THE MERCURY CATHODE AND ITS APPLICATIONS[1]

J. A. MAXWELL AND R. P. GRAHAM

Departments of Geology and Chemistry, McMaster University, Hamilton, Ontario, Canada

Received February 24, 1949

CONTENTS

I. HISTORICAL

"Professor Gibbs explained a new general method in analysis discovered by himself and brought to a certain degree of perfection by experiments. . . . The new method was simply to place the metal in solution in a beaker, add pure mercury, and connect the mercury with an electric battery. By the electric action the metal was thrown down on the mercury. It was necessary only to weigh the mercury and beaker beforehand, and then after the process to determine the metal by again weighing the vessel and the mercury. This method, he said, was applicable to mercury, tin, cobalt and other metals. . . . He did not despair of separating potassium and sodium by the process, although his experiments with these metals had not been completely successful.

"Professor Hunt said this process came with the beauty and force of a revelation; its simplicity recommended it. Every chemist would await further developments with great interest." (55)

---

[1] Financial support was received from the Research Council of Ontario. The authors also wish to acknowledge their indebtedness to Dr. H. S. Armstrong of the Department of Geology, McMaster University.

Thus it was that before the National Academy of Sciences in New York City on November 16, 1880, Professor Wolcott Gibbs made known the results of his investigations with the mercury cathode. Today, nearly seventy years later, with further development of his idea still in progress, the mercury cathode cell has become an extremely useful tool in analytical chemistry.

In 1883 Gibbs advanced further suggestions for the use of the mercury cathode.[2] He visualized not only the determination of the metal by measuring the increase in weight of the mercury but also, in certain separations, the determination of the anion by titrimetric or gravimetric methods.

About the same time that Gibbs introduced the mercury cathode, Luckow formed an amalgam by the electrolysis of a metal salt in the presence of metallic mercury (98) and, in 1885, gave directions for the determination of metals by plating them out as adherent amalgams on the inner surface of a platinum dish (99). A modification of this method was proposed in which the metallic mercury was replaced by mercuric chloride (166, 167).

Drown and McKenna (37), in 1891, pioneered an application that has now become an accepted procedure when they used the mercury cathode to separate iron from aluminum prior to the determination of the aluminum.

A notable change was suggested in 1898 by Paweck, who devised a rigid mercury cathode to replace the customary mobile one. His cathode, of brass wire mesh coated with mercury (122), was subsequently used for the determination of various metals (123). This work has been carefully evaluated by Böttger and his associates (17, 19).

In 1903 there appeared a paper by Edgar F. Smith entitled "On the Uses of a Mercury Cathode in Electrochemical Analysis" (153); it described his work on both the determination of various anions and the separation and determination of metallic cations. This was the first of many papers published on this subject by Smith and his students, who greatly enlarged the field of application of the mercury cathode and at the same time modified and improved the apparatus. They devised a more convenient single mercury cell and an ingenious double cell in which it was possible to determine anions, using a silver-coated anode (65). McCutcheon went even further in his investigation of anion determination and used a platinum gauze anode coated with lead, cadmium, bismuth, zinc, or copper (109).

A further contribution made by Smith and his students was the investigation and adoption of the rotating anode in place of the stationary type (79, 80), although doubts concerning its advantages were raised by others who favored simplicity and economy in the apparatus (13, 27, 158). Common ground for the two opposing views was provided by Frary, who devised magnetic methods for

---

[2] There is some confusion in the literature regarding Gibbs' later papers on this subject. The statements made in 1883 were contained in a paper read before the National Academy of Sciences also, but the only account of it is given by Gibbs himself in a later note (56), written for the purpose of correcting an error made in the reporting of one of his previous papers.

the agitation of the electrolyte when using a stationary anode; this removed the need for elaborate mechanical stirrers (48, 49).

In Germany the work of Böttger (15, 16, 17, 18, 19) and Baumann (4, 5) did much to promote the use of the mercury cathode, for these workers designed new types of cells and also introduced new methods of "breaking" the electrolysis and washing the amalgam. Work on the mercury cathode has been carried out also in Italy (106, 107), in France (43, 44, 45) and, in recent years, in the U.S.S.R. (54, 87, 88, 113, 151, 156, 160, 161, 165).

Development of the mercury cathode for the determination of elements continued apace in the United States. But in 1911 a new form of cell, devised by Cain for the purpose of separation only, made its appearance (22) and since then the use of the mercury cathode for determining an element (which was the original intent of Gibbs) has declined in favor of its use for separating certain elements from others. This application was developed using either the Cain cell or the simple arrangement of Drown and McKenna. In 1930 Melaven suggested a cell that eliminated almost all of the objectionable features of earlier cells, and that made possible easy and rapid separations. This cell in its original form is probably the best known of all cells, although modifications have generally increased its efficiency (135, 138, 143, 148, 169).

Other forms of cells were developed, for the purpose of both estimation and separation, of which the Bakelite cell for use with hydrofluoric acid (72), the cell employing a moving mercury cathode (41), and the glass–porcelain apparatus for the deposition of uranium (63) are the most noteworthy.

Of particular interest in cell design was the trend towards compactness, in order to facilitate the washing and, in some cases, the weighing of the cathode. Spoon-shaped cathodes, which were suspended in the electrolyte, were developed for determination (114, 163) and the English workers Chirnside, Dauncey, and Proffitt, in an effort to obtain a simple inexpensive cell, devised the first unitized apparatus for the separation of metals (27, 28). An extremely compact and convenient cell has been constructed in the Shell Development Laboratory (73, 119, 131, 171).

A very important development in recent years has been the adaptation of the mercury cathode to polarographic analysis by carrying out separations at controlled potential, as suggested by Lingane (89, 90, 91, 124). Not only can separations be made among groups of elements, but by careful control of the potential of the cathode, separations within the groups can be effected. By the introduction of a coulometer, it is possible to carry out determinations of various metals, an application that seems to complete the circle that began with Gibbs (161).

Furman and his associates have used the mercury cathode prior to the polarographic determination of minor amounts of impurities in uranium and its salts (50, 51, 52) by distilling away the mercury cathode (2.5 ml. in volume) in which the impurities had been deposited. The residue was then available for further treatment. It is thought that the method will be found useful in the analysis of many other metals, alloys, and compounds.

The mercury cathode has found application in the field of organic chemistry also. It has been used, for example, in the preparation of isopropyl alcohol from acetone (64) and for the reduction of ketones (147) and quinaldine (87, 88); in recent years controlled-potential electrolysis has been used to effect the reduction of one organic compound to another, after preliminary work to establish the optimum conditions had been carried out using the polarograph (97).

Thus, as if to compensate for the fact that all of Gibbs' expectations for the mercury cathode have not been realized, applications have been developed that he did not foresee.

Until recent years, work done with the mercury cathode has been concerned chiefly with the development of operational procedures and an extension of its application. There is comparatively little material available that deals with its theoretical aspects, apart from contributions on the subject of amalgam formation, decomposition and hydrogen overvoltage (31, 68, 71, 76, 77), and some papers on the intermetallic compounds formed in mercury (140, 141, 142.). Numerous textbooks include mention of the procedure as a means of separation, notably Lundell and Hoffman's *Outlines of Methods of Chemical Analysis* (103), and the more recent *Instrumental Methods of Analysis* of Willard, Merritt, and Dean (171). The section on the mercury cathode in Böttger's *Physikalische Methoden der analytischen Chemie* (17) is the most extensive general review that we have found and, with an earlier paper (19), is the major source of information on the rigid mercury cathode.

It is of interest to note the growth in the literature pertaining to the mercury cathode since Gibbs proposed the technique in 1880. From then until 1907 the number of papers averaged about one per year, but in the succeeding period of five years activity in this field reached its height and from a total of about 30 papers in 1907 the literature swelled to about 75 papers in 1912. A lean period followed with only an occasional paper appearing until in 1924 a revival of interest occurred. The last decade has seen rapid strides made in the range of application of this technique, one which was regarded by Drown and McKenna, as far back as 1891, as "one of the most valuable and suggestive contributions to the qualitative separation and determination of metals by electrolysis that has yet been made" (37).

II. APPARATUS

A. GENERAL

It has been mentioned that Gibbs visualized the mercury cathode for determining an element by weighing the mercury (or the entire cell) before and after the deposition of the metal. This idea was perpetuated by numerous succeeding workers, but gradually the study of the mercury cathode as a means of determination of an element was replaced by the study of its use in effecting separations. Descriptions of cells for both purposes, including a number of rather specialized ones, are given in the following sections; an effort has been made to include all types mentioned in the literature.

B. CELLS FOR DETERMINATIONS

1. Conventional types

The cell used by Gibbs was indeed very simple (55). The cathode consisted of a layer of pure mercury in a beaker with electrical contact to it made by a glass-enclosed platinum wire; the beaker and mercury were weighed before and after the electrolysis.

This simple apparatus subsequently underwent changes in shape and in manner of operation. The separate electrical contact to the mercury was replaced by a small platinum wire sealed into the bottom of the cell (4, 78, 116, 125) and some workers provided the vessels with little platinum feet (1, 15, 49), the whole being placed on a charged copper plate during operation. In the Smith–Howard cell (figure 1), a single mercury cup used extensively by Smith and his students and by others (12, 104, 112), the platinum wire contact was bent underneath the bottom of the beaker, a charged copper plate again being used.

