May 17, 1955 R. K. LADISCH 2,708,657

POLAROGRAPHIC CELLS

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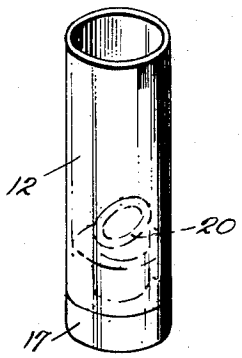


Fig. 1

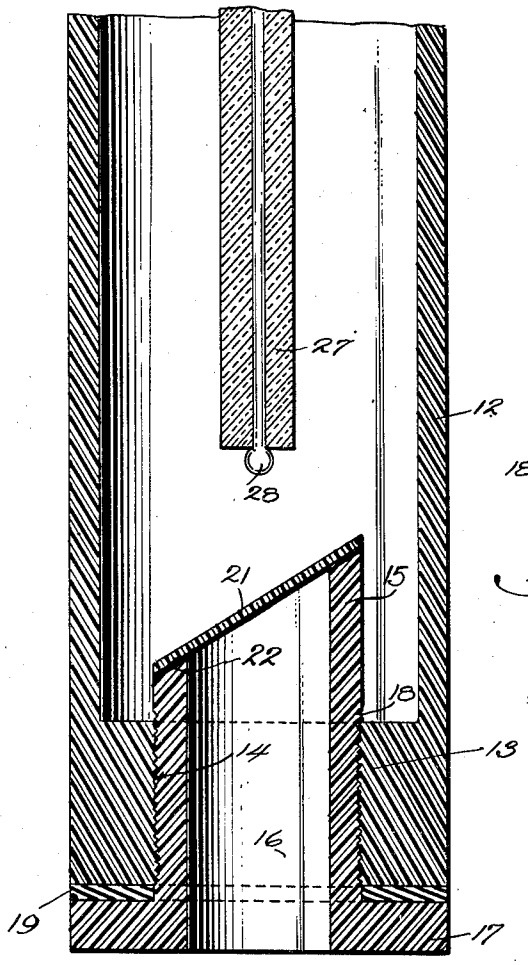


Fig. 3

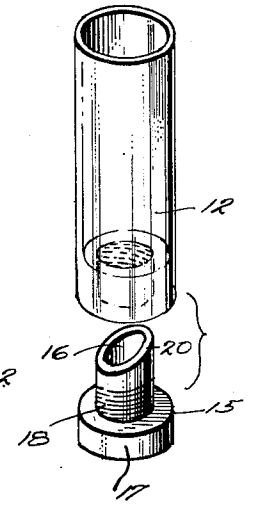


