April 19, 1955 R. K. LADISCH 2,706,712

PORTABLE POLAROGRAPHIC HALF CELL

Filed March 30, 1954 2 Sheets-Sheet 1

Fig. 1.

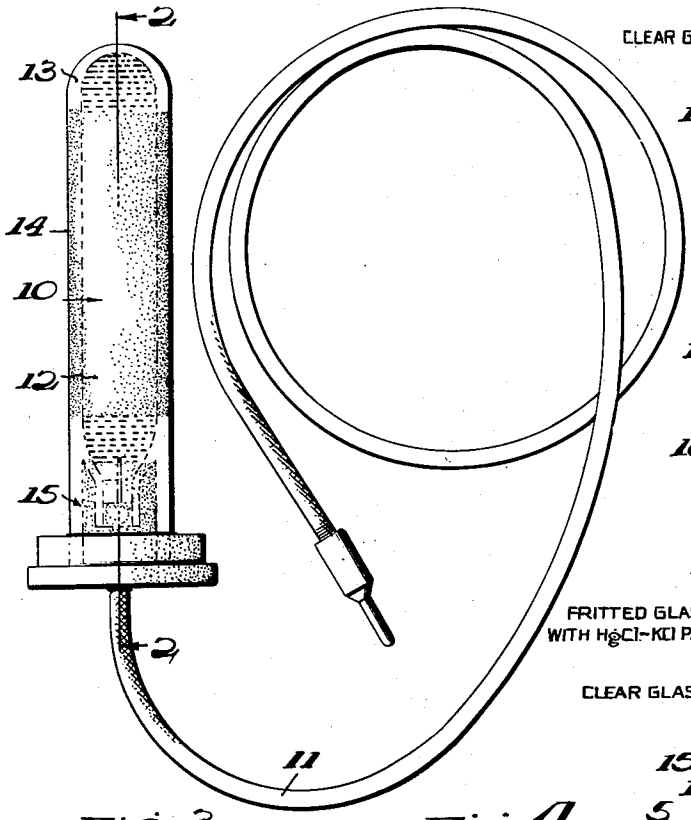


Fig. 2.

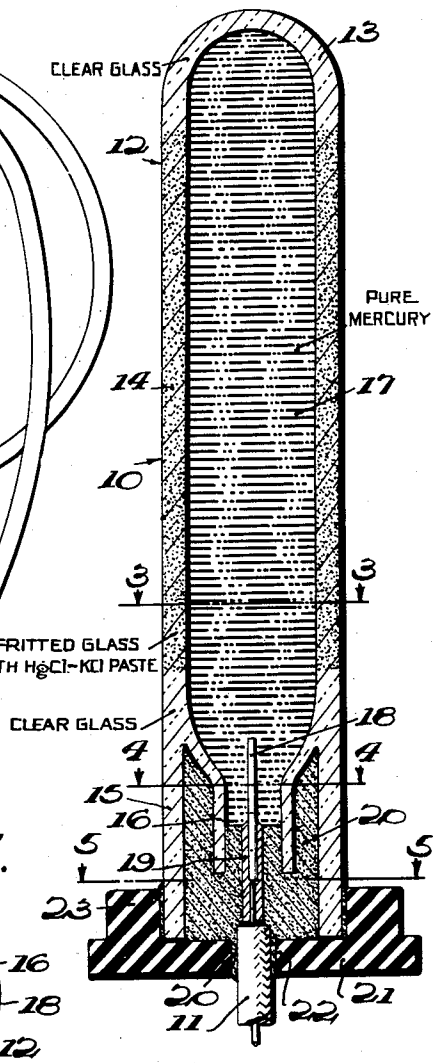


Fig. 3.

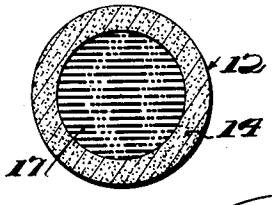
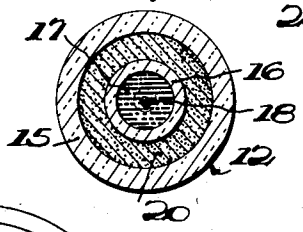


Fig. 4.



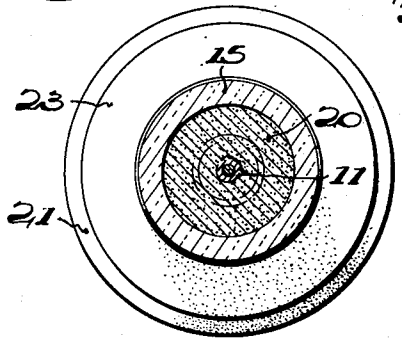


Fig. 5.