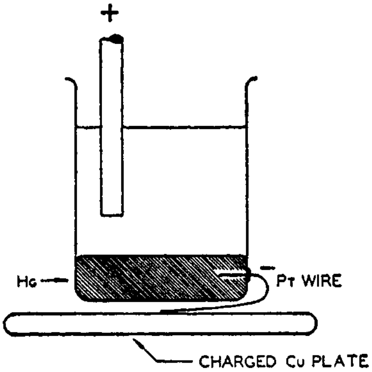

Fig. 1. The Smith–Howard cell

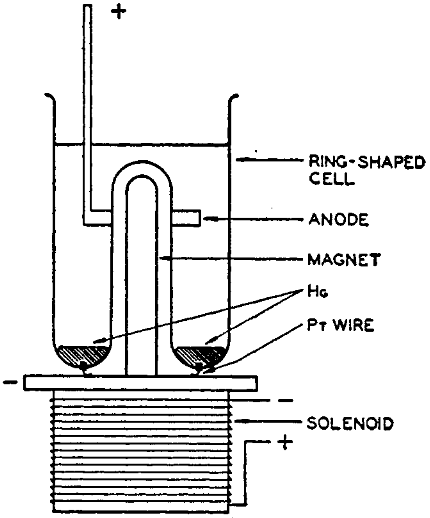

Fig. 2. The Frary cell

The size of the cell underwent a reduction as investigators sought to reduce the weight. One device used was the arching of the bottom to minimize the amount of mercury required (1, 15, 49, 116). Some investigators found it more convenient to remove the mercury to a porcelain crucible and weigh it apart from the cell, but this method was found to have disadvantages (46, 134).

The removal of the electrolyte was usually accomplished by siphoning, although Baumann introduced a method for its removal by fitting a small glass tap into an outlet in the side of the cell just above the level of the mercury (4). In order to conserve weight the tap was removed and replaced by a glass stopper before the cell was weighed.

In all these cells the anodes were introduced separately and were generally spiral-shaped. They were usually rotated, although this was considered unnecessary by some (12, 158). Frary devised an electromagnetic method (figure 2) for stirring which did away with the need for a motor or moving parts and considerably simplified the apparatus (48, 49).

2. Unitized types

The spoon-shaped mercury cathode of Moldenhauer is an interesting departure from the conventional type, and in manner of handling and in appearance has the compactness of a single unit. A glass cup is sealed to the side of a glass rod and mercury is placed in the cup, electrical contact with the mercury being made by means of a wire enclosed in the rod (114). The anode, which is rotated, consists of a small rectangular piece of platinum foil sealed into the end of a glass rod which in turn encloses a platinum wire. The weighed cathode is placed in a beaker containing the electrolyte.

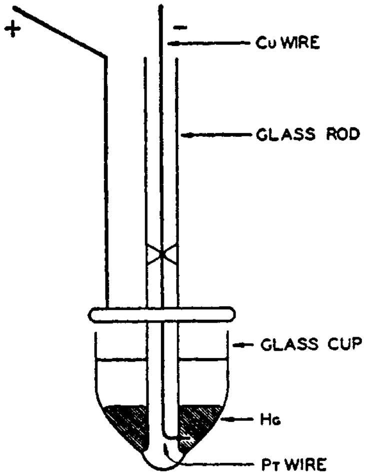

FIG. 3. The Tutundzic cell

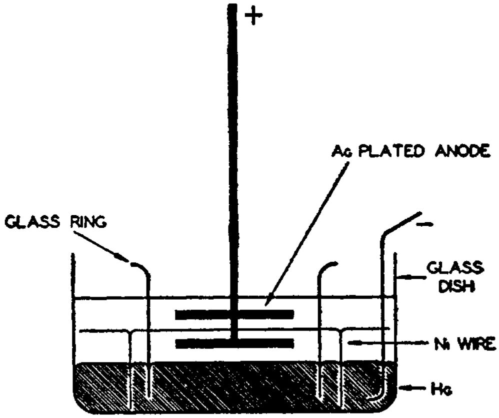

FIG. 4. The Hildebrand cell

A cathode of very similar nature was devised by Tutundzic (163), who used a flat disc of platinum gauze as the anode and placed it about the central axis of the cell (figure 3). The small cup is sealed to the end of the supporting glass rod, through which contact is made to the mercury, and the whole is rotated. The operational procedure is the same as that for the Moldenhauer cell.

3. Specialized types

One of the most interesting cells of a specialized nature is that devised by Hildebrand for the determination of anions (65, 127, 144, 155). It consists of a double mercury cup in which the amalgam is formed in the one compartment and decomposed in the other (figure 4). An inner glass ring is supported above the floor of the outer and larger compartment and mercury is added until the two compartments are sealed one from another. The solution to be electrolyzed is placed in the inner compartment and a dilute solution of sodium chloride, as a conductor, is placed in the outer one. The rotating anode is made of platinum gauze, coated with silver. Geith used a carbon anode in his modification of the Hildebrand cell (53), but later work (36, 57) showed it to be unsatisfactory.

A double cell which, in addition to separating the anode and cathode liquids, also permitted the use of high current densities was constructed by Groves and Russell (63). It consists of an unglazed porcelain cylinder, closed at one end and containing the electrolyte, inserted in a cylindrical glass container. Mercury and a suitable cathodic liquid are placed in the outer compartment and both units are cooled during operation of the cell. A rectangle of platinum foil, suspended inside the porcelain cylinder, serves as the anode.

A Bakelite cell for use with hydrofluoric acid solutions (such as those employed for the electrolytic deposition of tungsten) was devised by Jackson, Russell, and Merrill, who made use of both a hollow block of Bakelite and a Soxhlet extractor soaked in Bakelite varnish and fired (72). They also found it advisable to coat the platinum anode with lead dioxide.

For the determination of arsenic by its reduction to arsine, cells have been devised that permit the liberation of the arsine in a closed mercury cathode immersed in the electrolyte, and the subsequent removal of the gas to a Marsh–Berzelius or similar apparatus (3, 23).

Baxter and his associates, in their work on the atomic weights of cadmium and zinc, prepared small closed cells that contained both anode and cathode; thus possible loss of platinum by dissolution or of mercury by spurting (6, 7, 8, 9, 10) was eliminated. Laird and Hulett, who also used the mercury cathode for the investigation of the atomic weight of cadmium, used separate cups for anode and cathode and connected them by means of a siphon arrangement (86).

C. CELLS FOR SEPARATIONS

1. Simple beaker type

This form, which is similar to the Gibbs type of cell, was used by Drown and McKenna in the first application of the mercury cathode to the separation of interfering elements (37). When the mercury cathode became predominantly a means of separation rather than of estimation, the need for minimizing the weight of the cell disappeared. Beakers of 150–1000 ml. capacity, containing as much as 200 g. of mercury, were used (2, 20, 35, 38, 105, 108, 128, 162) and batteries of them have been installed in some laboratories (74, 121). The electrolyte is agitated either by rotation of the anode or by use of separate stirrers.

2. Separatory funnel type

The mercury cathode cells of this kind may be divided into two types.

(a) The Cain type

The Cain cell (22), which utilizes a slightly modified separatory funnel, permitted easier removal of the electrolyte and washings than had hitherto been the case (figure 5). Mercury is placed in the cell to within 1–2 mm. of the top of a small, inwardly projecting tube sealed to the stopcock entrance and itself filled with mercury. Electrical contact is made by a platinum wire sealed into the bottom of the funnel. This form has been adopted by others (51, 66, 70, 104, 113, 143). Blair modified it slightly by the addition of a hard rubber cone which rests on the flared end of the short inner tube; one end of the anode is screwed into the cone so that the anode may be kept in place while it rotates (14). In another modification, the drain tubulature projects from the lower side of the beaker-type cell (146).

In order to shorten the time of electrolysis when the presence of only small amounts of the elements sought necessitates the use of large samples, Steinmetz uses a 4000-ml. beaker as the basis of his separatory funnel and fastens the contact to the mercury, and the anode as well, inside the cell (157).

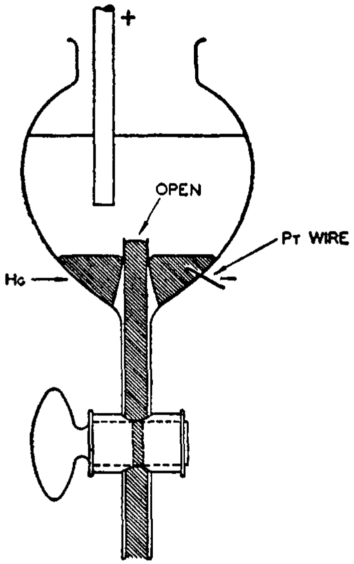

Fig. 5. The Cain cell

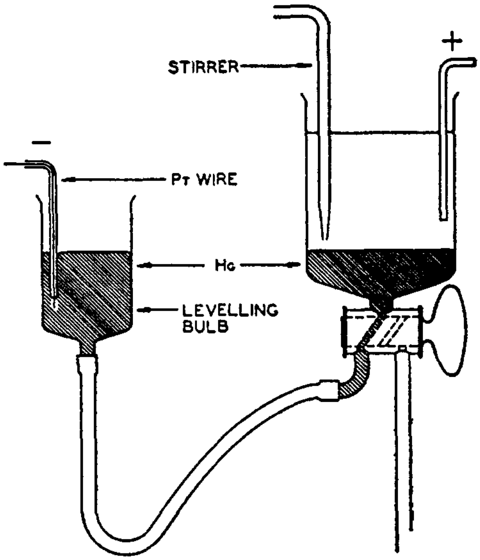

Fig. 6. The Melaven cell

(b) The Melaven type

The cell designed by Melaven (figure 6) is in common use today (2, 24, 42, 67, 111, 137, 145, 152, 170, 171) and its development was a notable step forward in the evolution of the mercury cathode. It has all the advantages of easy washing and removal of the electrolyte that are found in the Cain cell, and it generally eliminates the need of filtration to remove mercury carried over (with the attendant danger of decomposition of the less stable amalgams), which must be done when the Cain cell is used. The apparatus, which is a modified separatory funnel, has a conical base fitted with a three-way stopcock. One arm of the stopcock is connected to a levelling bulb that controls the level of the mercury in the cell and also carries the electrical contact to the mercury. Agitation is accomplished by a mechanical stirrer or by a stream of air. At the end of the electrolysis a clean separation of the mercury from the electrolyte is obtained by lowering the levelling bulb and draining out the mercury, keeping the circuit closed at all times.

A slight modification of the Melaven cell was made by Scherrer and Mogerman (148), who reduced the loss due to spraying by increasing the height of the cell to about 20 cm. Rocquet improved this modification by enclosing the tall electrolysis cell in a water-jacket (figure 7) and by introducing an extra branch in the tube connecting the levelling bulb and electrolysis vessel; this allowed the removal of spent mercury without the need for disconnecting the rubber tubing (138). He also made electrical contact with the mercury in this junction, rather than through the levelling bulb. A somewhat similar water-jacketed cell has been devised recently for use with high current densities (169).

