

PHOTOMETRIC IODINE MICROCOULOMETER*

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Of recent years coulometry is more widely spread among the analytical methods of modern physical chemistry. This electrochemical analytical procedure is based on Faraday's law: the quantity of the electric current required to produce the appropriate quantity of the reagent used for the determination and for the quantitative electrolytic reaction, respectively, of the substance is determined. These methods are mainly microanalytical procedures suitable for the determination of 10^{-4} — 10^{-7} gram-equivalent substance. This means that the corresponding quantity of current that is 1 — 10^{-3} coulomb has to be determined as precisely as possible.

These measurements require a very precise microcoulometer which is easy to handle. BOSE and CONTRAT's [1] generally known silver coulometer, as well as LEHNFIELD's [2] and WILSON's [3] mercurial microcoulometer, respectively, are very precise but difficult to handle and this fact a good while retarded the general use of coulometry. Consequently, the improvers of the method soon turned from the direct measurement of coulombs to the so-called "time-current" method, namely, employing an electrical source of stabilized current rate, the time of passing and the intensity of current were measured; for these measurements precise measuring devices are available.

Only in recent years did some successful attempts to come back to the direct coulometry occurred. Among these attempts PROSZT's [4] coulometer shaped to a dilatometer has to be mentioned in the first place; this device was employed with good results, even for coulometric semi-microanalyses [5]. The aim of my investigations was to construct a coulometer which is easy to handle and can be employed with the required accuracy in the entire field of coulometry.

During my investigations I employed the photometric method so far not used for coulometry.** My idea was that if I discover an electrochemically

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** After having begun my investigations in 1954, I could continue the work only after an involuntary interruption of 2 years. In the meantime T. C. FRANKLIN and C. C. ROTH [6] in July 1955 published their colorimetric coulometer. Working with different acid-base

quantitative reaction the final product of which is coloured and can be photometrically determined in small quantities, then this reaction may be used for the measurement of current quantities. The electrochemical production of iodine seemed to be the most suitable for this purpose.

Iodine was produced in electrochemical way for the first time by PARKER and ROBINSON [7]. Both these researchers and also W. S. RAMSEY [8] and P. S. TUTUNDZIC [9] employ a diaphragm-type cell; the latter use the reaction for coulometric analyses, too. When making an electrolysis in an alkaline medium, liberation of oxygen was observed. Under such circumstances the deposition potential of oxygen amounts to 0,88 V; this value is very close to the deposition potential of iodine of 0,53 V. To avoid this difficulty the electrolysis was made in an acidic medium, in this case we were not afraid of oxygen liberation, as in this medium the liberation potential of oxygen is 1.68 V. This process has been used, since quite a long time for coulometry, so that the already formed iodine was titrated with thiosulphate. Recently R. TAFT and D. H. LIESE [11] studied this reaction and found it to be 100 per cent electrochemical; and so appropriate for microcoulometry.

The photometric determination of a small quantity of iodine was elaborated by GROSS and collaborators [12] who determined in solutions of 50 ml volume 1—14 γ iodine, by means of a Coleman's spectrophotometer.