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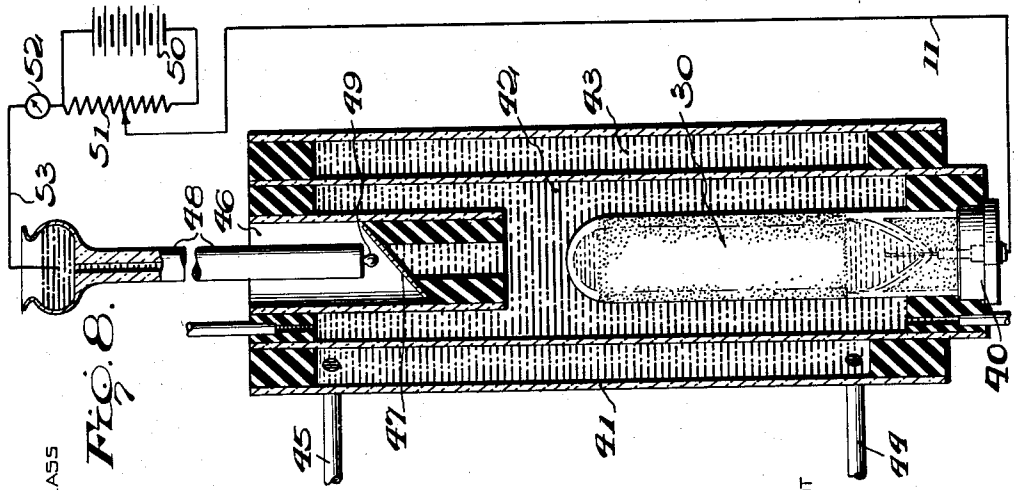


Fig. 8.

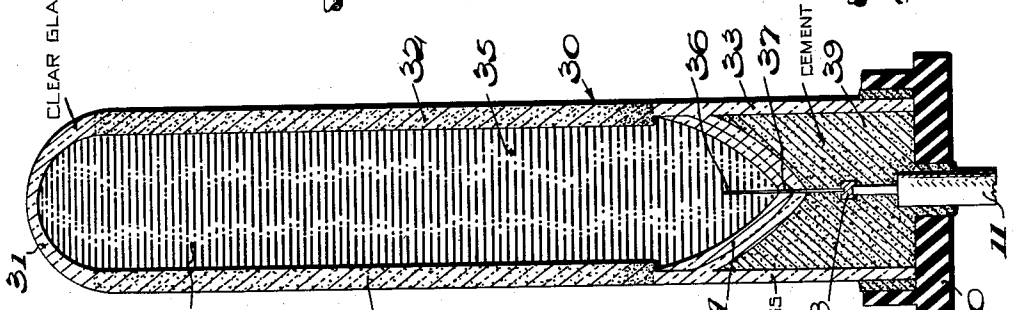


Fig. 7.

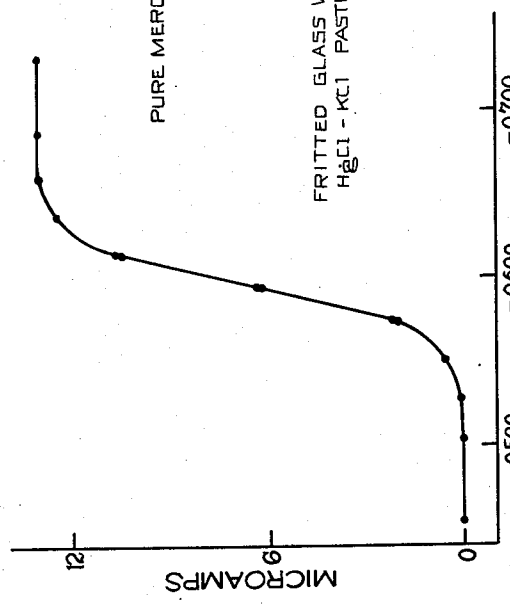


Fig. 6.

2 millimolar Cadmium waves in 0.1n KCl solution with the cells of Figs. 2 and 7.

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PORTABLE POLAROGRAPHIC HALF CELL

Rolf Karl Ladisch, Lansdowne, Pa., assignor to the United States of America as represented by the Secretary of the Army

Application March 30, 1954, Serial No. 419,941

5 Claims. (Cl. 204—195)

(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment to me of any royalty thereon.

The present invention relates to portable polarographic half cells such as are used in qualitative and quantitative analyses of certain solutions.