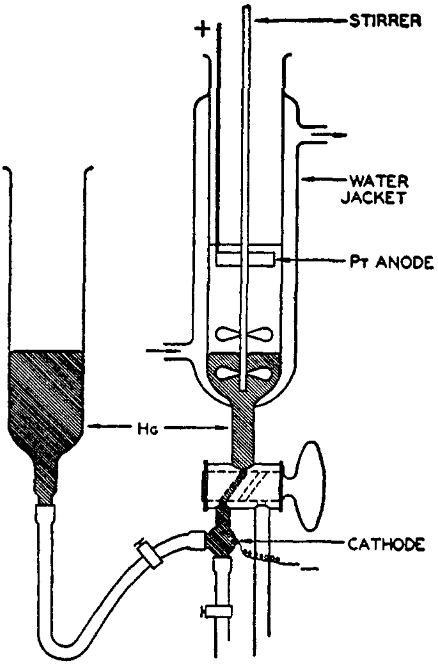

FIG. 7. Rocquet's modification of the Melaven cell

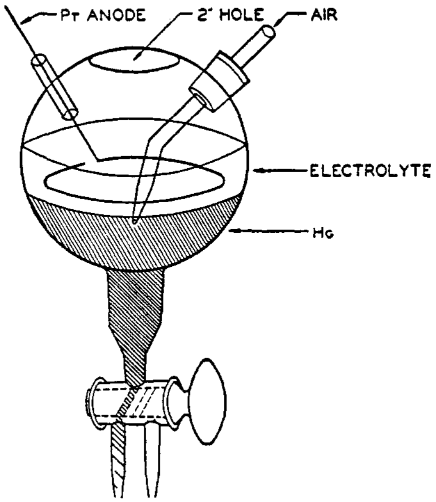

FIG. 8. Rabbitts' modification of the Melaven cell

In order to reduce the time of electrolysis, Rabbitts devised a cell which is a modification of the Melaven type and which minimizes certain disadvantages found in the latter cell (112a, 135). An inverted 700-ml. Florence flask has a 2-in. hole cut into the bottom and a three-way stopcock sealed into the neck (figure 8). Agitation is accomplished by means of a stream of air admitted through a tube sealed in the side of the cell. A modified thistle tube, fitted into the hole at the top, condenses the fine mist and spray formed during electrolysis. An Erlenmeyer flask serves as the levelling bulb, and about 4 kg. of mercury is used. The anode is a circle of platinum wire, 10 cm. in diameter, sealed into the side of the cell and lying about 0.5 cm. above the mercury surface. Ford (47) preferred to draw out the bottom of the flask to accommodate a stopcock, and admits the anode through a hole in the stopper carrying the thistle tube.

3. Unitized types

In an effort to dispense with costly apparatus, on which blame is laid for the comparatively little use made of the mercury cathode in analysis (27, 28), Chirnside, Dauncey, and Proffitt designed a unitized apparatus of a simple and inexpensive nature (figure 9). The anode is a cylinder of platinum foil supported by a platinum wire sealed into the bottom of a glass tube. The anode surrounds a similar glass tube, into the end of which is sealed a small loop of platinum wire, both glass tubes being fastened to the opposite sides of a grooved cork. Connections are made by means of wires dipping into mercury in the bottom of the tubes. The whole unit, which is about 20 cm. high, is allowed to rest against the lip of a 250-ml. beaker containing about 10 ml. of mercury, a cover glass being used to decrease loss due to spraying. The electrolyte is removed, on completion of the electrolysis, by a siphon (figure 9). The low cost of such a unit permits its use in a series of cells.

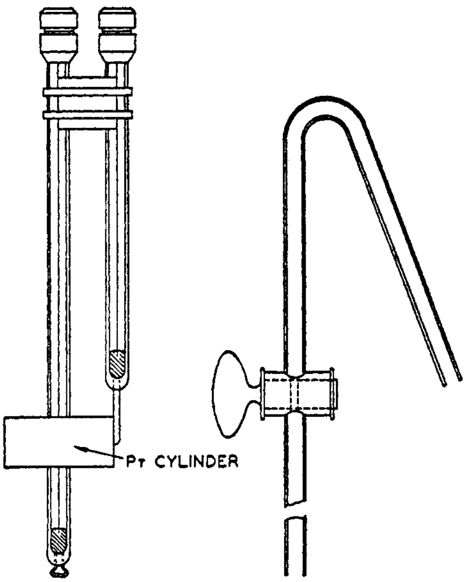

FIG. 9. Unitized cell, designed by R. C. Chirnside, L. A. Dauncey, and P. M. Proffitt

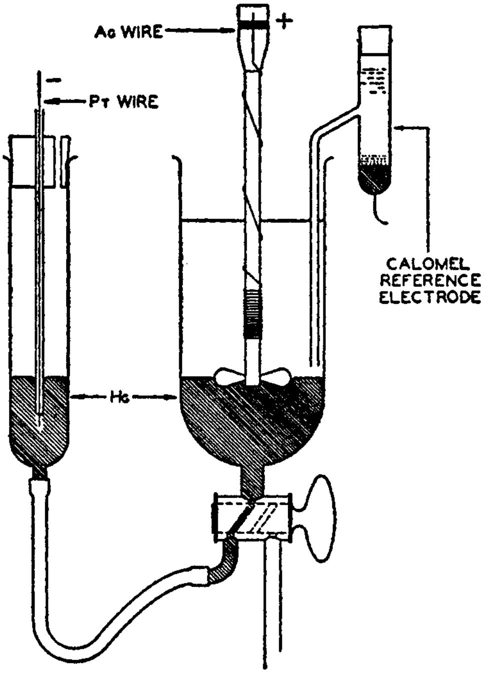

FIG. 10. Lingane's modification of the Melaven cell

This trend towards compactness has been further developed by Johnson, Weaver, and Lykken (73), who devised a compact, sturdy, self-contained immersion electrode, very similar to the Moldenhauer and Tutundzic cells described earlier. They sought efficiency and speed in removal of the mercury amalgam, elimination of the need for decantation and filtration, reduction of the overheating that accompanies high current densities, and ease and strength in handing. Their cell is washed quickly and easily and the mercury is changed readily. Both cathode and anode are contained in the single unit, the basis of which is a small cup supported at the center by a glass pole. This latter also carries the cathode lead, which is a copper wire connected at the bottom of the pole to a piece of tungsten wire that makes contact with the mercury. The anode is a disc of platinum gauze that fits over the center pole and is suspended by a platinum–iridium wire above the rim of the cup. The upper half of the unit is enclosed in a Bakelite cover which carries at the top the connections for the anode and cathode. A tall-form beaker of 250-ml. capacity is used in the electrolysis, and agitation of the mercury may be accomplished, if faster amalgamation is desired, by the use of a magnetic stirrer. Small fume-hoods over each unit have been added for use with hydrofluoric solutions (119). The cell is available commercially (131) and the preparation of a simple cell of this nature from laboratory materials has been described (171).

A commercial dual unit has recently been devised in which a magnetic circuit provides rapid countercurrent stirring of the mercury and the electrolyte, contained in beaker-type cells, at the deposition interface (37a).

4. Specialized types

In order to avoid solution of the deposited metal when the amalgam surface becomes saturated, Evans (41) constructed a cell employing a moving cathode. A thin thread of mercury is projected across the cell and falls to the bottom, after which it is drawn into a separatory funnel. After washing with a solution designed to regenerate it at least partially, it drops into a reservoir from which it again enters into the cell.

The addition of a saturated calomel reference electrode (figure 10) and the use of a silver-wire anode wrapped in a spiral about the propeller shaft used to keep the mercury–solution interface in rapid motion were the modifications of the Melaven cell made by Lingane for the separation of elements by means of a carefully controlled potential (89, 91). The further addition of a hydrogen–oxygen coulometer made possible the actual determination of an element (90). An H-type polarographic cell was used by Lingane, Swain, and Fields for the preparation of organic compounds (97). A discussion of these important applications of the mercury cathode is given later.

III. OPERATIONAL DETAILS

Many of the factors that influence the efficiency of the cell have not been studied with the care they deserve. One finds recorded in the literature—and usually without explanation—a bewildering array of acid concentrations, electrolyte and mercury volumes, electrolysis times and temperatures. Although some work has been done to lessen the confusion (119, 121, 152), much more is required. In the following sections these factors are discussed separately and an effort has been made to present the consensus of opinion.

A. NATURE AND CONCENTRATION OF THE ACID

The acid most commonly used is undoubtedly *sulfuric acid.* Although concentrations of this acid up to 5 *M* have been used (121), it is generally agreed that the concentration should be as low as possible without permitting precipitation to occur (28, 37, 73, 81, 152). The inefficiency of the cells reported by early investigators may have been due to their use of too high a concentration of acid (112), although the recording of acid concentrations in terms of "drops" makes this point somewhat obscure.

The use of *nitric acid* was avoided at first because it was believed that an error would arise due to the reduction of the nitrate ion and formation of an ammonium amalgam (101). Loss of weight due to the formation of a fine suspension of mercury has also been reported (19). This acid has, however, been used successfully in certain procedures (1, 12, 13, 80, 101, 155).

Hydrochloric acid has been little used, probably because of the corrosive action of the liberated chlorine upon the anode (8). Some procedures employing the acid have been developed (63, 73, 112, 155), but it is not usually recommended.

Perchloric acid has proven satisfactory, at least in the separation of iron (121, 169), and it is definitely advantageous in procedures involving the subsequent determination of sulfur (105). Apart from this, perchloric acid is not considered to have any advantage over sulfuric acid (73), but further study of its use would be welcomed.

There is some disagreement regarding the utility of *phosphoric acid* (73, 121). It appears, however, to be useful in certain methods for the removal of manganese (96, 170) and of iron (37). *Hydrofluoric acid* is favored for the deposition of tungsten in spite of the necessity of using special cells (44, 72).

