

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES]

IMPROVED APPARATUS FOR MICRO-ELECTROANALYSIS¹

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Two related problems which frequently arise in chemical analysis are (1) the separation, identification and determination of small quantities of metallic ions where the volume of the liquid sample may be limited, and (2) where the volume is large relative to the metal concentration and cannot be reduced owing to high salt concentration. Both these problems are efficiently handled by electroanalytical methods, provided that micro-technique is suitably applied.

These problems have been attacked by others along similar lines.² The most widely used cell for micro-electroanalysis is that of Pregl.³ The usefulness of this cell is somewhat limited by the employment of boiling for effecting agitation, and none of the other apparatus published is free from one or more of the following objections: (1) long time required for complete deposition; (2) structural fragility; (3) disparity in size and shape between electrodes, preventing simultaneous cathodic and anodic deposition; (4) absence of provision for agitation, or use of objectionable methods; (5) difficulty in washing electrodes.

The present paper describes two cells, for the respective purposes stated, in which these objectionable features are eliminated or minimized.

Apparatus

The Cell for Small Volumes.—The large outer vessel (Fig. 1), sealed to the electrode compartment at its base, is a water-jacket which can be heated by a micro-flame. Figure 2-I shows the glass frame which in the assembled cell fits inside the electrode vessel and serves to support both the electrodes and the pumping device. Its lower end is flared to form a conical bell having a diameter about 4 mm. less than that of the container. While the two electrodes are held very close together, they cannot make contact or become fouled by touching the glass wall of the container. The support permits a free circulation of the electrolyte. This circulation is accomplished by the tube shown in Fig. 2-II, which is held erect in the axis of the cell. A stream of bubbles of air or of an inert gas is introduced by means of this tube into the space under the bell and causes a continuous overflow of liquid over the top of the tube A that supports the inner electrode. At the same time the suction caused by the removal of the liquid from under the bell further assists circulation in this direction by drawing upon that portion of the electrolyte in the space between the outer electrode and the wall of the containing vessel. A rapid agitation is thus maintained whereby

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² Classen, "Quantitative Analyse durch Elektrolyse," 7th ed., Julius Springer, Berlin, 1927; Heinze, *Z. angew. Chem.*, **27**, 237 (1914); Riesenfeld and Möller, *Z. Elektrochem.*, **21**, 137 (1915); Brenneis, *Mikrochemie*, **9**, 385 (1931).

³ Pregl, "Quantitative Organic Microanalysis," 2d ed., translated by Fyleman, P. Blakiston's Sons, Philadelphia, 1930.

the whole of the electrolyte is forced through the inter-electrode space several times a minute.

The electrodes are two platinum gauze cylinders 15 mm. high, the one having an inside diameter of 9 mm., the other, 18 mm., weighing 0.8 g., and 1.5 g., respectively.

The Cell for Large Volumes.—This cell is designed for the separation of small quantities of metals from large volumes of solution, when concentration of the sample is undesirable. Provision is made for the continuous and rapid circulation of the large liquid volume through the space between the micro-electrodes.

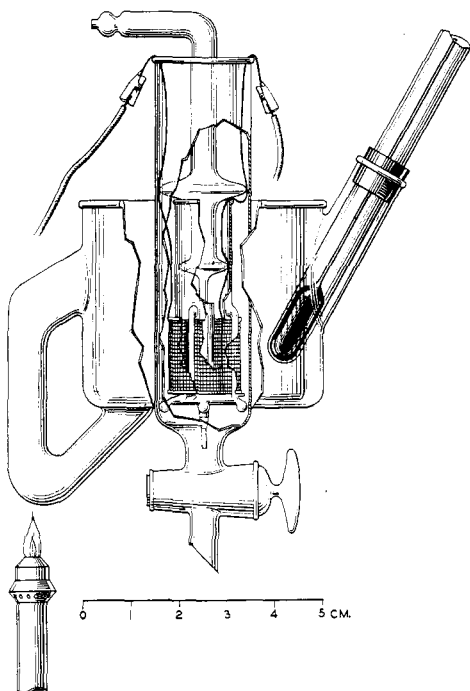


Fig. 1.—General view of cell for small volumes.

to permit the escape of the air used for pumping.