Fig. 2

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Fig. 4

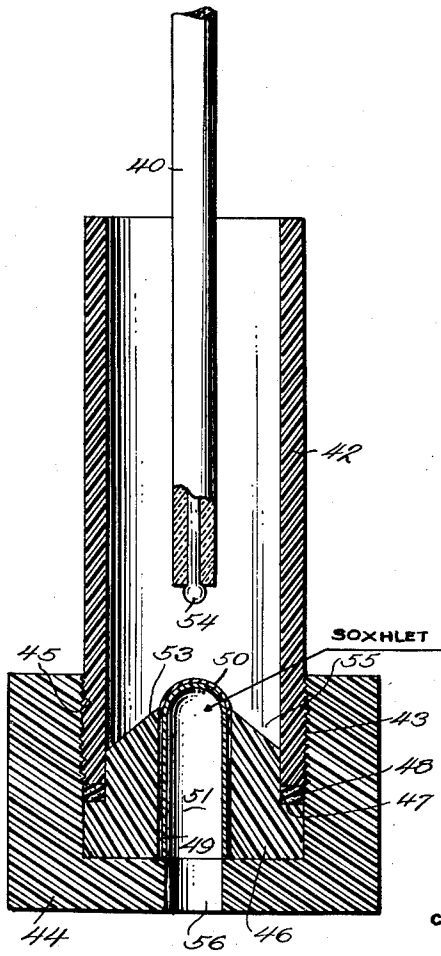
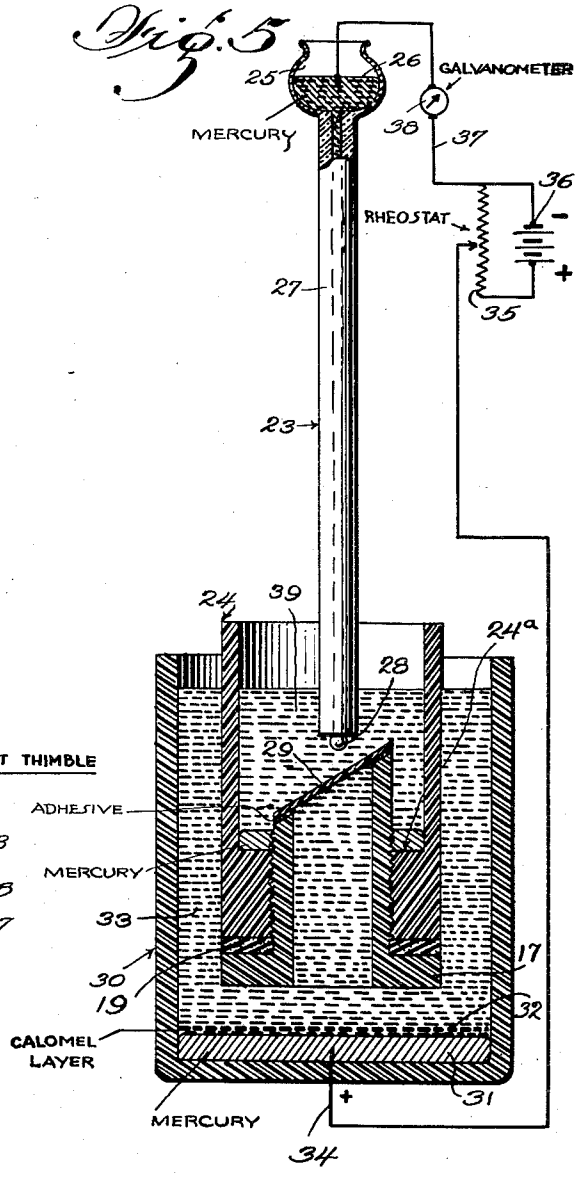


Fig. 5



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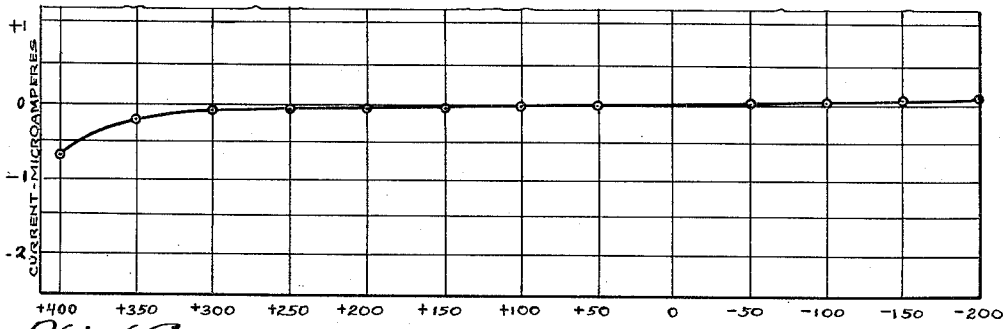