In using a polarograph for studying diffusion currents, a calomel half cell is most commonly employed as a reference electrode in series with the dropping mercury electrode. Half cells in wide use, such as those described by J. J. Lingane and H. A. Laitinen in Ind. Eng. Chem., Anal. Ed., Vol. 11, p. 504 (1939) and G. S. Smith in The Analyst, Vol. 75, p. 215 (1950), cannot be moved about freely because shaking them sometimes causes inaccuracies of 1—3 millivolts or even more, and full accuracy may not be restored until five or six hours have elapsed. Besides, these prior art structures must be kept in an upright position to main the original cleanliness of the platinum contact.

This invention aims to provide a non-polarizable, rugged half cell of low ohmic resistance, especially made to confine the mercury in a rigid support, so that the electrical contact between the platinum wire and the mercury is not disturbed under the conditions of polarographic procedure. A specific object is to confine the mercury by material which is porous to the mercury when the latter is subjected to pressure. The preferred porous material is glass frit; when choosing a frit of the proper size the area of the mercury can be made equal to or several times larger than that of the mercury pool in a conventional half cell.

The present application is a companion to my pending applications Serial Nos. 372,411 and 373,928 filed respectively August 4, 1953 and August 12, 1953, each of which shows a portable half cell of different construction.

In the accompanying drawings forming a part of this specification,

Fig. 1 is a full size elevation of one form of the half cell, showing a conventional lead for the contact wire;

Fig. 2 is an enlarged longitudinal section, omitting the lead;

Figs. 3, 4 and 5 are respectively cross sections on lines 3—3, 4—4 and 5—5 of Fig. 2;

Fig. 6 is a reproduction of a curve made from actual tests with the half cell;

Fig. 7 is a longitudinal section through another form of the half cell; and

Fig. 8 is a diagrammatic sectional view partly in elevation showing a set-up, including the half cell of Fig. 7, for analyzing a solution by polarographic methods.

Referring particularly to the drawings, Fig. 1 shows the completed half cell **10** with a lead **11** coupled thereto. The half cell **10** comprises a generally tubular glass body **12** (Figs. 2–5) having a clear glass closed upper end **13**, a fritted glass cylindrical body portion **14**, and a clear glass lower end portion **15** which is open. In making the fritted glass body portion **12**, fritted glass parts with nominal maximum pore sizes of 40 microns and 5 microns were used at random. A glass tube **16** of about half the diameter of the tubular end **15** is fused inside said tubular end **15** so that tube **16** is coaxial with the tubular end **15** but terminates short of the lower extremity of said tubular end. Calomel-potassium chloride paste is deposited within the porous fritted glass wall **14** by means of suction with a water injection pump, in a manner similar to ordinary filtration practice. After this depositing, the interior of the tubular cell is cleaned by washing with distilled water. Then air is sucked through the fritted glass until the latter becomes dry. Then the interior of the cell is filled with pure mercury **17** by pouring the mercury in through the open end of the body **12**, which is of course inverted for this step. Some of the mercury stands in tube **16** as shown. Then the contact wire **18** (platinum or tungsten) is inserted in the mercury, after having been electrically and mechanically connected to the end of lead **11** by means of soft solder **19**. Finally, the lower end of the half cell is sealed by means of a mass of cement **20** which is placed inside the open tubular end **15** and inside the lower end of tube **16**. Cement **20** should have good dielectric characteristics and when it sets or hardens it provides a rigid support or anchorage for the contact wire **18**. The bottom of the glass tube is closed by a rubber or similar stopper **21** having a central opening **22** through which lead **11** passes, and having a circular flange **23** which surrounds the tubular end **15**. When the parts are assembled, some of the cement **20**, while still plastic, will flow through opening **22** and into the space between flange **23** and the outer wall of tubular end **15**; and when the cement hardens the rubber stopper will be secured tightly to the tubular end **15**, also lead **11** will be firmly secured to the rubber stopper and hence to the half cell assembly.

The modification shown in Figs. 7 and 8 comprises a half cell **30** essentially the same as the one shown in Figs. 1–5 except that it has no open end through which the mercury may be poured, hence it is more difficult to make. The half cell **30** has a generally tubular glass body including a clear glass closed upper end **31**, a fritted glass cylindrical body portion **32**, a tubular clear glass lower end portion **33**, which is open, and a fused wall **34** closing and sealing the lower end but terminating short of the lower extremity of the glass body. In making the fritted glass body portion **32**, fritted glass parts with nominal maximum pore sizes of 40 microns and 5 microns were used at random.