The outer electrode (J in Fig. 4-II) is a cylinder of perforated platinum sheet or heavy gauze and is permanently fixed in place, snugly against the wall of the electrode chamber, by a stout platinum wire welded to the electrode and fused through the glass wall. The inner electrode (L in Fig. 4-II) is of platinum gauze, similar to that used for the small cell, and that portion of the lead wire in contact with the solution is enclosed in glass. The central electrode fits over the tube E with a clearance of about 0.5 mm. The clearance between the electrodes is 3 to 4 mm. In order to permit the removal of the inner electrode from the cell without interrupting the current, it is convenient to connect the platinum lead wire to the binding post by a short length of flexible tinsel cord with a small spring clip.

When the quantity of the ion in question is extraordinarily small and it is desired merely to effect a separation, the weighable electrode just described is conveniently replaced by that shown in Fig. 4-III. The deposit may then be dissolved in a drop of acid and subjected to microscopic identification tests or colorimetric estimation.

Figure 3 shows the cell container and accessory parts, and details of construction and assembly are given in Fig. 4. The size of the large reservoir B should accord with the volume of liquid to be electrolyzed. Within the tube C in Fig. 3 four internal glass projections, as shown in cross-section in Fig. 4-I, provide support at D for the tube E (Fig. 4-II), which in turn holds the inner electrode in position and includes a device for washing the deposit (see Experimental Section). Circulation of the electrolyte is effected by an air-pump similar to that used for the small cell. The small clearance between E and the tube C, and the crowding of the electrodes into this space, cause the velocity of flow through the inter-electrode space to be relatively great, thus accelerating the electrolysis. The bulb F above the electrode space serves to affect turbulent flow, as indicated by the arrows in Fig. 4-I, and thereby to bring about a desirable increase in agitation at this point. The stopper H is notched parallel to its axis

On account of its small active area, this disk electrode is particularly useful for the concentration of such small quantities as might escape observation when deposited on the larger cylindrical electrode.

Manipulation.—Successful practice of microchemical technique requires an almost meticulous attention to manipulative detail. It is therefore necessary to give somewhat elaborate descriptions of those manipulations involved in the operation of these cells that are not obvious from the drawings.

Electrodes.—The electrodes are first cleaned by immersion in hot, concentrated nitric acid, followed by rinsing with distilled water. They are next heated to dull redness in the oxidizing portion of a small Bunsen flame, then cooled and weighed on the Kuhlmann microbalance.⁴ The electrodes should of course always be handled with suitable forceps.

Assembly of the Cells

(a) **Cell for Small Volumes.**—After the electrodes have been weighed and assembled (Fig. 2-I), the unit is lowered into the cell vessel containing the solution to be electrolyzed, the volume of which is then so adjusted that its level coincides with the upper end of the tube A in Fig. 2-I. The air tube is now introduced as indicated, and bubbles admitted at

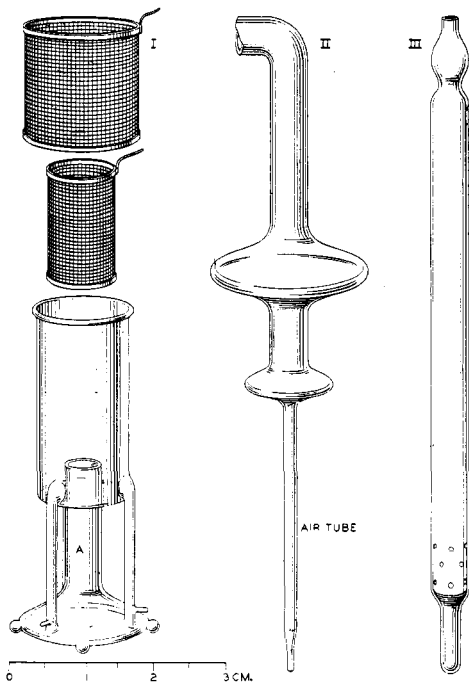


Fig. 2.—Detail of cell for small volumes.

such a rate that the liquid may be seen to flow regularly over the top of the tube A. Too much air should, of course, be avoided, since it may cause excessive spraying of the electrolyte. When the electrical connections are made, the apparatus is now ready for the electrolysis.