Fig. 6

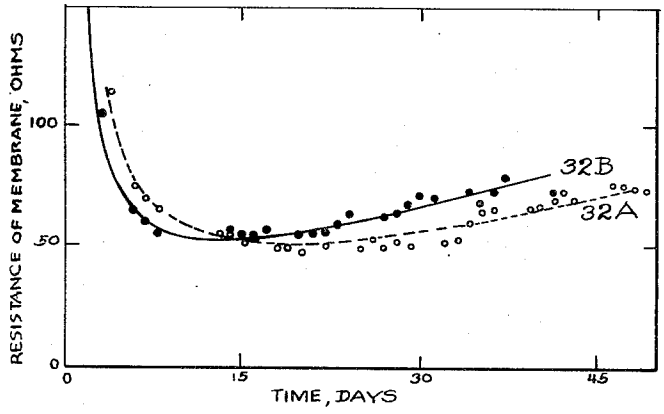


Fig. 7

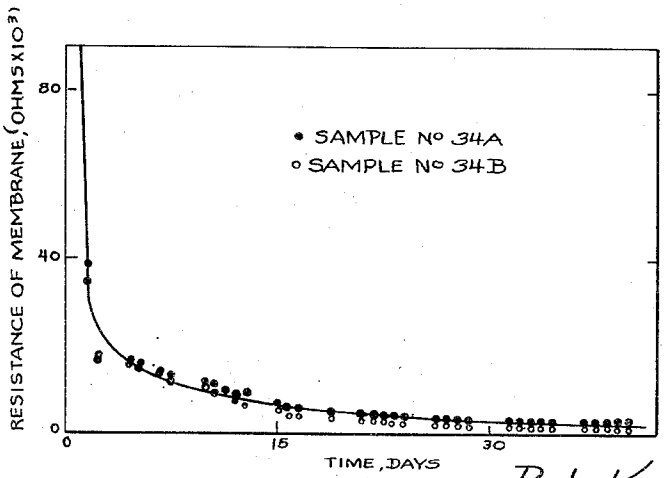


Fig. 8

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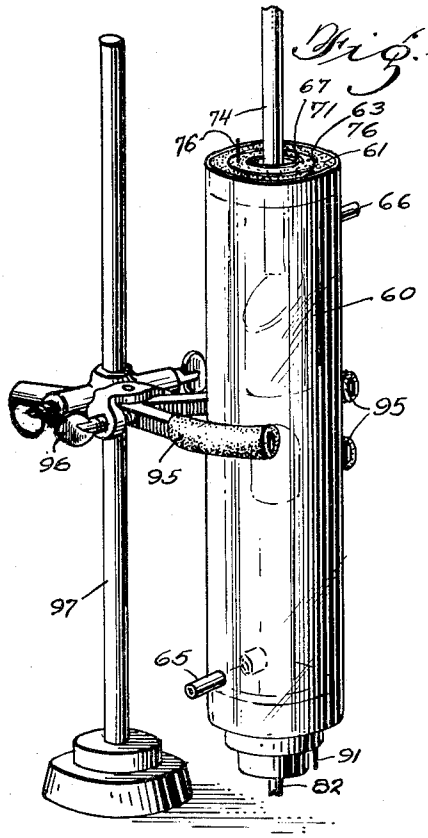
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POLAROGRAPHIC CELLS

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Fig. 10



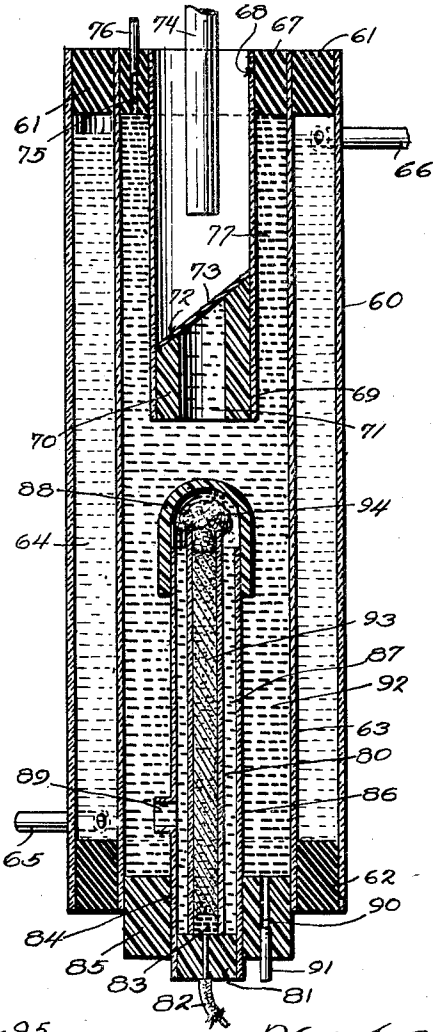
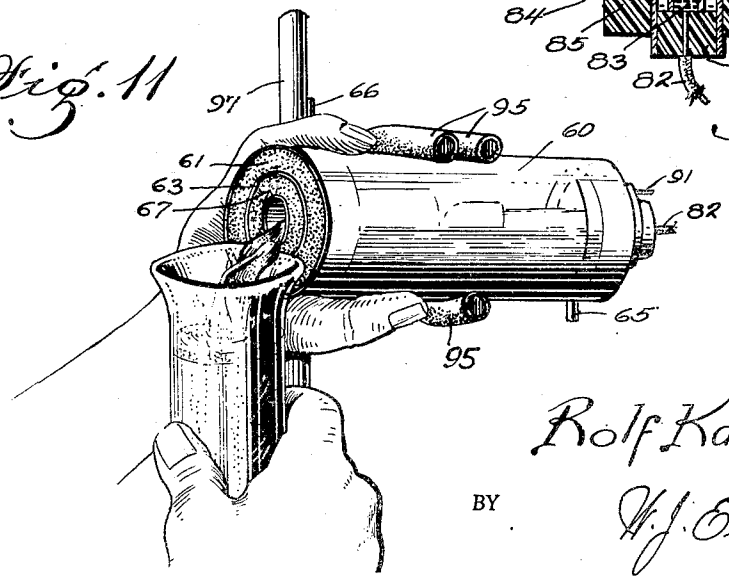


Fig. 9

Fig. 11



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United States Patent Office 2,708,657 Patented May 17, 1955

2,708,657

POLAROGRAPHIC CELLS

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Application April 10, 1951, Serial No. 220,325

11 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.