The use of *organic acids*, such as citric, tartaric, oxalic, and acetic, has been found to require excessively long electrolysis times and sometimes to yield irregular results (12), although it is reported that acetic acid is superior to sulfuric acid in the separation of iron in manganese and aluminum bronzes (67) and of cadmium (19). Acetic acid has also been used in the separation of iron in steel (169).

B. AMOUNT OF MERCURY

The amount of mercury is governed by the use to which the cell is to be put, whether as a means of estimation or of separation. When weighing of the cell was contemplated, early workers sought to reduce the weight as much as possible and normally used 40–80 g. of mercury (1, 4, 78, 83, 116). When the use of the cell as a means of separation became predominant, the need for conservation of weight disappeared and the amount of mercury used soared rapidly. Simpson concluded that the amount of mercury used had little effect on the efficiency of zinc removal (152). Others have found that the amount of iron remaining in solution was roughly inversely proportional to the area of the cathode surface (119). The lower limit is controlled by the tendency of amalgams to become viscous, a property that hinders the clean separation of amalgam and electrolyte. The amount of mercury used is in general between 200 and 600 g., although Rabbitts uses 4 kg. (135).

C. AGITATION OF ELECTROLYTE AND MERCURY

The earliest workers made no attempt to stir the electrolyte. Smith and his students were the first to propose the rotating anode, with which increased efficiency of deposition was claimed (79, 80, 81). Its use became rather general (1, 5, 38, 83, 84, 105, 155) and where a stationary anode was used, agitation was accomplished by other mechanical means (24, 35, 66, 111, 135, 148, 170). Benner investigated the difference in rate of deposition with rotating and stationary anodes; he found that more rapid deposition is achieved by the former but he considered the gain more than offset by the simplicity and lower cost of the latter (12, 13). Frary placed a ring-shaped cell about one pole of a magnet and obtained stirring of the electrolyte in the cell by magnetic currents (48, 49). By using high current densities, e.g., 0.28 amp./cm.^{2}, later investigators believed that the gas evolution alone was sufficient to stir the electrolyte (27, 152, 158).

Agitation of the mercury surface has also been recommended (36, 66, 89, 93, 96, 135, 148, 155, 164, 169, 170, 171) and, in some instances, is considered to be essential. A fresh unsaturated surface naturally favors more efficient deposition and in the reduction of various organic compounds, for example, it has been found that higher yields are obtained by continuous renewal of the mercury surface (88). Furman found that the hydrogen overvoltage was lowered by the incorporation in the mercury of traces of platinum, iron, copper, and other metals; this resulted in the incomplete deposition of certain other metals from solution. He also found that some elements, when present as major constituents, prevent depression of the cathode potential to the level necessary for the complete deposition of certain metals (51, 52). In the Lingane cell agitation is accomplished by the use of a stirrer which agitates both the electrolyte and mercury surface. In other cells stirring is done by means of a stream of air through a tube dipping into the mercury, or by a glass-enclosed iron bar floating on the mercury surface and rotated magnetically.

It would thus seem that agitation of the electrolyte, and in some instances of the mercury also, is considered necessary. The debatable point seems to be whether or not stirring by gas evolution alone is satisfactory, or if recourse must be had to other means.

D. TIME AND TEMPERATURE OF ELECTROLYSIS

There is a confusing array of electrolysis times scattered throughout the literature, but it is significant that as more work was done on the mercury cathode the time necessary for electrolysis was reduced considerably.

In discussing the matter of electrolysis time, the use to which the cell is being put must be considered. When it was used in its early history for purposes of determination the necessarily small volume of electrolyte and mercury employed permitted the use of only low current densities, with a correspondingly long period of electrolysis. Smith and his students carried out electrolyses in about 10–15 min., but the amount of metal deposited was usually only 0.1–0.5 g. (79). Larger amounts required several hours and electrolyses usually were allowed to continue over night (116). Certain metals, such as tungsten and molybdenum, require much longer periods of electrolysis than do others, such as copper and zinc.

When attention was turned to the application of the mercury cathode in separations, reduction of the time element became a necessity, for it was usually desirous that much larger amounts of an element should be deposited than had heretofore been the case. This objective was achieved by the use of larger cells (135, 166), changes of mercury (73), and higher current densities (28). Concentration of the electrolyte has been found to reduce the time necessary for satisfactory deposition (27, 28, 79, 155), bearing in mind again that certain metals are deposited with more difficulty than are others (145, 148). A study of the efficiency of removal of iron, copper, and nickel with time has been made by Ford (47), who found that iron is deposited more rapidly when the other metals are present.

Although no definite statement can be made, owing to the many factors that influence the duration of electrolysis, the electrolysis period for the deposition of a 2–5 g. sample seldom exceeds 2 hr. and is usually much less (14, 22, 27, 135). The time factor need no longer be a deterrent to the use of the mercury cathode in analysis.

Relatively little has been said about the matter of temperature, it usually being taken for granted that the electrolyte is heated to the boil by the operation of the cell. Baumann devised a small heating device for his cell (4), whereas others made a cooling device a part of their apparatus (63, 64, 74, 112, 138, 143, 169). All procedures for the determination of boron emphasize the necessity of keeping the electrolyte below 30°C.

Chirnside, Dauncey, and Proffitt introduced the idea of the "hot-start," in which the electrolyte is heated to boiling before the electrolysis, as opposed to the "cold-start" in which the electrolysis is begun with the electrolyte at room temperature (27). On the other hand, such preliminary heating has been found of little value (152). The boiling action does serve to agitate the solution, and the condensing water vapor keeps the sides of the cell free of electrolyte, but there is also the danger of loss by too violent boiling, and appreciable dissolution of the mercury may occur (169).

E. CURRENT DENSITY

Precise statements about the most advantageous current density for use with certain metals cannot be made because the various investigators show little agreement on the subject (28). Some authors fail to report cathodic surface areas and thus no calculations of the current densities they employed can be made.

Generally, the current density used is the highest possible without there occurring undue boiling of the electrolyte (148), but when a number of cells are in operation it may be found desirable to determine the optimal current density in order to reduce the cost of operation. Up to a point, the amount of metal remaining in solution is found to be roughly in inverse proportion to the current density (119, 152) but the higher current densities (above 0.3 amp./cm.^{2}) may serve only to cause excessive evaporation. In his work on the efficiency of the separation of zinc from aluminum in die-casting alloys, Simpson found (152) that there was an optimal current density.

F. CELL POTENTIAL AND CONTROLLED-POTENTIAL ELECTROLYSIS

In most papers in this field, information on cell potential is rather sparse, emphasis being laid on the current density employed. Generally it appears that a potential of 5 to 10 v. is satisfactory, with the average potential across the cell about 6 to 7 v. With reference to zinc it was found that changes between 13 and 25 v. had little effect upon the efficiency of zinc removal (152).

Reference has been made earlier in this paper to the use of the mercury cathode in the young and growing field of controlled-potential electrolysis. The excellent reviews by Lingane (92, 93, 94, 95) have served as a basis for the following brief summary.

In polarography it is frequently necessary that the interference of a certain element or elements be eliminated. Separations by controlled-potential electrolysis are a convenient means of achieving the desired end, and have the advantage that they do not introduce extraneous reagents nor incur the losses associated with coprecipitation phenomena. A mercury cathode is particularly suited to such separations, because information about the appropriate cathode potential and about the composition of the solution is readily available by the use of the polarograph. A notable advantage is that "several metals may be successively separated from the same solution without removing it from the electrolysis cell; after each separation a small sample is taken with a pipette and polarographed" (92).

The use of a hydrogen–oxygen coulometer, together with a larger silver-wire anode and a stream of an inert gas to effect the removal of dissolved air, makes possible the determination of an element by the measurement of the quantity of electricity passed during the complete reaction at an electrode (90, 92, 94, 171). Again, the use of a mercury cathode enables the prediction of optimum electrolysis conditions from the known polarographic characteristics of the substance being determined. The hydrogen–oxygen coulometer provides a continuous indication of the progress of the electrolysis and the successive determination of several metals from the same solution is being investigated.

Controlled-potential electrolysis is particularly applicable in the preparation of organic compounds ("polarographic syntheses") by reduction at a mercury cathode. Information on the proper cathode potentials can be readily obtained by a study of the polarographic characteristics of the substance to be reduced and, by the use of a special H-cell which prevents mixing of the anodic and cathodic liquids, reductions hitherto impossible or unsatisfactory by means of chemical reducing agents can be achieved easily (97).

"Electrochronometric analysis," in which measurement of the time necessary for the deposition of an element in a mercury cathode, at a given current, serves as a means of determining the element (161), is closely related to Lingane's "coulometric analysis."

Use has been made also of the amalgam obtained from a mercury cathode separation as the dropping electrode in an amperometric cell. It is considered a particularly convenient method for the determination of certain elements present in trace quantities (164a).

TABLE 1

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

* Also elements 58–71 (partial deposition of lanthanum and neodymium has been reported).

Heavy solid lines enclose elements that can be quantitatively deposited in the mercury cathode.

Broken lines enclose elements that are quantitatively separated from the electrolyte, but are not quantitatively deposited in the mercury.

Light lines enclose elements that are incompletely separated.

IV. APPLICATIONS

The following is a brief summary of the work that has been done on the applications of the mercury cathode in analysis. The subject has been treated from the standpoint both of the individual element and of the class of substance to which the method may be applied.

Table 1, which is essentially that appearing in *Outlines of Methods of Chemical Analysis* by Lundell and Hoffman (103), shows that roughly one-third of the elements are deposited in the mercury cathode, either completely or partially. It will be seen in the following section that under certain special conditions some elements not included in the enclosed portions of table 1 may also be deposited.

A. BY ELEMENTS

Group IA (Li, Na, K, Rb, Cs, Fr): These elements are usually considered to remain in the electrolyte after completion of the electrolysis and under ordinary circumstances they do so, this being the basis of a separational procedure prior to the polarographic determination of the alkalies (73, 119). The remarkable work done by Smith and his students would appear, however, to have fulfilled Gibbs' hope that it might be possible to separate and to determine sodium and potassium by the mercury cathode method (59, 85), at least when these two alone are present in the solution.