(b) **Cell for Large Volumes.**—The volume of the solution to be

⁴ For very precise work Riesenfeld and Möller² have suggested a preliminary electrolysis of pure, dilute nitric acid for the purpose of stabilizing the weights of the electrodes by saturating them with hydrogen and oxygen, respectively, before weighing. Our experience, however, has indicated that the errors from this source are generally below those of weighings made on microbalance of the Kuhlmann type, and may therefore be disregarded.

the fall of the current to a negligible value, the electrodes may be safely removed.

If the excessive dilution of the electrolyzed solution involved in this method is objectionable, the following arrangement may be used. The device shown in Fig. 2-III, which minimizes the quantity of wash water when only the inner electrode is to be weighed, consists of a glass tube, of outside diameter slightly less than the diameter of the electrode. The lower end terminates in a short, solid process which fits loosely into the central overflow tube A. For a distance of 1 cm. from the end, the walls of the tube are perforated by a number of small holes. The open end of this tube is connected, by rubber tubing, to a reservoir containing distilled water, the flow being controlled by a suitable pinchcock. At the completion of the electrolysis, the air tube is withdrawn from the cell and this special washing tube inserted. The cell is drained slowly, while the wash water is admitted at the same rate through the perforations. At the same time, and without interrupting the current, the electrode is drawn up over the tube A until it occupies a position level with the perforations on the washing tube. The electrode, held in this position, is withdrawn together with the washing tube from the electrolyte: at the time it is pulled through the liquid surface it is surrounded by nearly pure wash water. If the holes in the washing tube are sufficiently fine, and these indicated operations are executed rapidly and skilfully, the electrolyte suffers a minimum amount of dilution.

In the large cell, the central supporting tube which holds the electrode in position has a perforated lower wall similar to that just described, and the technique of washing is identical with that used in the small cell. When the small disk electrode is used, however, another washing arrangement is employed. Before beginning the washing the cup S (Fig. 4-III) is filled with water which is held in place by the bulb Q ground into S. When the electrode is withdrawn, the water is released and trickles down through the meshes of the disk as the latter moves upward.

After removal from the cell, the deposits are further washed with re-distilled alcohol and ether and dried for two to five minutes in an oven at 90°. They are then protected in stoppered test-tubes until weighed.

Experimental

Many uses for these cells will suggest themselves. A few typical examples will be given in which the two cells, singly or in conjunction, enable the microanalyst to carry out difficult determinations with precision and expedition.

Traces of Zinc in Aluminum Solutions.—To 250-cc. portions of solutions of zinc sulfate and aluminum sulfate of the indicated compositions, was added enough potassium hydroxide to redissolve the aluminum hy-

droxide and furnish about 5% in excess. The solutions were electrolyzed in the large cell at room temperature for four hours, under 3.5 volts. Since the purest reagents that could be obtained for preparing these synthetic solutions contained considerable amounts of iron, the deposited zinc was contaminated with this metal, causing a dark appearance and a spongy texture. In order to purify the deposit it was redissolved and the iron precipitated as the hydroxide between P_H 4 and 5. The zinc was then repleted from the filtrate on a coppered electrode in the *small* cell.

TABLE I
DETERMINATION OF TRACES OF ZINC IN ALUMINUM SOLUTIONS

Aluminum present, mg.	Zinc present, mg.	Zinc found, mg.	Error, parts per thousand
5000.0	1.000	1.012	+12
5000.0	0.500	0.483	-34
5000.0	.200	.193	-35
5000.0	.100	.099	-10
			Average = 23 ⁵

A practical application of this procedure occurs in the analysis of aluminum-base die-cast alloys having very low (about 0.01%) zinc contents. Preliminary results indicate the superiority of this method over the sulfide separation.