This invention relates to improvements in polarographic cells of the dropping mercury electrode type, 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. The solution of the calomel half cell containing chloride ions and the test solution with the dropping mercury electrode are electrically connected through a bridge which will permit ionic transport. Agar gels (about 2 per cent agar and 98 per cent water) are commonly employed to make the connection between the two solutions. However, it is known that agar gels allow chloride ions to migrate into the test solution to an appreciable extent, and therefore are inadequate for analyses where chloride ions interfere with the diffusion current of the test substance. (See Lingane, "Polarographic theory, instrumentation, and methodology," in Analytical Chemistry, January 1949, page 48, column 2, last paragraph.) Measurements have shown that chloride ions migrate from a saturated potassium chloride solution into distilled water through various agar plugs of 0.8 in. diameter and 0.24 in. thickness, at agar contents from 2 to 4 per cent, at a rate of 13 to 17 mg. KCl per half hour. Exchanging the water against a buffer solution consisting of 0.05 molar sodium acetate, 0.05 molar acetic acid, 0.01 per cent methyl red in a mixture (75:25) of methyl alcohol and distilled water, the shape of the residual current curve was greatly affected in the positive range of applied potential. The duration of the experiments varied between six and 148 hours. The rate of migration of KCl was steadily increasing to the above-mentioned values during the first eight hours in the use of an agar plug with concurrent changes in the shape of the residual current and the internal cell resistance. Because of these facts the quantity and quality of the test substance cannot be calculated accurately. Sometimes agar plugs become erratic after a short time for no apparent reason. Because of these drawbacks, Kolthoff and Matsuyama during their experiments described in Ind. Eng. Chem., Anal. Ed., 17:615 (1945) inserted the agar bridges into the tubes just before each polarogram was run, which obviously is time-consuming and prohibitively expensive if a large number of tests are to be made.

Various expedients have been resorted to to overcome this problem, including use of potassium nitrate bridges between the calomel electrode and the test solution, with agar blocks separating the potassium nitrate solution from the calomel electrode solution and also from the test solution. Other attempts to solve the problem are discussed on page 50 of Lingane, "Polarographic theory, instrumentation, and methodology"; see Fig. 13 also. These

attempts have been unsatisfactory because they greatly complicate the set-up and do not obviate the likelihood of contamination by migration of chloride ions; furthermore, they introduce a number of liquid junctions which can cause discrepancies in the readings. Moreover, the problem cannot be solved by considerably increasing the thickness of the agar block because this raises the resistance of the circuit to a prohibitive figure.

I have made the surprising discovery that by using certain very thin resin films or membranes to separate the test solution from the calomel electrode, it is possible to reduce the permeability with respect to potassium chloride to such a low level that the test solution is practically not disturbed by migrating chloride ions, while at the same time the resistance of the circuit is reduced to low enough values to be practicable, and in many cases is much lower than in the conventional prior art set-ups referred to above. These very thin membranes are of the order of 0.001 in. in thickness. Uniformity of thickness of these resinous membranes is not essential. The important considerations are low permeability to chloride ions and reasonable electrical resistance values.

In the preferred form of the invention, the polarographic cell is made entirely of cellulose acetate including the film or membrane. After an analysis, both the mercury and the test solution may be poured out of the open top of the cell and a new solution may be poured in, with a minimum of time consumed in making sure that contamination is obviated. Usually the only precautions necessary are a rinsing of the interior of the cell three times with distilled water. The cell itself may have cylindrical exterior walls so that it is easily made and readily supported by a swinging clamp fixed to a vertical stand to facilitate inverting the cell to pour out the mercury and the test solution, then rinsing as described and introducing a new test solution.