To complete the half cell, the part delivered by the glass blower was placed in a desiccator and was evacuated by means of a high vacuum pump for at least an hour. Still under vacuum, triple distilled mercury was admitted through a funnel in the lid of the desiccator in such a fashion that the mercury filled the space around the wall of fritted glass. The mercury penetrated through the wall (when made of coarse glass frits) as soon as the desiccator was returned to atmospheric pressure, to fill the entire interior of the half cell, as indicated at **35**. (If the frits were of 5 microns pore size, a pressure of 75 p. s. i. gage from a nitrogen cylinder was applied to the mercury to accomplish the same result. This latter operation was done in a stainless steel bomb, to which the glass half cell body, including the mercury, had been transferred from the desiccator.) After filling the half cell, any excess mercury clinging to the outside walls was shaken off. A paste made of KCl solution (special for calomel cells, into which 0.35 per cent by weight of agar had been dissolved) plus calomel (special for calomel cells) was brushed onto the outer surface of the fritted glass body portion **32**. Electrical contact with the mercury is made by fusing a tungsten wire **36** through aperture **37** in wall **34**, which is accomplished before filling the half cell with mercury. A piece of soft solder **38** mechanically and electrically connects wire **36** to lead **11**, and a mass of insulating cement **39** (like cement **20**) closes the lower end portion **33** and anchors the lead to the assembly. Finally, a flanged rubber stopper **40** (like stopper **21**) is fitted on the lower end of the half cell body, being secured by cement **39** as Fig. 7 indicates.

Referring to Fig. 8, the half cell of Fig. 7 has its principal portion immersed in a sealed container **41** containing KCl solution **42**, with a surrounding water jacket **43** (having connections **44** and **45** with a thermostated water bath) to keep the temperature of the half cell substantially constant. Also located in the sealed container **41** above the half cell is an open vessel **46** closed at the lower end by a very thin resinous membrane **47** whose under surface is in direct contact with the KCl solution **42**. My pending application Ser. No. 220,325 filed April 10, 1951, discloses vessel **46** in more detail. The open vessel **46** contains the solution to be tested by the apparatus (not shown) and a dropping mercury electrode **48** drops mercury **49** into the test solution in the well known manner. A battery **50** with a rheostat **51**, a galvanometer **52**, and a lead **53** to the dropping mercury electrode, are also

shown. The circuit is completed by lead 11 which is connected to the rheostat 51. As the technique of using the described polarographic apparatus is well understood, no description thereof will be undertaken.

The half cell of Figs. 7 and 8, like the half cell of Figs. 1–5, even when handled frequently during an analysis, will perform satisfactorily. Both cells are obviously rugged and compact and are easily handled and packaged. With the conventional mercury pool electrode, great care had to be exercised to arrive at equally precise results, but in routine polarographic analysis, precise results cannot be expected from the conventional electrode.

The potential of the half cells described herein was checked in saturated KCl solution against a saturated calomel electrode, in combination with a potentiometer and a galvanometer. The average deviation of all cells tested was 0.3 millivolt; these small deviations decreased even further after the cells came to equilibrium over night.

Polarographic analyses of 2.00 millimolar cadmium sulfate in 0.1 normal KCl solution were conducted in a Lingane-Laitinen H-cell. The test compartment was separated from the reference electrode by an agar plug as usual. For comparison, a conventional mercury pool-calomel reference electrode in saturated KCl solution was placed in the bottom of the H-cell adjacent to the test compartment, the half cells herein described being likewise immersed in the saturated KCl solution above the mercury pool electrode. The surface area of the mercury pool was 3.8 sq. cm. In view of the fact that the potential of the pool electrode may become inaccurate under certain conditions, this electrode was prepared with extreme care, and once it had been set up in the thermostated H-cell, it was neither removed nor mechanically disturbed. The pool electrode was renewed whenever significant changes in its potential (as measured against a calomel electrode) became apparent despite the precautions taken. Removal of the test solution and clearing of its compartment were done with a suction tube. The test solution was free from oxygen by purified nitrogen prior to the analysis, and nitrogen was passed over the solution during the analysis as is usual. The drop time of the capillary used was checked during each run at the half wave potential; it maintained a value of 4.89 ± 0.01 sec. The $m^{2/3}t^{1/6}$ value was found to be 1.83 at an applied potential of -0.700 v. versus SCE, at which the magnitudes of the diffusion currents were determined. The capillary cell equipment was kept at $25° \pm 0.1°$ C. by means of a thermostat control. A well known commercial manual polarograph was employed. The IR drop across the polarographic circuit was measured. All data were corrected for the IR drop and the residual current.