Separation of Small Quantities of Lead Present as an Impurity

(a) **Lead from Zinc.**—The data in Table II were obtained on 250-cc. portions of zinc sulfate-lead nitrate solutions of the indicated compositions, to each of which were added nitric acid to 2% and 25 mg. of copper sulfate, the latter functioning as a depolarizer which increases the hydrogen overvoltage and prevents the cathodic reduction of quadrivalent lead (Classen,² p. 226). Electrolysis was carried out at 60–70° for three hours at a potential difference of 2.8 volts. The final determination of the plated lead was made volumetrically as recommended by Lucas and Grassner.⁶

TABLE II
DETERMINATION OF TRACES OF LEAD IN ZINC SULFATE

Zinc present, mg.	Lead present, mg.	Lead found, mg.	Error, parts per thousand
10000.0	0.500	0.502	+ 4
10000.0	.200	.195	-25
10000.0	.100	.096	-40
			Average = 23

⁵ The precisions reported in Tables I to V, inclusive, are not to be regarded as representing the best that can be obtained: these data are presented merely as illustrations of types of separation to which the cells are applicable.

⁶ Lucas and Grassner, *Mikrochemie*, Emich Festschrift, 199 (1930).

(b) **Lead from Nickel.**—The experimental procedure and conditions were similar to those in (a), except that the nickel was present as the c. p. nitrate. Table III shows the results.

TABLE III
DETERMINATION OF TRACES OF LEAD IN NICKEL NITRATE

Nickel present, mg.	Lead present, mg.	Lead found, mg.	Error, parts per thousand
5000.0	0.500	0.495	-10
5000.0	.200	.196	-20
5000.0	.100	.092	-80
			Average -37

Similar results were obtained for traces of lead in aluminum solutions.

Separation of Small Quantities of Copper

(a) **Copper in Water.**—On the electrolysis at 60° for three hours under an e. m. f. of 4.0 volts of 250 cc. of distilled water containing 0.01 mg. of copper and 1% of sulfuric acid, using the small disk cathode, a dark-colored deposit was obtained. On exposure to the moist fumes of nitric acid the deposit dissolved instantly as shown by the brightening of the electrode. The electrode with adhering droplets of copper nitrate solution was then dipped into a drop of 10% potassium thiocyanate solution acidified with acetic acid, held on a microscope slide, and exposed to pyridine vapors. The characteristic yellowish-green needles of copper pyridine thiocyanate appeared. The dilution in this case amounted to 4 parts of copper in one hundred million.

(b) **Traces of Copper in Nickel Solutions.**—Table IV shows results obtained on electrolysis of nickel nitrate solutions 1% in nitric acid and 2% in sulfuric acid, containing the indicated small quantities of copper. A potential difference of 3.0 volts was applied for four hours at 60–70°. The copper plate obtained was dissolved, redeposited in the small cell and weighed.

TABLE VI
DETERMINATION OF COPPER IN NICKEL SOLUTIONS

Nickel present, mg.	Copper present, mg.	Copper found, mg.	Error, parts per thousand
5000.0	0.100	0.103	+30
5000.0	.200	.196	-20
5000.0	.500	.502	+ 4
5000.0	1.000	1.008	+ 8
			Average =15

Similar results were obtained for traces of copper in zinc solutions.

Determination of Impurities in Reagent Chemicals.—Incidental to this work, it was observed that the labels on "c. p." reagent chemicals sold

by prominent manufacturers are often misleading. Table V gives examples, and emphasizes the delicacy of micro-electroanalytical methods.