Referring to the accompanying drawings forming a part of this specification,

Fig. 1 is a perspective view of one form of polarographic cell embodying the invention, the electrodes, the circuit and the test solution being omitted;

Fig. 2 is an exploded view of the cell of Fig. 1;

Fig. 3 is an enlarged longitudinal section through the cell of Fig. 1, showing the lower or discharge end of the dropping mercury electrode, the thickness of the membrane being greatly exaggerated;

Fig. 4 is a longitudinal section on the scale of Fig. 3 showing another form of cell embodying the invention;

Fig. 5 is a wiring diagram including the cell of Figs. 1–3;

Fig. 6 is a typical residual current curve obtained by using a cell embodying the invention;

Figs. 7 and 8 show internal cell resistance curves with certain cellulose acetate membranes used in the cells of the invention;

Fig. 9 is a longitudinal section through another form of polarographic cell made particularly to facilitate pouring out its contents;

Fig. 10 is a perspective view of the cell of Fig. 9 shown supported in normal position; and

Fig. 11 is a similar view showing the contents being poured out.

Referring particularly to the drawings and first to Figs. 1, 2 and 3, the preferred polarographic cell comprises a hollow outer shell or casing 12 which has cylindrical outer walls and is open at the top. At its lower end, which is also open but is intended to be sealed, the shell or casing has an annular flange or thickened portion 13 which is screw threaded on the interior as indicated at 14. A combined closure and membrane support 15 is

generally tubular, has a central bore 16, and a base flange 17 of the same outside diameter as the shell or casing 12. Screw threads 18 on the outer wall of the tubular closure member 15 engage threads 14 to permit the closure member 15 to be screwed into the shell or casing. Both the casing and the closure member 15 are preferably made entirely of cellulose acetate. A resilient washer 19 of a suitable synthetic rubber or plastic is shown interposed between the annular shoulder provided by the base flange 17 and the lower end of the cylindrical shell or casing, thereby to seal the screw joint. The casing does not require threading and the use of a washer; if made in two tightly fitting sections, these sections may be cemented together by means of a suitable solvent or adhesive. At its upper end the tubular closure member 15 is beveled as at 20, and the preferred angle of said bevel is from 30° to 45° relative to the longitudinal axis of the cell body; but the invention is not limited to any particular angle. A thin resinous membrane 21, preferably of cellulose acetate, is fixed by an adhesive layer 22 to said beveled upper end 20. Preferably membrane 21 is only about 0.001 in. thick, has an area exposed to the solutions of about 3 sq. cm., and is readily removable for replacement with another membrane; however, adhesive 22 forms a seal so long as the membrane is untouched. The described construction constitutes a hollow receptacle closed at the bottom and open at the top, with a thin membrane secured on the interior in a position such that it will receive the globules or drops of mercury from the dropping mercury electrode.

Now referring to Fig. 5, which shows the manner of using the described cell, a dropping mercury electrode 23 is supported in any suitable manner, as by a clamp, not shown, directly above the cell 24. This dropping mercury electrode consists of an open reservoir 25 containing a supply of mercury 26 and a capillary tube 27 open to and extending downwardly from reservoir 25 and adapted to discharge a series of drops of mercury, one of which is shown at 28, directly upon the upper inclined surface of membrane 29. Capillary 27 may be constructed in accordance with the priniciples discussed by Muller in J. Am. Chem. Soc., 66:1019 (1944). The cell may be supported within a beaker or other open or closed container 30 holding a standard calomel half cell. A pool of mercury 31 is in the bottom of container 30, and a calomel layer 32 floats on the mercury in contact with a calomel solution 33. A lead 34 is immersed in said mercury pool to make a good electrical connection and is coupled with a rheostat 35 shunted across a battery 36, while another lead 37 is coupled to the negative side of the battery and is electrically connected to the mercury 26 in reservoir 25. Battery 36 represents any source of uniform current; conveniently a storage battery, 4 v. or 6 v., is used. A galvanometer 38 is in series with lead 37. The sensitivity of the galvanometer may be regulated by means of the well known Ayrton shunt, not shown, which should have a total resistance equal to the critical damping resistance of the galvanometer. A millivoltmeter (not shown) may also be coupled in the circuit.

The solution to be tested is shown at 39 and preferably stands at the same level as the saturated calomel solution 33, so that the pressures on opposite sides of membrane 29 are substantially equal. Mercury drops from capillary 27 at regular intervals fall on the slanting upper surface of membrane 29 and slide off down into the annular recess 24*a* provided on the inside of the cell.