Experimental

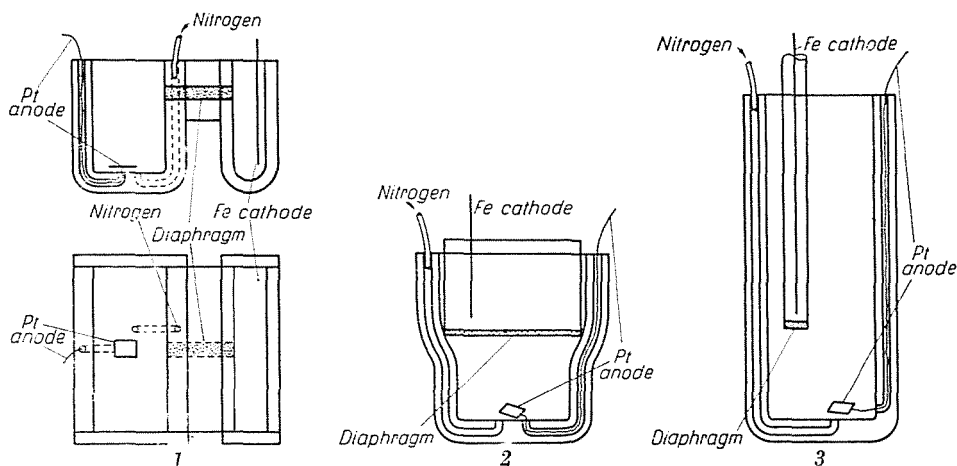
Solutions. Twice recrystallized C. P. chemicals were used to prepare the solutions. Extreme care had to be taken that the KJ should be free of iodate. When necessary, KJ was prepared by the reaction between C. P. KHCO_3 and C. P. HJ and heated in H_2 stream was used. The dissolution was performed in twice distilled water [12].

The anolyte consisted of 8 ml 0,1 N H_2SO_4 and 8 ml starch solution (2 g/l) after the mixing of which 1 g KJ was added and the solution diluted to 100 ml. The starch solution was prepared every other week, and in order to prevent oxidation of the anolyte, it was added to the solution immediately before the measurement. The composition of the anolyte is identical to that used by GROSS [12] for photometric determinations; conforming with our experiments, this composition proved to be excellently suitable for electrolysis. The catholyte consisted of 0,1 N H_2SO_4 .

According to TAFT [11], the metal platinum could be used as an anode. Platinum spiral was employed to increase the surface. Both platinum and iron could be used as cathode.

indicators they determined the colour of these indicators in colorimetric way generating electrolytically acid and base, respectively. Each indicator can be used in a very narrow interval but by varying them and employing other redox system, a measuring limit of about 0,01—1 coulomb could be reached.

Apparatus. Our intention was to complete the electrolysing cell of our coulometer so that the anode space could be used at the same time as photometric cuvette too. The electrodes and diaphragms could hardly have been used in the cuvettes of the Pulfrich photometer without it standing in the way of the passing light beam. The colour of the starch iodide is measured at a visible light (5750 Å); therefore the cuvettes made of plexiglass proved



Figs. 1—3. Different designs of cells

to be very suitable. A great advantage of the plexiglass is its excellent workability, rendering the mounting of the necessary aids possible (electrode, diaphragm, etc.) in the wall of the cuvette. The only disadvantage of the plexiglass as against glass is that it is softer and can be more easily cut and scratched. Therefore the two windows standing in the way of the light were later changed for optical glass which was stuck with Araldit 101 to the plexiglass. If carefully handled, cuvettes made of plexiglass could be satisfactorily used.

Various kinds of cuvettes were constructed (Figs. 1—3) and these could be used with equally good result. In every construction, the anode and cathode chambers are connected by diaphragms. In case of № 1 execution the diaphragm consists of agar-agar glue made with saturated KCl solution; this glue was inserted into the wall of the anode and cathode chambers, placed beside each other. In the apparatus № 2 and № 3 the diaphragm consisted of a glass filter of a G 4 porosity. As a matter of course, in case of every execution, care had to be taken that the level of the catholyte and anolyte should be equal so that the volume of the anolyte would not change, the catholyte and anolyte were not to mix, and the concentration of the iodine should not undergo a change.

The connection of the anode was conducted to the bottom of the cuvette through a hole bored into the wall of the plexiglass cuvette. In order to remove

the iodine formed from the vicinity of the anode, as quickly as possible, and to ensure an uniform iodine concentration of the solution, nitrogen was introduced into the solution near the anode during the electrolysis, to get uniformly mixed solution. With the help of continuous bubbling of the inert gas, the oxidizing effect of the air, that is the possibility of the following reaction



is also excluded. The introduction of nitrogen was also through the hole bored in the wall of the plexiglass cuvette. Naturally, the bubbling was interrupted during the reading of the photometer.