It has been reported (65, 153, 155) that sodium can be separated by electrolysis of a solution of sodium chloride in the single mercury cup; the procedure was to reverse the current at the end of the electrolysis and to estimate sodium by titration of alkali in the solution. This method was applied to potassium also (155), and it is reported that lithium, cesium, and rubidium may also be determined from solutions of their chlorides (155).

Peters used the Hildebrand double cup in his investigations of the electrolysis of sodium chloride (127), and Lukens, who worked with potassium chloride, found it necessary to deposit mercury on the platinized lower edge of the inner ring of the Hildebrand cell to reduce errors due to seepage (100).

It has been suggested by others that the alkali metals could be separated from one another (155) using the double cup, and a method for the determination of sodium and potassium in mixed chlorides has been proposed (65, 109). Further, the ability of certain metals to remain in the inner cup while others, including the alkalies, migrate to the outer compartment, is said to permit the separation of the alkalies from magnesium, or from calcium provided that magnesium also is present (102, 109). Similar separations of the alkalies from iron, aluminum, and uranium have also been investigated (109, 155). Modifications of the Hildebrand cell have also been used for the determination of the alkali metals (36, 53, 57), and electrolysis at a controlled potential has been proposed as a means of direct analysis of the alkali metals by separation using a silver anode and mercury cathode (124).

Group IIA (Be, Mg, Ca, Sr, Ba, Ra): In the ordinary method of electrolysis with the mercury cathode these elements remain in the electrolyte and can thus be separated for subsequent determination. This has been done for calcium (119) and magnesium (2, 27, 35).

Again it has been reported that barium and strontium have been separately determined by electrolysis in the single mercury cup (32, 153, 155). In the double cup these elements and calcium, as noted above, pass to the outer compartment but magnesium remains in the inner cup and, if calcium is present, will prevent it from leaving also, at ordinary potentials (33, 102, 155). Raising the potential sufficiently is said to separate calcium and magnesium (109). This should enable numerous separations to be carried out, both among this group itself and from other elements such as aluminum, iron, the alkalies, and the rare earths (60, 102, 109, 155). The only work done on beryllium involves the removal of other elements such as chromium, iron, and nickel by electrolysis, allowing the subsequent determination of the beryllium (24, 27, 54, 116).

Group IIIB (Sc, Y, rare earths, Ac): For the most part the elements comprising this group are not deposited in the mercury cathode, the exceptions being lanthanum and neodymium, for which partial deposition has been reported

(103). When electrolyzed in the double cup, lanthanum, yttrium, cerium, praseodymium, and neodymium remain in the inner compartment with the formation of hydroxides (109, 110); offering the possibility of separation from alkali and alkaline earth elements (109, 155).

The single cup has been used to separate iron from cerium (24, 168) and the rare earths as a group (13, 80, 116).

Group IVB (Ti, Zr, Hf, Th): Of these elements, only hafnium is unrepresented in the literature. Titanium has been deposited from a hydrochloric acid solution (63) and it is reported that, together with zirconium and thorium, it decomposes to a hydroxide in the inner compartment of the double cup (109, 110). Under ordinary conditions, however, these elements remain in the electrolyte and separations of thorium (119, 137, 153), of titanium (74, 110a, 153, 155, 156, 157), and of zirconium (74, 153, 155) from iron and other elements have been carried out.

Group VB (V, Nb, Ta, Pa): In this group only vanadium has received any attention. Groves and Russell succeeded in slowly depositing it in their special cell, whose cathodic compartment contained a fine suspension of sodium vanadate in 1 *M* sulfuric acid (63). In the Hildebrand double cup, vanadium is said to remain in the inner compartment (109). It is, however, usually found in the electrolyte under normal conditions, and Cain first applied his new cell to the separation of iron from vanadium (22), a method now in common use (2, 24, 38, 104, 157). Smith separated vanadium from molybdenum in this manner also (155). Lingane and Meites used a phosphoric–sulfuric acid solution to prevent interference from manganese and molybdenum when determining vanadium in steel (96).

Group VIB (Cr, Mo, W, U): These metals are deposited with difficulty on mercury, and under ordinary conditions wolfram and uranium remain in the electrolyte.

The determination of chromium received attention very early in the history of the mercury cathode, but difficulty was caused by the instability of the amalgam formed when a solution of the sulfate was electrolyzed (79, 116, 155). Removal of chromium by the mercury cathode has been found very useful in analysis of alloys, and improvements that permit satisfactory separation have been suggested by numerous investigators (22, 28, 40, 50, 73, 74, 119, 164).

Molybdenum was deposited from a hydrochloric acid solution of molybdic acid by Férée (43) and from sulfuric acid solution by later investigators (101, 112, 116, 119, 155), who stressed the importance of the correct acidity in effecting a deposition, although Chilesotti was not successful in either medium (26). This method is considered to be an excellent way to separate molybdenum from vanadium (155), although the use of phosphoric acid is recommended for prevention of the precipitation of the molybdenum (96).

Férée succeeded in depositing wolfram by electrolysis of a hydrofluoric acid solution containing tungstic acid (44), but efforts by others to duplicate this failed (33, 34, 117) until Jackson and Russell, using their special Bakelite cell, achieved partial deposition (72). It has also been partially deposited from sulfuric acid solution (101) but normally remains in the electrolyte.

Uranium usually remains in the electrolyte also and separations of iron and other metals from uranium have been carried out (21, 25, 50, 51, 52, 74, 135a, 153); nevertheless Férée reported that he deposited it from a hydrochloric acid solution of uranous chloride (45). Later investigators could not obtain deposition from this medium but were successful using uranyl sulfate in sulfuric acid (63). Sutton reduced uranyl sulfate, chloride, or perchlorate to U^{+4} and then titrated back to U^{+6}, using ceric sulfate (159). In the double cup uranium and chromium remain as hydroxides in the inner compartment (109).

Group VIIB (Mn, Tc, Re): Rhenium is quantitatively deposited on the cathode, but manganese is incompletely deposited on the anode and in the mercury (29, 37, 103, 121). Much work has been done in an effort to obtain quantitative deposition of manganese, and among the various suggestions offered are the use of nitric acid (37), phosphoric acid (96, 170), and acetic acid (67), and a high current density (27, 148).

Group VIII (Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt): Iron was one of the first metals deposited on the mercury cathode (56), and good results were obtained in its estimation by this method (13, 79, 153, 155). The separation of iron is probably the most prevalent application of the mercury cathode at present (2, 22, 37, 103, 119, 121, 135, 157). Böttger recommends the presence of hydrazine sulfate as a depolarizer for ready deposition of iron from acid solution (18). The determination of nickel by deposition has been successfully carried out in sulfate solution (13, 18, 56, 79, 153, 155), although it is reported that poor results were obtained with a rigid cathode (19). Numerous separations of nickel from such elements as aluminum (20, 27, 28, 67), magnesium and beryllium (27, 28), uranium (21), and vanadium (121) have been made. Cobalt has a history very similar to that of nickel, being deposited from sulfuric acid solution (56, 79), although Smith reports that it does not form an amalgam with equal ease (155). The presence of hydrazine sulfate has again been found advantageous for work with cobalt (18). Of the remaining six elements of the group, rhodium, platinum, and palladium are quantitatively deposited, iridium is completely deposited with difficulty, osmium is quantitatively separated but some of it is volatilized at the anode, and ruthenium is incompletely deposited in the mercury although none is volatilized (103).

Group IB (Cu, Ag, Au): Copper has been determined satisfactorily by deposition from a sulfuric acid solution (1, 13, 56, 79, 130, 153, 154, 155). Benner used nitric acid (12), as did Kimley, who regarded this method as superior to the use of platinum electrodes when the copper must be determined from a strongly acid solution (78). This method has also proven very useful when removal of copper is desired (28, 119, 145, 148). Lingane separated copper and the members of the copper group by controlled-potential electrolysis (89), and later on determined copper coulometrically (90). Trishin determined it in the presence of zinc in a similar manner (161).

Both silver, from nitric acid solution (1, 12, 80, 155), and gold, using the chloride (155), have been determined, since both are quantitatively deposited with ease. Alders and Stähler noted that the mercury cathode method was particularly suited to the nobler metals (1).

Group IIB (Zn, Cd, Hg): Deposition of zinc as an amalgam was suggested by Gibbs (56) and by both Luckow (99) and Vortmann (166). The mercury cathode method is particularly suited for deposition of this metal (155, 170)—Sand considered the Paweck amalgam electrode to be the best means of deposition (144)—and considerable work has been done on both the quantitative determination of zinc (13, 15, 19, 78, 79, 153, 161) and in the field of separation (35, 119, 145, 152). Böttger recommends the addition of a small quantity of nickel amalgam before electrolysis, and of sodium acetate before breaking the current (18). It is interesting to note that it was because of the low results obtained by Price that doubts concerning the reliability of the mercury cathode first arose (132, 133, 134) and this resulted in careful reëxamination of the procedure (83, 130). Baxter and his associates used special mercury cathode cells for the determination of the atomic weight of zinc (6, 9).

Cadmium has been deposited quantitatively from a solution of its sulfate (12, 80, 125, 155) and the method has been used to determine the atomic weight of cadmium using bromide and chloride solutions, as well as the sulfate (7, 8, 10, 69, 86, 126, 134a). It is also deposited in the presence of nitric acid (12), and the latter acid is the best medium for mercury (1, 80, 155). Böttger found that the use of a nickel or cobalt amalgam prevented the formation of mercurous chloride when mercury was deposited from a solution of mercuric chloride (18). Vortmann deposited cadmium and mercury as amalgams in a platinum dish, using an oxalate solution as the electrolyte (166).