Referring to Fig. 4, which shows a modified and somewhat less desirable form of cell, the lower end only of dropping mercury electrode 40 is shown within a polarographic cell consisting of an outer shell or casing 42 having the form of a cylinder, with screw threads 43 cut on its lower end. A cup-like support 44 surrounds the lower end of the shell or casing 42 and has threads 45 engaging threads 43. A closure member 46 fits within support 44 and has an annular shoulder 47 for clamping a resilient washer 48 thereby to seal the screw joint. The closure member 46 has a central bore 49 for receiving a thin membrane 50 (of the same characteristics, though not of the same dimensions, as membrane 21). A Soxhlet thimble 51 may hold the membrane 50 in bore 49 so that its upper end projects like a rounded dome above the conical upper surface 53 of closure member 46 and directly beneath the dropping mercury electrode 40. Membrane 50 is cemented, or tightly adhered by means of a solvent, to the surface of bore 49 or to the lip of conical upper surface 53 to obtain a tight seal. Mercury from the drops 54 forming on the lower end of electrode 40 will collect in the recess 55 after striking the rounded surface of the membrane. The test liquid is poured in the shell or casing 42, exactly as shown in Fig. 5, and the calomel half cell is placed in a container (not shown) which, like container 30 of Fig. 5 surrounds the lower part of the cell. The solution of the calomel half cell makes contact with the under surface of membrane 50 through a central port 56 in the bottom wall of support 44. In lieu of the thimble 51, any porous inert material such as fritted glass may support the membrane 50 while permitting the solution to reach the under surface of the membrane.

In lieu of cellulose acetate membranes or films, I may employ cellulose nitrate (pyroxylin) or partially or substantially denitrated cellulose nitrate films. Compared with a 2% agar plug, the permeability of these films is very low, as Table I shows:

Table I

Film	Thickness (in.)	Resistance (ohms)	Permeability (mg. KCl/0.5 hr.)	Calculated Permeability (mg. KCl/sq. cm./hr.)
2% agar plug	0.24	2,850	15.00	9.5.
Pyroxylin	very thin	1,800	0.15	
Substantially denitrated cellulose nitrate.	do	4,500	0.10	
Cellulose acetate, film No. 32, after 6 weeks.	0.0010	50–70	0.25–0.40	0.17–0.27.
Cellulose acetate, film No. 34	0.0012	1,500	less than 0.05	less than 0.03.

The electrical resistance of the two cellulose acetate films (Nos. 32 and 34) was initially high but dropped off sharply and reached a very low stabilized value at the end of thirty days. The reason for this sharp drop in electrical resistance is that the membrane as freshly prepared contains no water or ions from the solutions, but upon being immersed in the solutions, it swells and absorbs water and electrolytes, gradually comes into equilibrium with the solutions and develops a substantially stable resistance value. The membrane samples 32A and 32B of Fig. 7 were used to separate saturated KCl from saturated KNO_3, and membrane samples 34A and 34B of Fig. 8 were used to separate the same solutions.

Two separate runs of cellulose acetate film No. 32 were carried out. Permeability values at various intervals for these two runs are shown in the following table, wherein the separate runs are distinguished by the symbols 32A and 32B.

Table II

Duration (weeks)	32A		32B	
	Permeability, mg. KCl/ 0.5 hr.	Calculated Permeability, mg. KCl/ sq. cm./hr.	Permeability, mg. KCl/ 0.5 hr.	Calculated Permeability, mg. KCl/. sq. cm./hr.
1	0.25	0.17	0.28	0.19
2	0.28	0.19	0.28	0.19
3	0.33	0.22	0.28	0.19
4	0.40	0.27	0.28	0.19
5	0.38	0.25	0.25	0.17
6	0.33	0.22	0.25	0.17

The changes in electrical resistance of this film will be fully understood from the curves of Fig. 7. Two separate runs were also carried out with cellulose acetate film No. 34. These are designated 34A and 34B in Fig. 8, which reveals the changes in electrical resistance of these films.

Referring to Fig. 6, a residual current curve is shown which is typical of the curves obtained by use of the described cell during ordinary routine analysis. No precautions were taken except to wash the cell out three times with distilled water and supporting electrolyte, respectively, which is standard procedure. The supporting electrolyte consisted of 33.38 g. of hydrated aluminum nitrate, $Al(NO_3)_3.9\ H_2O$, C. P.; 0.10 g. of gelatin, U. S. P.; and nitric acid, C. P.; to produce a pH value of 1, in aqueous solution made up to one liter. The aluminum present corresponded to 0.09 molar concentration. The curve was made when using a capillary having a respective capillary constant of 1.431 at +200 millivolts and 1.457 at —150 millivolts of applied voltage. Temperature of the electrolyte was 24.5°±0.1° C. Note the very low residual current even in the positive range of applied voltage, where chloride ions usually interfere to such an extent that special precautions must be taken when agar plugs are used, and even then the results of the analysis are reliable only to a certain degree.