TABLE V
ANALYSIS OF "PURE" CHEMICALS

Manufacturer	Chemical	Excerpt from label	Lead found
A	Zinc sulfate	"Heavy Metals, <0.001%"	0.01%
B	Zinc sulfate	"Heavy Metals, 0.000%"	0.0015%
C	Zinc sulfate	(Impurities not indicated but ostensibly negligible)	Trace
A	Nickel sulfate	"Tested Purity"	0.045%
C	Nickel nitrate	(Impurities ostensibly negligible)	0.0005%

The following are typical examples of the uses of the cell for small volumes.

Determination of Nickel.—The solution used contained, in one liter, 40 g. of ammonium sulfate, 340 cc. of ammonia solution and 0.19740 g. of nickel as nickel sulfate; 5-cc. portions were used for the determinations, here as well as in the following examples. The air used for stirring was passed first through concentrated ammonia solution; this not only prevented the loss of ammonia from the electrolyte but maintained in it a practically constant concentration of the dissolved gas. The conditions for the best deposit proved to be rather critical, and were as follows: e. m. f., 2.4–2.5 volts (60–70 milliamperes);⁷ time, fifteen to twenty minutes; temperature 60°. Seven such samples were analyzed. The average weight of nickel recovered was 0.988 mg. (0.987 mg., present), the average deviation of the results from this average being ± 0.002 mg., with a maximum deviation of 0.004 mg.

Determination of Tin.—For this determination ammonium sulfide was found to give more satisfactory results as electrolyte than did oxalic acid. As recommended by A. Fischer,⁸ the electrode was first prepared by depositing a thin coat of copper, followed by one of tin from an oxalate solution. The electrolyte consisted of ammonium monosulfide solution containing sodium sulfite (to prevent formation of free sulfur). The best conditions for the electrolysis were found to be: e. m. f., 1.2 volts (1200 milliamperes); time, twenty to thirty minutes; temperature, 60°. After the electrolysis the electrode was washed with water, alcohol, carbon bisulfide, alcohol and ether, in the order given. Several samples, each containing 0.995 mg. of tin, were analyzed. Average weight of tin recovered: 0.996 mg.; average deviation from this average: ± 0.003 mg.; maximum deviation, 0.005 mg.

⁷ It is not practicable to give current densities, since the area of a fine gauze electrode is not accurately estimable.

⁸ Fischer, *Z. anorg. Chem.*, **42**, 382 (1904).

Determination of Zinc.—The difficulties met in the macro-determination of zinc are also operative here, and require special attention in working out a satisfactory procedure. From caustic solutions the deposit, while perfectly adherent, tends to assume a bluish-gray, granular form, in which it is subject to some oxidation. Three factors were found to favor this objectionable form: too high a temperature, too low an alkali content, and evolution of hydrogen at the cathode. Electrolytes weakly acid or containing cyanide were entirely unsatisfactory. Experiments showed, however, that by suitably regulating the important variables the caustic medium could be used to give accurate and precise results. The best conditions for the electrolysis, which must be strictly maintained to assure good results, are as follows: temperature, 25°; potassium hydroxide concentration, 10%; e. m. f., 3 volts (150 milliamperes); time, fifteen minutes. Cathodic evolution of hydrogen was prevented by giving the platinum gauze a thin preliminary plate of copper. Since the zinc deposit is very soluble in 10% caustic solution, especial precautions must be taken to wash out all traces of the electrolyte before interrupting the current; errors as great as 5% have been observed from carelessness here. Eleven analyses were made. With 0.898 mg. of zinc present (as c. p. zinc sulfate), the average weight of zinc recovered was 0.899 mg. The average deviation from this average was ± 0.003 mg., and the maximum deviation 0.013 mg.

Summary

1. Two new cells for micro-electroanalysis are described, both suitable for separating extremely small quantities of metallic ions from solutions, but the one designed to electrolyze a few cc., and the other several hundred cc.
2. Descriptions are given for the following determinations employing the cell for large volumes: traces of zinc in aluminum sulfate solutions; traces of lead in zinc sulfate and in nickel nitrate solutions; traces of copper in water and in nickel nitrate solutions; impurities in "chemically pure" reagents. For the small cell the following determinations are described: traces of nickel, of tin and of zinc.

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