Group IIIA (B, Al, Ga, In, Tl): Of the four metals in this group, only aluminum is not deposited in the mercury cathode, and this has long served as the basis of a method for the separation of interfering elements from aluminum, both when the latter is present in large amounts or in micro-amounts (2, 20, 24, 27, 35, 37, 54, 67, 99, 113, 116, 120, 128, 129, 138, 148, 150, 151, 160, 169). Gallium is quantitatively deposited, indium may be deposited quantitatively and has been determined in this manner (84), and thallium has been investigated by Morden, who considers deposition in a mercury cathode to be the most satisfactory electrolytic method for the metal, provided a little zinc is deposited simultaneously (115, 155). Good results were obtained in the electrolysis of thallium sulfate using a mercury-coated platinum cathode in the presence of gallic acid and lead; nitric acid and ammonium hydroxide caused low results (30). Attempts have also been made to deposit thallium on a platinum dish by Vortmann's method (1), and on a lead-plated anode (109).

The determination of boron has been facilitated by the use of the mercury cathode to remove interfering elements (24, 75, 105, 162), since boron is not deposited in the mercury.

Group IVA (C, Si, Ge, Sn, Pb): Germanium and tin are both quantitatively deposited in mercury. Kollock and Smith determined tin by deposition from sulfuric acid solution (80) but hydrochloric acid solution is reportedly more satisfactory (119). Although lead is quantitatively separated, some of it is partially deposited on the anode and suggestions for minimizing the anodic deposit include use of an alkaline solution (166), the rigid mercury cathode (19), and deposition as an amalgam on a platinum dish (1, 155). Lingane separated lead from other members of the copper group using controlled-potential electrolysis (89) and also determined it coulometrically (90).

Group VA (N, P, As, Sb, Bi): Of this group only bismuth is quantitatively deposited in mercury and although considerable care is necessary (80, 155), this method is considered to be the best electrolytic method for its determination (12, 70). It has also been determined by deposition as an amalgam on a platinum dish (166) and coulometrically (90), but only fair results are reported with the rigid electrode (19). Parks, Johnson, and Lykken were not successful when they applied their cell to its separation, and this was also the case with arsenic and antimony (119).

Arsenic, although it is quantitatively separated, is partly volatilized as arsine at the cathode, while antimony is only partially deposited in the mercury and partly volatilized at the cathode as stibine (103). The volatilization of arsine in special closed cells has been made the basis of a method for the determination of arsenic (3, 23, 136, 139). Alders and Stähler separated arsenic from lead but did not succeed in effecting the separation of lead from antimony (1). Vortmann recommends deposition of antimony from a sodium sulfide solution but he could not deposit arsenic quantitatively (166).

Group VIA (O, S, Se, Te, Po): Polonium is quantitatively deposited in the mercury, while selenium and tellurium, being reduced to the elemental state, remain suspended in the electrolyte and can be quantitatively removed by filtration (103). Alders and Stähler were not able to separate lead from selenium (1).

The determination of sulfur, as the sulfate ion, has been carried out with ease after the removal of interfering elements by electrolysis of a perchloric acid solution of the material (105).

Group VIIA (F, Cl, Br, I, and the anions in general): The anions received much attention from Smith and his students. By the use of a silver-plated platinum-gauze anode the chlorides, bromides, and iodides of the alkaline earths and the alkali metals have been determined (58, 65, 102, 109, 153, 155, 167) and similarly chlorine in hydrochloric acid and bromine in hydrobromic acid (61, 155), although Gooch and Read report consistently low results in their electrolysis of hydrochloric acid (62). In addition to the halides, several other anions including phosphate, ferrocyanide, ferricyanide, thiocyanate, and carbonate have been determined with the silver anode (65, 155) and it has been suggested that an anode coated with calcium hydroxide would make possible the determination of fluoride (102, 155). Ammonium chloride, bromide, and thiocyanate were electrolyzed in the double cell and both the cation and anion assessed (109, 155). An attempt was also made to separate ferrocyanide and ferricyanide by means of the double cell (82).

B. BY CLASS OF SUBSTANCE

The widest practical application of the mercury cathode, insofar as one can judge from the literature, is in the field of alloys, both ferrous and nonferrous.

The mercury cathode has been applied to the determination of vanadium in plain carbon (24, 38), chrome-vanadium (22, 104), and other alloy steels (2, 24, 96); of aluminum in plain carbon (11, 24, 37, 138, 160) and in chromium (74, 128), nickel (27), and other alloy steels (20, 169), and of boron in plain carbon steel (24, 39, 75, 105) and in other alloys containing boron (162). Beryllium has been determined in plain carbon (24) and nickel alloy steels (24, 27), as has also magnesium (27, 86a), cerium (24), titanium and zirconium (74; 110a), and sulfur (105) after removal of interfering elements by the mercury cathode.

In the nonferrous alloys aluminum has been determined in bearing metals and solder (145, 148), in brasses (2, 40, 148), in manganese and aluminum bronzes (67, 151), in gun-metal and tin alloys (40, 131a, 148), and in magnesium and its alloys (2). The same separational procedure has been applied to the determination of aluminum in zinc-base die-casting alloys (2, 35, 152) and magnesium can be determined in these alloys in the same manner (2, 35), a well as in aluminum and its alloys (2). Sodium has been determined in aluminum by use of a modified double cell (53).

Removal of the iron in ferrosilicon (119), in ferrotitanium (156a), and of the chromium as well in ferrochromium (28) facilitated the determination of titanium, calcium, and aluminum in these alloys. Vanadium (14), aluminum (37), and cerium (11, 168) have been determined in iron in this manner.

The mercury cathode is used in industrial laboratories to remove large amounts of interfering elements from iron ore and smelter samples (25, 42, 119, 156) in order to facilitate the subsequent determination of calcium, aluminum, magnesium, titanium, sodium, and uranium. Smith suggested a method for the estimation of mercury in cinnabar (155) in which final determination of the mercury is made by weighing it as an amalgam. Geith applied a modified Hildebrand cell to the determination of sodium in clay (53).

V. Summary

In discussions of the advantages of the mercury cathode cell the claim has been made that it permits separations to be effected rapidly and without the introduction of foreign salts that may contaminate a precipitate or be otherwise objectionable. But these are not so much advantages of the mercury cathode method as they are of electrolytic methods of separation.

What are the advantages of the mercury cathode cell as compared with the conventional platinum cathode cell? Everyone is familiar with the care that is often necessary during an electrolysis using a platinum cathode to ensure that an adherent deposit is obtained. By its amalgamation with an element, the mercury cathode removes all questions of the satisfactory nature of the deposit and, of equal importance, the amalgamation protects the deposited metal from oxidation. Certain metals can be amalgamated that cannot be deposited on platinum because of hydrogen evolution; the high overvoltage of hydrogen on mercury is, of course, well known.[3] Mercury holds an almost unique place among

---

[3] "A mercury electrode is of especial value . . . since the supersaturation of the hydrogen can attain a far higher value upon the smooth surface of the liquid metal than it can on ordinary solid electrodes."—Wilhelm Ostwald, 1895 (118).

cathodic materials because of the ease with which a fresh unstrained surface may be obtained (149). Taken together these are formidable advantages, and as a result certain separations involving the mercury cathode are unrivalled for rapidity and convenience.

It is true that there are certain objections to the mercury cathode cell when used for the determination rather than the separation of an element. The very nature of the cathode requires extreme care in handling (15, 116), for tiny droplets of mercury are easily lost; it is believed that this is the source of many of the low results obtained by some investigators. There may also be mentioned the difficulties in washing and in drying the amalgam (155, 170). Again, losses may occur during the washing of the amalgam (78, 83) and during the drying of the amalgam (owing to the explosive evaporation of the alcohol or ether used in the process). Another error may be introduced by the solvent action of the electrolyte on the glass of the cell in basic solutions (1), although not in acidic ones (130). The reduction of the size of the cell, with accompanying reduction in the amount of mercury, led to difficulties with small surface area, although modifications were introduced that made the most of the available mercury (1, 15, 41, 49, 116, 125). The removal of the electrolyte by decantation or by siphoning, necessitating subsequent filtration to remove particles of mercury carried over, was another problem but again one that has been, at least partially, overcome.

The possibility of an error arising through evaporation of mercury at the elevated temperature of the electrolysis has been investigated and found to be negligible (130). The problem of purifying mercury for further use has been largely eliminated because satisfactory simple purification methods have been devised (121). Cells have been simplified (27, 135) and even a series of them can be constructed at modest cost. The Melaven, Frary, beaker, and unitized types can be obtained from supply houses.

The mercury cathode cell is in use in several industrial and university laboratories where it is regarded as a valuable analytical tool, but it is by no means used as widely as it could be or should be. This rapid method is especially useful in the analysis of alloys and minerals wherein it is often necessary to remove large concentrations of one element in order to make possible the determination of a trace concentration of another by polarographic or other methods. In the field of rock analysis its use as a rapid method for the determination of the alkali and alkaline earth elements, and for the separation of these elements one from another—always a troublesome problem—should be studied further. And there are interesting possible applications in the separation of elements such as copper, nickel, and chromium from the more abundant elements of rocks. Much ground must yet be tilled before an end to the applications of the mercury cathode cell is in sight, but the instrument is established as an integral part of the analytical laboratory.

VI. References

(1) Alders, H., and Stähler, A.: Ber. **42,** 2685 (1909); also reported in Z. anal. Chem. **49,** 445 (1910).

(2) *A.S.T.M. Methods of Chemical Analysis of Metals*. American Society for Testing Materials, Philadelphia (1946).