Referring to Fig. 9, which shows a polarographic cell embodying the invention and containing a calomel half cell of known construction, a cylindrical casing **60**, which may be of glass or a transparent plastic, supports a rubber stopper **61** in its upper end and another rubber stopper **62** in its lower end. An inner cylindrical shell **63** is coaxial with casing **60** and is secured by friction or by an adhesive (not shown) to the stoppers **61**, **62**, both of which have bores of sufficient size to receive the shell ends. Thus the shell **63** forms with the stoppers **61**, **62** and the casing **60** an annular chamber or space **64** suitable for a water jacket to maintain a substantially constant temperature within the polarographic cell, water flowing in through supply tube **65** near the lower end of casing **60** and flowing out through tube **66** near the upper end of said casing. An annular stopper **67** is fixed within the upper end of shell **63** and has a central bore **68** in which the upper end of a plastic cell vessel **69** is held by friction. Cell vessel **69** is cylindrical and open at the top but is closed at its lower end by a plug **70** having a central bore **71** and provided with a beveled upper end **72**. A resinous membrane **73**, like membranes **21** and **29**, is secured and sealed by an adhesive (not shown) upon the beveled upper end **72**. Cell vessel **69**, plug **70** and membrane **73** may all be of cellulose acetate or other suitable material which is inert to the test solution and the metallic mercury dropping from the capillary **74** upon the membrane. Capillary **74** is inserted into the cell vessel **69** prior to the start of the test and is removed after the readings are taken; it is like the capillary **27** of Fig. 5. A port **75** is provided in stopper **67** and has a plug **76** closing it but being manually removable; this construction permitting the potassium chloride solution **77** to completely fill the space between the water jacket and the cell vessel **69** and to flow out through

port **75** when stopper **67** is inserted, after which plug **76** seals the opening.

Supported within shell **63** is a known type of calomel half cell characterized by its portability and capability of withstanding handling without loss of its contents. This calomel half cell includes a tube **80** open at the top and secured at its lower end to and sealed by a plastic plug **81**. A lead or wire **82** is passed through plug **81** and into the interior of tube **80** to make electrical contact with a pool of mercury **83** at the bottom of the tube. An outer tube or housing **86** surrounds tube **80** and receives plug **81** at its lower end, providing an annular chamber **87** therebetween for receiving potassium chloride solution. The tube or housing **86** is frictionally held within the bore **84** of a stopper **85** which in turn is frictionally held within the lower end of shell **63** to close the latter. A rubber cap **88** closes the upper end of the outer tube or housing **86** and a nipple **89** affords communication between chamber **87** and the interior of shell **63**. Stopper **85** has an air port **90** closed by a plug **91** which permits complete filling of the space **92** between the water jacket and the housing **86** by potassium chloride solution. Tube **80** is substantially filled with a pasty mass **93** of mercury mixed with calomel placed above the mercury pool **83**, and a porous wad **94** of cotton or glass wool closes but does not seal the tube at the top. Such a calomel half cell may be inverted or roughly handled without losing its usefulness.

Casing **60** is held upright by a three-fingered clamp **95** fixed by a thumbscrew **96** to a stand **97** and capable of being turned 90° or more about a horizontal axis thereby facilitating pouring out the test solution and the rinsing solution, as will be understood by comparing Figs. 10 and 11. While the necessary tubing connections are not shown, a stream of purified nitrogen gas may be introduced into the test solution prior to the test, cooperating with an exhaust for the air so that oxygen is removed from above the test solution; this is in accordance with a known technique employed to obviate dissolved oxygen, which is reducible at the dropping mercury electrode.

While my invention has been described in terms of the preferred arrangement in which the thin resin membrane which separates the test solution from the calomel half cell is located directly under the dropping mercury electrode, this arrangement is not necessary for the proper functioning of the resin membranes. The resin membrane may be oriented in any convenient manner required for a given dropping mercury electrode and polarographic cell arrangement. It is not necessary for the mercury to contact the resin membrane at all. If more convenient, the membrane support **15** might connect with the polarographic cell at a 90° angle or other angle instead of being inserted in the lower end of the polarographic cell. The resin membrane may be off to one side of the polarographic cell and may lie in a plane parallel to the axis of the dropping mercury electrode or may assume any other convenient angle and position in the polarographic cell.