The optimum length of the cuvette, that is the optical layer thickness, amounts to 50 mm. A reference solution the composition of which was identical with that of the anolyte, was used in a cuvette fully corresponding to the anode chamber. In Hungary very few laboratories possess spectrophotometers; therefore our coulometer was elaborated by employing the generally known Pulfrich photometer with filter № 5 (5750 Å). This is a less sensitive instrument than the spectrophotometer; consequently, 15—200 micrograms iodine could be measured in 50 ml solution. This means that in the case of 30 ml anolyte volume, only $8 \cdot 10^{-3}$ — $4 \cdot 10^{-2}$ coulomb could be determined. The determinable current quantity is, however, dependent on the concentration; therefore our measuring limit could be changed, to a great extent, if different anolyte volumes are used, keeping the layer thickness at an identical value. Therefore identical iodine quantity yields different concentrations and different light transmissions. By using cuvettes (*Fig. 3*) which, keeping to a layer thickness of 50 mm, are usable with 15—90 ml anolyte volumes, the measuring limit was very broad: $5 \cdot 10^{-3}$ — $1 \cdot 10^{-1}$ coulomb could be determined (*Fig. 4*).

With the object of extending the measuring limit further, the aforementioned experiments were performed with the same apparatus, employing an anolyte containing no starch at all. In this case the tawny colour of the formed iodine was measured. In the literature there is no process described for the photometric determination of the formed iodine. According to our experiments, the maximum appears at 4360 Å. Using a № 9 violet filter of the Pulfrich photometer, the determination of $8 \cdot 10^{-2}$ —1 coulomb became possible (*Fig. 5*).

Accordingly, with the aid of our photometric iodine coulometer, measurements are possible within very broad limits, between $3 \cdot 10^{-3}$ coulomb and 1 coulomb. This makes possible the coulometric determination of 10^{-4} — 10^{-7} gram-equivalent quantities.

The calibration of the coulometer was carried out by the "time-current" method, measuring the passing time of the current with an electric stopwatch and the current intensity with a calibrated milliammeter.

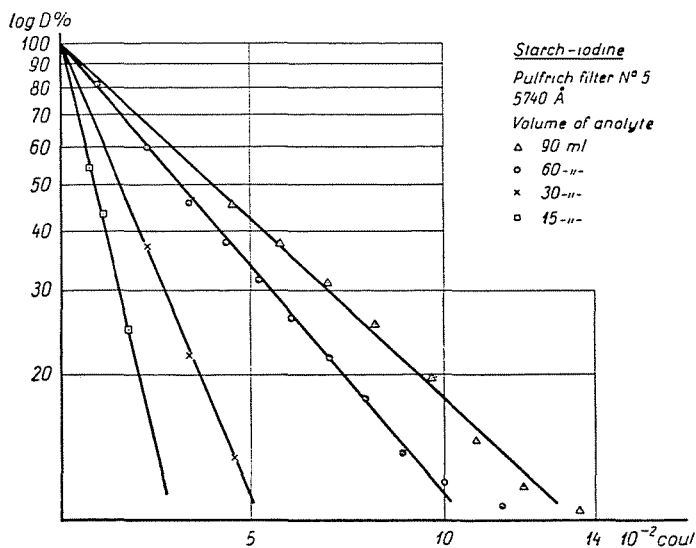


Fig. 4. Extinction of starch-iodine chromogen formed, plotted against numbers of coulomb with different volumes of anolyte