(3) Aumonier, F. S.: J. Soc. Chem. Ind. **46,** 341T–5T (1927).
(4) Baumann, P.: Chem. Ztg. **35,** 854–5 (1911).
(5) Baumann, P.: Z. anorg. Chem. **74,** 315–50 (1912); also reported in Z. anal. Chem. **52,** 210 (1913).
(6) Baxter, G. P., and Grose, M. R.: J. Am. Chem. Soc. **38,** 868–73 (1916).
(7) Baxter, G. P., Grose, M. R., and Hartmann, M. L.: J. Am. Chem. Soc. **38,** 857–67 (1916).
(8) Baxter, G. P., and Hartmann, M. L.: J. Am. Chem. Soc. **37,** 113–31 (1915).
(9) Baxter, G. P., and Hodges, J. H.: J. Am. Chem. Soc. **43,** 1242–51 (1921).
(10) Baxter, G. P., and Wilson, C. H.: J. Am. Chem. Soc. **43,** 1230–41 (1921).
(11) Beeghly, H. F.: Anal. Chem. **21,** 241–6 (1949).
(12) Benner, R. C.: J. Am. Chem. Soc. **32,** 1231–7 (1910).
(13) Benner, R. C., and Hartmann, M. L.: J. Am. Chem. Soc. **32,** 1628–36 (1910).
(14) Blair, A. A.: *Chemical Analysis of Iron*, 8th edition, pp. 199–200. Lippincott and Company, Philadelphia (1918).
(15) Böttger, W.: Ber. **42,** 1824–39 (1909); also reported in Z. anal. Chem. **48,** 763 (1909).
(16) Böttger, W.: Chem. Ztg. **34,** 1033 (1910).
(17) Böttger, W.: *Physikalische Methoden der analytischen Chemie, Teil II, Elektroanalyse.* Akademische Verlagsgesellschaft, Leipzig (1936).
(18) Böttger, W.: Z. anal. Chem. **128,** 421–31 (1948).
(19) Böttger, W., Block, N., and Michov, M.: Z. anal. Chem. **93,** 401–22 (1933).
(20) Brophy, D.: Ind. Eng. Chem. **16,** 963 (1924).
(21) Buckminster, I. H., and Smith, E. F.: J. Am. Chem. Soc. **32,** 1471–7 (1910).
(22) Cain, J. R.: Ind. Eng. Chem. **3,** 476–81 (1911).
(23) Callan, T., and Parry Jones, R. T.: Analyst **55,** 90 (1930).
(24) Chemists, U. S. Steel Corporation: *Sampling and Analysis of Carbon and Alloy Steels*. Reinhold Publishing Corporation, New York (1938).
(25) Chernichov, I., and Guldina, E.: Z. anal. Chem. **96,** 257–63 (1934); Chem. Abstracts **28,** 3026 (1934).
(26) Chilesotti, A.: Z. Elektrochem. **12,** 146 (1906).
(27) Chirnside, R. C., Dauncey, L. A., and Proffitt, P. M.: Analyst **65,** 446–52 (1940).
(28) Chirnside, R. C., Dauncey, L. A., and Proffitt, P. M.: Analyst **68,** 175–80 (1943).
(29) Chlopin, N. J.: Z. anal. Chem. **107,** 104–7 (1936).
(30) Chrëtien, A., and Longi, Y.: Bull. soc. chim. **11,** 245–9 (1944).
(31) Coehn, A.: Z. anorg. allgem. Chem. **25,** 430–35 (1900).
(32) Coehn, A., and Kettembeil, W.: Z. anorg. allgem. Chem. **38,** 198–212 (1904).
(33) Collenberg, O. O., and Backer, J.: Z. Elektrochem. **30,** 230 (1924).
(34) Collenberg, O. O., and Nilsson, K.: Z. Elektrochem. **31,** 555 (1925).
(35) Craighead, C. M.: Ind. Eng. Chem., Anal. Ed. **2,** 188–90 (1930).
(36) Drossbach, P.: Z. anorg. allgem. Chem. **165,** 149–56 (1927).
(37) Drown, T. M., and McKenna, A. G.: J. Anal. Chem. **5,** 627 (1891); also reported in Trans. Inst. Mining Engrs. **20,** 242 (1891).
(37a) *Dyna-Cath*, Special Bulletin, Eberbach and Son Company, Ann Arbor, Michigan; also in Anal. Chem. **22,** 25A (1950).
(38) Etheridge, A. T.: Analyst **53,** 423 (1928).
(39) Etheridge, A. T.: Analyst **54,** 141–4 (1929).
(40) Etheridge, A. T.: Analyst **67,** 9–11 (1942).
(41) Evans, B. S.: Analyst **60,** 389–93 (1935).
(42) Farnham, G. S.: Private communication.
(43) Férée, J.: Compt. rend. **122,** 733 (1896).
(44) Férée, J.: Bull. soc. chim. **19,** 213 (1898).
(45) Férée, J.: Bull. soc. chim. **25,** 622 (1901).
(46) Filippo, H.: Chem. Weekblad **6,** 2269; through Kimley, W. S.: J. Am. Chem. Soc. **32,** 637–8 (1910).

(47) Ford, E. G.: Unpublished work from the Research and Development Laboratories, Canadian Westinghouse Company, Ltd., Hamilton, Ontario, 1949.
(48) Frary, F. C.: Z. Elektrochem. **13,** 308 (1907).
(49) Frary, F. C.: J. Am. Chem. Soc. **29,** 1592 (1907); also reported in Z. angew. Chem. **20,** 1897 (1907).
(50) Furman, N. H.: Chem. Eng. News **26,** 2490–2 (1948).
(51) Furman, N. H., and Bricker, C. E.: United States Atomic Energy Commission, MDDC–691.
(52) Furman, N. H., Bricker, C. E., and McDuffie, B.: J. Wash. Acad. Science **38,** 159–66 (1948).
(53) Geith, R.: Chem. Ztg. **46,** 745 (1922).
(54) Gerke, F. K., and Lyubomirskaya, N. V.: Zavodskaya Lab. **6,** 746–8 (1937).
(55) Gibbs, W.: Chem. News **42,** 291 (1880); also reported in Z. anal. Chem. **22,** 558 (1883).
(56) Gibbs, W.: Am. Chem. J. **13,** 571 (1891).
(57) Ginsberg, H.: Z. anorg. allgem. Chem. **167,** 183–4 (1927).
(58) Goldbaum, J. S.: J. Am. Chem. Soc. **33,** 35–50 (1911).
(59) Goldbaum, J. S., and Smith, E. F.: J. Am. Chem. Soc. **30,** 1705 (1908).
(60) Goldbaum, J. S., and Smith, E. F.: J. Am. Chem. Soc. **31,** 900–2 (1909).
(61) Goldbaum, J. S., and Smith, E. F.: J. Am. Chem. Soc. **32,** 1468–71 (1910).
(62) Gooch, F. A., and Read, H. L.: Am. J. Sci. **28,** 544–52 (1909); also reported in Z. anorg. allgem. Chem. **64,** 287–97 (1909).
(63) Groves, R., and Russell, A. S.: J. Chem. Soc. **1931,** 2805–14.
(64) Haggerty, C. J.: Trans. Am. Electrochem. Soc. **56,** 421 (1929).
(65) Hildebrand, J. H.: J. Am. Chem. Soc. **29,** 447 (1907).
(66) Hillebrand, W. F., and Lundell, G. E. F.: *Applied Inorganic Analysis.* John Wiley and Sons, Inc., New York (1929).
(67) Holler, A. C., and Yeager, J. P.: Ind. Eng. Chem. Anal. Ed. **14,** 719–20 (1942).
(68) Hoogland, J. G.: Discussions of the Faraday Society **1,** 200–203 (1947).
(69) Hulett, G. A., and Quinn, E. L.: J. Am. Chem. Soc. **37,** 1997–2000 (1915).
(70) Ibbotson, F., and Aitchison, L.: *The Analysis of Non-Ferrous Alloys,* 2nd edition. Longmans, Green and Company, London (1922).
(71) Iofa, Z. A., and Pichkovskaya, Z. B.: Doklady Akad. Nauk S.S.S.R. **59,** 265–8 (1948); Chem. Abstracts **42,** 6215a (1948).
(72) Jackson, K. S., Russell, A. S., and Merrill, J. L.: J. Chem. Soc. **1929,** 2394–8.
(73) Johnson, H. O., Weaver, J. R., and Lykken, L.: Ind. Eng. Chem. Anal. Ed. **19,** 481-3 (1947).
(74) Kar, H. A.: Metals & Alloys **6,** 156–7 (1935).
(75) Kar, H. A.: Metals & Alloys **9,** 175 (1938).
(76) Kerp, W., and Böttger, W.: Z. anorg. allgem. Chem. **25,** 1–71 (1900).
(77) Kettembeil, W.: Z. anorg. allgem. Chem. **38,** 213–31 (1904).
(78) Kimley, W. S.: J. Am. Chem. Soc. **32,** 637–41 (1910).
(79) Kollock, L. G., and Smith, E. F.: J. Am. Chem. Soc. **27,** 1255 (1905); also reported in Proc. Am. Phil. Soc. **44,** 137 (1905).
(80) Kollock, L. G., and Smith, E. F.: J. Am. Chem. Soc. **27,** 1527 (1905).
(81) Kollock, L. G., and Smith, E. F.: J. Am. Chem. Soc. **29,** 797 (1907).
(82) Kollock, L. G., and Smith, E. F.: Proc. Am. Phil. Soc. **46,** 341 (1907).
(83) Kollock, L. G., and Smith, E. F.: Trans. Am. Electrochem. Soc. **14,** 59 (1908).
(84) Kollock, L. G., and Smith, E. F.: J. Am. Chem. Soc. **32,** 1248–50 (1910).
(85) Kolthoff, I. M., and Sandell, E. B.: *Textbook of Quantitative Inorganic Analysis,* revised edition, p. 156. The Macmillan Company, New York (1947).
(86) Laird, J. S., and Hulett, G. A.: Trans. Am. Electrochem. Soc. **22,** 385–96 (1912).
(86a) LaRochelle, A. E., and Fournier, J. A.: Am. Foundryman **17,** 65-6 (1950).
(87) Levchenko, V. V.: J. Gen. Chem. (U.S.S.R.) **17,** 1656–8 (1947); Chem. Abstracts **42,** 2187 (1948).

