strong.

When the electrode **20** is rotated rapidly within a solution or the like being measured, the minute currents generated by the electrode **20,** upon plating and deplating of particular solutes at its contacts **24, 28,** are conducted to external meansuring circuitry (not shown) through a pair of cylindrical brush members **30, 32,** or the like. One of the brush members, for example the brush member **30** is secured directly to the central conductive support **22** such that an electrical path is established to the central or disc contact member **24** through the conductive support **22,** which projects outwardly and preferably centrally of the brush members **30, 32** for connection to suitable rotation means. The brush member **30** can be shrunk-fitted on the central support **22** and/or an electrically conductive epoxy resin can be interposed therebetween to ensure a reliable, electrical engagement. The brush member **32** can be similarly mounted on the conductive tube **26,** or alternatively as shown, the brush member **32** can be formed integrally with the conductive tube **26.** The brush member **30** likewise can be fabricated integrally (not shown) with the central rod **22.** In any event a reliable conductive path is established between the brush member **32** and the ring contact **28.**

As apparent from the foregoing, the brush member **32,** the conductive tube **26,** and the ring contact **28** must be maintained reliably in electrical isolation from the brush contact **30,** the central conductive support **22** and the disc contact **24.** In addition to thoroughly isolating the ring contact **28** and associated components from the central or disc contact **24** and associated components, it is vitally important that the overall electrode structure **20** be leak-proof. That is to say, it is essential that a liquid or other material being subjected to electroanalysis with the electrode **20** be excluded from electrical contact with any other conductive component of the electrode **20**, such as the conductive support rod **22** or the conductive tube **26**, or the "non-contact" surfaces of the contacts **24, 28**, to avoid erroneous readings.

One arrangement for leak-proofing the electrode **20** and for electrically isolating its disc and ring contacts **24, 28**, includes the use of non-conductive sheath or sleeve members **34, 36.** The inner diameter of the outer sheath member **34** desirably is slightly smaller than the outer diameter of the conductive tube **26** such that upon forcing the outer sheath **34** thereover a compression fit results along the length of the conductive tube **26** and at the outer periphery of the ring contact **28.** Such compression fit forms an impenetrable seal along the interface between the conductive tube **26** and the outer sheath **34,** and particularly between the end portion **38** of the outer sheath and the adjacent peripheral surfaces of the ring contact **28.** Accordingly no fluid, in which the electrode **20** may be partially immersed, can penetrate into any portion of the junction between the ring contact **28** and the outer sheath member **34.** Of course, the lengths of the conductive tube **26** and of juxtaposed components of the electrode **20** can be varied depending upon the extent to which the disc and ring contacts **24, 28** will be inserted into a fluid monitored by the electrode **20.** Desirably the outer sheath **34** extends along the length of the electrode **20** a greater portion of the overall electrode length than that which is intended to be inserted into the aforementioned fluid.

Desirably the sheath members **34, 36** are fabricated from Teflon (a Trademark owned by Dupont for 2 bromo 1, 1, 1, 2 tetrafluoroethane) or the like because of its toughness and imperviousness, but sufficient plasticity to enable the sheath **34** to be forced over the relatively oversized conductive tube **26.** Another advantage in the use of Teflon plastic for this purpose is its almost complete inertness and concomitant negligible effect upon the readings or measurements obtained from the electrode **20.** Depending upon the application of the invention, however, other materials such as the epoxy resins can be employed although the latter are not as inert as Teflon. The outer sheath **34** electrically isolates the conductive tube **26** from the solution or other fluid in which the electrode **20** is partially immersed.

The inner sleeve or sheath **36** can be fabricated from Teflon plastic as mentioned previously and thus provides a reliable, electrical isolation between the ring and disc contacts **24, 28** between which the end portion **40** of the inner sheath is inserted and also between the conductive tube **26** and its cylindrical brush contact **32** on the one hand and the conductive central electrode support **22** on the other. Desirably, the inner diameter of the inner sheath **36** is somewhat smaller than the outer diameter of the central support **22** such that when forced therein a compression seal is established between the inner sheath **36** and the juxtaposed surfaces of the central support **22** and the disc contact **24.** This prevents any possibility of liquid penetration between the inner sheath end portion **40** and the contact disc **24.**

On the other hand the outer diameter of the inner sheath **36** is sized such that, when the sheath has been mounted on the central support rod **22** as aforesaid, the outer diameter of the inner sheath **36** is somewhat larger than the inner diameter of the conductive tube **26** and of its brush member **32.** In consequence a similar compression fit is established between the brush member **32** and the conductive tube **26** and the ring contact **28** on the one hand and the juxtaposed outer surfaces of the inner sheath member **36** on the other, when the aforementioned components are forced over the assembly comprising the inner sheath **36** and central support **22.** There is, in turn, no possibility of liquid penetration between the outer surface of the inner sheath end portion **40** and the adjacent inward surfaces of the ring contact **28.** By employing the various compression fits described previously, the contact or immersible end portion **42** of the electrode **20** is virtually hermetically sealed, and there is no liklihood of spurious readings from unwanted fluid penetration along the non-contact or embedded surfaces of the contacts **24, 28.**