Furthermore, it is to be understood that while the cylindrical shell or casing **12** and the closure member **15** are preferably made of cellulose acetate, they may be made of any other suitable plastic which will not of itself introduce discrepancies into the measurement. Also it will be understood that the shell of the polarographic cell does not have to be cylindrical. The preferred form is cylindrical for convenience and low cost.

I claim:

1. A polarographic cell comprising an upright casing open at the top and adapted to hold the test solution, a membrane support within said casing, a bottom wall attached to said casing and providing a mercury-collecting well or trough within the casing, and a very thin non-selective resinous and slightly permeable membrane fixed to said membrane support and being generally dis-

posed centrally of the casing, said membrane being inclined so that it will shed drops of mercury striking it, the membrane support being constructed and arranged to permit a saturated calomel electrode solution to contact said membrane on the under surface.

2. The invention defined in claim 1, wherein the membrane support is hollow and has its upper end disposed at an acute angle to the longitudinal axis of the casing, and the membrane is flat and is removably secured along its edges by an adhesive to said upper end, the central portion of the membrane being free of contact with the support and adapted to be contacted by said solution.

3. The invention defined in claim 1, wherein the membrane support is partly a Soxhlet thimble over one end of which the membrane is laid so as to form a dome-like structure which the drops of mercury may strike.

4. A polarographic cell assembly adapted to be utilized for rapid analysis of a series of test solutions by polarographic methods, comprising, in combination, a portable reference electrode including a mercury pool and means enclosing said pool constructed and arranged to obviate spilling or movement of the mercury when the electrode is tilted or inverted; a test solution container which has a thin non-selective resinous membrane adapted to contact the test solution and at least in part closing the container, said test solution container having an open top adapted to receive a dropping mercury electrode; said thin resinous membrane having been stabilized to have a very low electrical resistance; a second container at least partially surrounding the test solution container and substantially inclosing the portable reference electrode; an electrolytic solution filling the second-mentioned container and contacting said membrane on the surface thereof which is opposite to the surface contacted by the test solution, and adapted to permit free electronic migration between the dropping mercury electrode and the portable reference electrode; a receptacle surrounding the containers and providing a liquid-containing jacket surrounding said containers and adapted to maintain the reference electrode, the test solution container and said electrolytic solution substantially completely stable thermally; plural means to hold the jacket, the second-mentioned container, the test solution container and the portable electrode container immovable with respect to each other so that all the mentioned parts form a unitary assembly capable of being supported in any position; and means supporting said unitary assembly pivotally so that a test solution may be poured into the open top of the test solution container, and after a set of readings has been taken by polarographic methods and the dropping mercury electrode has been withdrawn from the test solution container, the test solution and the mercury contained in it may be poured out of the inverted test solution container without disturbing the support or impairing the operativeness of said unitary assembly upon being restorted to an upright position and refilled with test solution.

5. A unitary cell assembly for polarographic analysis comprising, in combination, a normally closed container holding an electrolytic solution so as to obviate spillage of said solution when said container is inverted; a substantially rigid reference electrode immersed in said electrolytic solution, said reference electrode including a mercury pool and means enclosing said pool constructed and arranged to obviate spilling or movement of the mercury when the electrode is tilted or inverted; a test compartment having an open top and being rigidly held by said container and also being in contact with said electrolytic solution; a non-selective permeable wall rigidly secured within said test compartment; said electrolytic solution communicating with the test compartment solely through the non-selective permeable wall; said test compartment having means adjacent to said permeable wall for collecting mercury drops falling into the test compartment from a dropping mercury electrode; and pivotal means for supporting said assembly so that it may be inverted to pour out the test solution in the test compartment.

6. The invention defined in claim 5, wherein a jacket for thermostating said assembly surrounds the container and is rigidly secured to the container to form an integrated assembly therewith which may be inverted without affecting the operability of the cell assembly.

7. The invention defined in claim 5, wherein the permeable wall is of regenerated cellulose having a thickness of the order of 0.001 inch.

8. The invention defined in claim 5, wherein the permeable wall is of cellulose acetate having a thickness of the order of 0.001 inch.

9. The invention defined in claim 5, wherein the non-selective permeable wall is inclined so that it will shed drops of mercury striking it, a mercury-collecting trough being formed in the test compartment below said permeable wall.

10. The invention defined in claim 9, wherein the permeable wall is of regenerated cellulose having a thickness of the order of 0.001 inch.

11. The invention defined in claim 9, wherein the permeable wall is of cellulose acetate having a thickness of the order of 0.001 inch.

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