(88) Levchenko, V. V.: J. Gen. Chem. (U.S.R.R.) **18,** 1237–44 (1948); Chem. Abstracts **43,** 955 (1949).
(89) Lingane, J. J.: Ind. Eng. Chem., Anal. Ed. **16,** 147–52 (1944).
(90) Lingane, J. J.: J. Am. Chem. Soc. **67,** 1916–22 (1945).
(91) Lingane, J. J.: Ind Eng. Chem., Anal. Ed. **17,** 332–3 (1945).
(92) Lingane, J. J.: Discussions of the Faraday Society **1,** 203–12 (1947).
(93) Lingane, J. J.: Anal. Chim. Acta **2,** 584–601 (1948).
(94) Lingane, J. J.: Anal. Chem. **21,** 58–9 (1949).
(95) Lingane, J. J.: Record Chem. Progress (Kresge-Hooker Sci. Lib.) **10,** 1–8 (1949).
(96) Lingane, J. J., and Meites, L.: Anal. Chem. **19,** 159–61 (1947).
(97) Lingane, J. J., Swain, C. G., and Fields, M.: J. Am. Chem. Soc. **65,** 1348–53 (1943).
(98) Luckow, C.: Z. anal. Chem. **19,** 15 (1880).
(99) Luckow, C.: Chem. Ztg. **9,** 338 (1885); also reported in Z. anal. Chem. **25,** 113 (1886).
(100) Lukens, H. S.: J. Am. Chem. Soc. **35,** 1472–82 (1913).
(101) Lukens, H. S.: Trans. Am. Electrochem. Soc. **52,** 309 (1927).
(102) Lukens, H. S., and Smith, E. F.: J. Am. Chem. Soc. **29,** 1455 (1907).
(103) Lundell, G. E. F., and Hoffman, J. I.: *Outlines of Methods of Chemical Analysis*, pp. 94–5. John Wiley and Sons, Inc., New York (1938).
(104) Lundell, G. E. F., Hoffman, J. I., and Bright, H. A.: Ind. Eng. Chem. **15,** 1064–9 (1923).
(105) Lundell, G. E. F., Hoffman, J. I., and Bright, H. A.: *Chemical Analysis of Iron and Steel.* John Wiley and Sons, Inc., New York (1931).
(106) Magri, G., and Ercolini, G.: Atti reale accad. Lincei **16,** 331; through reference 155, page 257.
(107) Magri, G., and Ercolini, G.: Gazz. chim. ital. **37,** 179 (1907); through reference 155, page 257.
(108) Mahin, E. G.: *Quantitative Analysis*, pp. 136–7. McGraw-Hill Book Company, Inc., New York (1932).
(109) McCutcheon, T. P.: J. Am. Chem. Soc. **29,** 1445 (1907).
(110) McCutcheon, T. P., and Smith, E. F.: J. Am. Chem. Soc. **29,** 1460 (1907).
(110a) Maxwell, J. A.: Unpublished work, McMaster University, 1949.
(111) Melaven, A. D.: Ind. Eng. Chem., Anal. Ed. **2,** 180 (1930).
(112) Merrill, J. L., and Russell, A. S.: J. Chem. Soc. **1929,** 2389–93
(112a) Mines Branch Laboratories (Ottawa, Canada): Unpublished methods of analysis of iron and steel.
(113) Molchanov, S. P.: Zavodskaya Lab. **5,** 1518–19 (1936).
(114) Moldenhauer, W., Ewald, K. F. A., and Roth, O.: Z. angew. Chem. **42,** 331–4 (1929); also reported in Z. anal. Chem. **81,** 467 (1930).
(115) Morden, G. W.: J. Am. Chem. Soc. **31,** 1045 (1909).
(116) Myers, R. E.: J. Am. Chem. Soc. **26,** 1124–35 (1904).
(117) Neumann, B., and Richter, H.: Z. Elektrochem. **30,** 474 (1924).
(118) Ostwald, W.: *The Scientific Foundations of Analytical Chemistry*, pp. 94–5. The Macmillan Company, London (1895).
(119) Parks, T. D., Johnson, H. O., and Lykken, L.: Anal. Chem. **20,** 148–51 (1948).
(120) Parks, T. D., and Lykken, L.: Anal. Chem. **20,** 1102–6 (1948).
(121) Pavlish, A. E., and Sullivan, J. D.: Metals & Alloys **11,** 56–9 (1940).
(122) Paweck, H.: Z. Elektrochem. **5,** 221 (1898).
(123) Paweck, H., and Walther, E.: Z. anal. Chem. **64,** 89–96 (1924).
(124) Penther, C. J., and Pompeo, D. J.: Anal Chem. **21,** 178–80 (1949).
(125) Perdue, W. L., and Hulett, G. A.: J. Phys. Chem. **15,** 147–54 (1910).
(126) Perdue, W. L., and Hulett, G. A.: J. Phys. Chem. **15,** 155–65 (1910).
(127) Peters, C. A.: Am. J. Sci. **32,** 365–85 (1911); also reported in Z. anorg. allgem. Chem. **74,** 127–51 (1912).

(128) Peters, F. P.: Chemist Analyst **24,** No. 4, 4–10 (1935).

(129) Phillips, D. F.: Mettalurgia **35,** 169–71 (1947).

(130) Porter, A. H., and Frary, F. C.: Trans. Am. Electrochem. Soc. **14,** 51–8 (1908); also reported in Z. angew. Chem. **22,** 166 (1909) and Z. Elektrochem **15,** 240 (1909).

(131) *"Precision" Mercalyzer*, Special Bulletin, Precision Scientific Company, Chicago, Illinois.

(131a) Price, J. B., and Payne, S.T.: Analyst **74,** 641–5 (1949).

(132) Price, T. S.: Trans. Faraday Soc. **3,** 88 (1907); also reported in J. Soc. Chem. Ind. **26,** 345 (1907).

(133) Price, T. S.: Chem. News **97,** 89–90 (1908).

(134) Price, T. S., and Judge, G. H. B.: Trans. Faraday Soc. **2,** 85 (1906).

(134a) Quinn, E. L., and Hulett, G. A.: J. Phys. Chem. **17,** 780–98 (1913).

(135) Rabbitts, F. T.: Anal. Chem. **20,** 181–2 (1948).

(135a) Rabbitts, F. T.: Can. Mining J. **70,** 84–6 (1949).

(136) Ramberg: Lunds Univ. Årsskr. N.F. (ii) **14,** No. 21; through Aumonier, F. S.: J. Soc. Chem. Ind. **46,** 341T (1927).

(137) Rider, B. F., and Mellon, M. G.: Anal. Chim. Acta **2,** 370–6 (1948).

(138) Rocquet, P.: Rev. mét. **40,** 276–83 (1943).

(139) Rogers, D., and Heron, A. E.: Analyst **71,** 414–17 (1946).

(140) Russell, A. S., Cazalet, P. V. F., and Irvin, N. M.: J. Chem. Soc. **1932,** 841–51.

(141) Russell, A. S., and Irvin, N. M.: J. Chem. Soc. **1932,** 891-8.

(142) Russell, A. S., Kennedy, T. R., and Lawrence, R. P.: J. Chem. Soc. **1934,** 1750–5.

(143) Rynasiewicz, J.: Anal. Chem. **21,** 756 (1949); also in United States Atomic Energy Commission AECD-2240.

(144) Sand, H. J. S.: *Electrochemistry and Electrochemical Analysis*, Vol. 2. Blackie and Son, London (1940).

(145) Sandell, E. B.: *Colorimetric Determination of Traces of Metals.* Interscience Publishers, Inc., New York (1944).

(146) Sargent and Company: *Scientific Apparatus and Methods*, Winter Bulletin, pp. 3–5 (1948–49).

(147) Schall, C., and Kirst, W.: Z. Elektrochem. **29,** 537–46 (1923).

(148) Scherrer, J. A., and Mogerman, W. D.: J. Research Natl. Bur. Standards **21,** 105–11 (1938).

(149) Schofield, R. K.: Science Progress **24,** 209–14 (1929).

(150) Sherman, M.: Die Castings **5,** 23 (1948).

(151) Shubin, M. I.: Zavodskaya Lab. **5,** 407–11 (1936).

(152) Simpson, D. H.: Unpublished work, McMaster University, 1945.

(153) Smith, E. F.: J. Am. Chem. Soc. **25,** 883–92 (1903).

(154) Smith, E. F.: J. Am. Chem. Soc. **26,** 1614 (1904).

(155) Smith, E. F.: *Electroanalysis.* Blakiston's Son and Company, London (1919).

(156) Sportenko, P. I.: Zavodskaya Lab. **7,** 1431 (1938).

(156a) Sportenko, P. I.: Zavodskaya Lab. **8,** 96 (1939); Chem. Abstracts **33,** 9188.

(157) Steinmetz, M. H.: Ind. Eng. Chem., Anal. Ed. **14,** 109 (1942).

(158) Stoddard, J. T.: J. Am. Chem. Soc. **31,** 385 (1909).

(159) Sutton, J.: Natl. Research Council Can., Pub. No. **1591** (1945).

(160) Temirenko, T. P.: Zavodskaya Lab. **13,** 621–3 (1947).

(161) Trishin, F. I.: Zhur. anal. Khim. **3,** 21–8 (1948); through Ashley, S. E. Q.: Anal. Chem. **21,** 73 (1949).

(162) Tschischewski, N.: Ind. Eng. Chem. **18,** 607–8 (1926).

(163) Tutundzic, P. S.: Z. anorg. allgem. Chem. **202,** 297–304 (1931).

(164) Tutundzic, P. S.: Z. anorg. allgem. Chem. **215,** 19–22 (1933).

(164a) Vandenbosch, V.: Anal. Chim. Acta **2,** 583 (1948).

(165) Vorobev, A. L.: Zavodskaya Lab. **6,** 891 (1937); through Johnson, H. O., Weaver, J. R., and Lykken, L.: Ind. Eng. Chem., Anal. Ed. **19,** 481–3 (1947).

(166) Vortmann, G.: Ber. **24,** 2749 (1891).

(167) Vortmann, G.: Monatsh. **26,** 674–83 (1895).

(168) Westwood, W., and Mayer, A.: Analyst **73,** 275–82 (1948).

(169) Wiberley, S. E., and Bassett, L. G.: Anal. Chem. **21,** 609–12 (1949).

(170) Willard, H. H., and Diehl, H.: *Advanced Quantitative Analysis*, p. 58. D. Van Nostrand Company, Inc., New York (1943).

(171) Willard, H. H., Merritt, L. L., and Dean, J. A.: *Instrumental Methods of Analysis,* pp. 193-4, 198–9. D. Van Nostrand Company, Inc., New York (1948).