When the inner sheath member **36** has thus been installed on the central conductive support **22**, an end flange **44** of the inner sheath **36** desirably is seated flushly against the adjacent surfaces of the brush member **30** for the conductive support **22**, as evident from FIG. **3.** Subsequently, when the assembly comprising the support **22**, brush member **30**, and inner sheath **36** is forced into the conductive tube **26** and its brush member **32** and ring contact **28**, a juxtaposed surface of the brush member **32** is likewise seated against the opposite side of the inner sheath flange **44.** The flange **44**, then, not only ensures electrical isolation between the brush members **30, 32** but can also delimit the proper positioning of the conductive tube **26** and associated components upon the electrode structure **20.** It will be apparent, of course, that the inner sheath flange **44** can be omitted and the brush members **30, 32** assembled with an isolating air gap therebetween, in place of the flange **44.**

When the electrode **20** is thus assembled it can be rotated more or less rapidly, while in contact with a fluid medium to be monitored, by suitable rotation means such as an ASR rotator supplied by the Pine Instrument Company, Grove City, Pennsylvania. Owing to the compact construction of the electrode **20** and the provision of the aforementioned compression fit, the electrode **20** can be rotated at speeds in excess of 10,000 RPM.

From the foregoing it will be seen that a novel and efficient Electrode for Electroanalytic Studies has been disclosed. The descriptive and illustrative materials employed herein are utilized for purposes of exemplifying the invention and not in limitation thereof. Accordingly, numerous modifications of the invention will occur to those skilled in the art without departing from the spirit and scope of the invention. Moreover, it is to be understood that certain features of the invention can be used to advantage without a corresponding use of other features thereof.

We claim:

1. A rotatable electrode construction for electroanalysis of a fluid, said construction comprising a first contact and a second contact spaced therefrom, conductive members electrically engaging said first and said second contacts respectively for establishing conductive paths thereto, means for electrically isolating said first and said second contacts from one another and said conductive members from one another, brush members mounted respectively on said conductive members and spaced from said contacts, and means for sealing said contacts and said conductive members against the entry of said fluid so that said fluid is prevented from contacting said conductive members and non-contact surfaces of said first and said second contacts, at least one of said contacts being fabricated from glassy-carbon.

2. The combination according to claim **1** wherein said first contact is a disc-shaped member, and said second contact is a ring-shaped member surrounding said disc member.

3. The combination according to claim **2** wherein both of said contacts are fabricated from glassy-carbon.

4. The combination according to claim **2** wherein said disc-shaped contact and said ring-shaped contact are mounted flushly in a face surface of said electrode construction.

5. The combination according to claim **2** wherein the conductive member of said first contact is an elongated rod extending along the length of said electrode construction, said brush members are mounted concentrically of said rod, and said rod protrudes outwardly and coaxially of said brush members from a side thereof remote from said contacts.

6. The combination according to claim **2** wherein said conductive members are a rod and tube extending from said first and said second contacts respectively, and non-conductive sheath members are closely fitted between said rod and said tube and around said tube respectively in sealing and electrically isolating relationship.

7. The combination according to claim **1** wherein said first contact is fabricated from glassy-carbon and said second contact is fabricated from one of the group consisting of platinum, gold, silver, palladium, other noble metals, and glassy-carbon.

8. The combination according to claim **1** wherein said first and said second contacts are mounted flushly in a face surface of said electrode construction.

9. The combination according to claim **1** wherein said brush members are cylindrical and are spaced in tandem along the length of said electrode construction.

10. The combination according to claim **1** including means for rotating said electrode construction.

11. A rotatable electrode construction for electroanalysis of a fluid, said construction comprising a first contact and a second contact spaced therefrom, conductive members electrically engaging said first and said second contacts respectively for establishing conductive paths thereto, means for electrically isolating said first and said second contacts from one another and said conductive members from one another, and means for sealing said contacts and said conductive members against the entry of said fluid so that said fluid is prevented from contacting said conductive members and non-contact surfaces of said first and said second contacts, at least one of said contacts being fabricated from glassy-carbon, said first contact being a disc-shaped member, said second contact being a ring-shaped member surrounding said disc member, said disc member being fabricated from glassy-carbon, and said ring member being fabricated from platinum.

12. A rotatable electrode construction for electroanalysis of a given fluid, said construction comprising a central conductive support terminating in a first contact member, a conductive tube spacedly surrounding at least a portion of the length of said support and terminating in a second contact member disposed adjacent said first contact member but spaced therefrom, a pair of brush members spacedly mounted on said structure and electrically engaging said support and said tube respectively, an electrically isolating sheath member disposed between said tube and its brush and contact members on the one hand and said support and its brush and contact members on the other, said sheath member extending into a gap between said brush members and into a gap between said contact members, and means for electrically isolating the outer surfaces of said tube and the adjacent outer surfaces of its contact.

13. The combination according to claim **12** wherein said sheath member has a flange at one end thereof for extension into the gap between said brush members.

14. The combination according to claim **13** wherein said outer sheath member is press-fitted about said conductive tube.

15. The combination according to claim **12** wherein at least said first contact member is fabricated from glassy-carbon.

16. The combination according to claim **12** wherein said isolating means includes an outer sheath member closely fitted about the outer surfaces of said tube and the outer pheripheral surfaces of said second contact member.

17. The combination according to claim **12** wherein said sheath member is pressed-fitted between said support and said conductive tube.

18. The combination according to claim **12** wherein said conductive tube and its brush member are formed integrally.

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