To detect possible time-dependent changes in potential of the cells herein described, five curves were drawn consecutively with readings based on the same test solution. Approximately 45 minutes elapsed between the first and the last measurements. The heights of the diffusion currents at an applied voltage of -0.600 v. versus SCE (i. e., close to the half wave potential) agreed with each other to better than ± 0.5 per cent.

Fig. 6 shows the 2 millimolar cadmium sulfate curves obtained with the conventional mercury pool-calomel reference electrode and the two half cells described herein. The values measured for the curves often coincided.

The diffusion currents measured at an applied potential of -700 mv. with the herein described half cells were within the ranges of 13.05 ± 0.05 microamperes for the 2 millimolar solution. The half wave potentials were read from individual curves for each reference cell at $\frac{1}{2}\ i_d$ (where i_d is the average diffusion current in microamperes during the life of the drop of mercury). The readings agreed with each other within 597 ± 0.5 millivolts. The comparative resistances in ohms were as follows:

Test Solution	Conventional Hg Pool Electrode	Half Cell Call Fig. 2	Half Cell Cell Fig. 7
2 millimolar	1,160	1,120	1,140

From the above it is clear that the resistances of the cells described herein are of the same magnitude as that of the conventional mercury pool electrode.

The diffusion current constant was calculated on the basis of the original Ilkovic equation with $m^{2/3}\ t^{1/6}$ being 1.83. The electrolysis was not diffusion controlled, since no maximum suppressor was present. The value found in this manner for Ia was 3.58, which is in very good agreement with the data of Buckley and Taylor (Res. Natl. Bur. Stand. Vol. 34, p. 97, 1945) who obtained 3.54 for cadmium ion in the absence of a maximum suppressor. The half wave potential of 597 ± 0.5 mv. agrees well with Lingane's value of 599 ± 2 mv. (J. Am. Chem. Soc., Vol. 61, p. 2099, 1939).

Although the portable calomel half cells of this invention have been described with particular reference to their use in polarographic analyses, because of the great importance of having a reference electrode in such analyses which is very stable, it is to be understood that the portable half cells of my invention may be used wherever calomel reference electrodes are needed.

What I claim is:

1. A portable polarographic half cell comprising a unitary generally tubular body having an upper wall providing a closed upper end, a lower end, and a chamber on the inside which is completely filled with mercury, the side walls of the tubular body being principally of porous fritted glass, and a calomel-potassium chloride paste all of which is on or in said porous fritted glass walls; a conductor entering the lower end of the tubular body and making electrical contact with the mercury in the chamber; and means to secure the conductor immovably upon the half cell.

2. A portable polarographic half cell comprising a unitary tubular body having a closed upper end of clear glass, a main body portion of porous fritted glass, calomel-potassium chloride paste all of which coats or impregnates the fritted glass, and a lower end of clear glass; the interior of the body providing a chamber, and mercury completely filling said chamber; a conductor extending through said lower end into the chamber and making electrical contact with the mercury therein; and sealing means closing said lower end and securing said conductor against movement within the chamber.

3. The invention defined in claim 2, wherein the sealing means includes a mass of cement principally contained within the lower end of the body and surrounding said conductor, said sealing means also including a rubber stopper fitting over the lower end of the tubular body and confining the cement, said rubber stopper having a central aperture through which the conductor extends, part of the cement forming a layer or film between the rubber stopper and the lower extremity of the tubular body and another portion of the cement surrounding the conductor at the area where it passes through said central aperture.

4. A portable polarographic half cell comprising a generally tubular body having a closed upper end made of clear glass, a porous fritted glass portion extending for the principal length of the body, a clear glass lower end portion which is open, and an internal tubular portion fused to the walls of the lower end portion and extending coaxially therewith, said tubular portion having a diameter materially less than the diameter of the lower end portion and terminating short of the extremity of said lower end portion, the interior of the body being hollow, mercury completely filling said interior, a paste of calomel and potassium chloride all of which coats or impregnates the porous fritted glass portion, a conductor in contact with the mercury and extending out through said lower end portion, and means sealing the lower end portion and securing said conductor.

5. A portable polarographic half cell comprising a generally tubular completely closed body having a closed upper end made of clear glass, a porous fritted glass portion extending for the principal length of the body, a clear glass lower end portion which is closed, the interior of said body being hollow, mercury completely filling said interior, a paste of calomel and potassium chloride all of which coats or impregnates the porous fritted glass portion, a conductor in contact with the mercury and extending out through said closed lower end portion, and means securing said conductor to the lower end of said body.

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