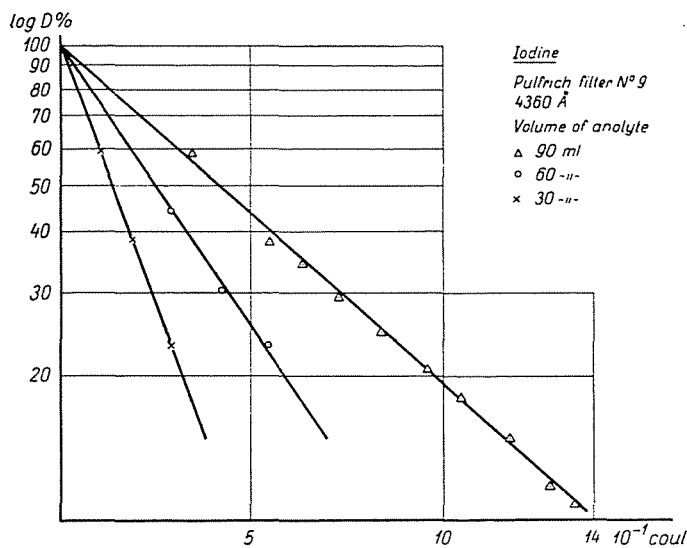


Fig. 5. Extinction of iodine formed, plotted against numbers of coulomb with different volumes of anolyte

With a view to controlling the measuring accuracy, a number of measurements were made with different current rates (0,1—20 mA) and current densities, respectively. The results of the measurements are shown in Fig. 6. It may be seen that within the afore-said measuring limit the maximum error amounts to 10%.

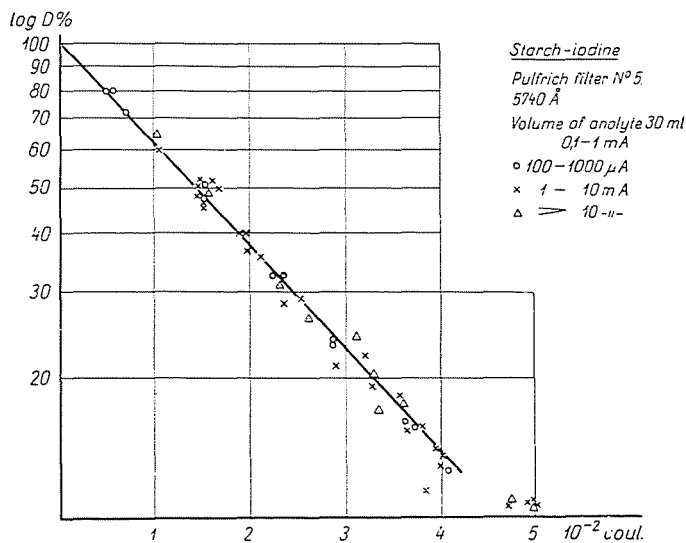


Fig. 6. Reproducibility of the data

A further increase of the measuring limit of our photometric coulometer is also possible. For example, when employing a spectrophotometer, our system using the $2J^- \rightarrow J_2 + 2e$ reaction is presumably suitable for determining one order of magnitude more coulombs, that is 10^{-4} coulomb too, and with other electrolytic systems a nearly infinite possibility of variations can be made. Thus *e. g.* TUTUNDZIC [14], together with his collaborator, established the conditions the maintenance of which assures the electrolytic oxidization of manganous salts to permanganates, with a current yield of 100%. Keeping to this experimental directions, and using the anolyte also as a reference solution, some preliminary experiments were made, and it was found that with this reaction the photometric coulometer makes the determination even of whole coulombs possible.

The photometric coulometer elaborated by the author is suitable in every field of coulometry to determine the required current quantity quickly and with appropriate accuracy.

The author is indebted to Professor János PROSZT for his interest and valuable advices given throughout these investigations.

Summary

In coulometry, a new branch of the electrochemical analyses necessitates the measurement of small current quantities with as high an accuracy as possible. Consequently, the elaboration of coulometers easy to handle was needed.

A photometric iodine coulometer suitable for this purpose and based on the photometry by Pulfrich photometer of electrolytically formed iodine was elaborated by the author.

The measuring limit of this method is very broad: $3 \cdot 10^{-2}$ —3 coulombs can be determined with a maximum error of 10%; this makes the coulometric determination of 10^{-2} — 10^{-5} gram-equivalent quantities possible. When using other systems, instead of the iodide-iodine reaction, e. g. electrolytic production of KMnO_4 , the measuring limit can be greatly increased.

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