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Coulometric Calibration of Microvolumetric Apparatus*

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Coulometric titration provides a simple and accurate means to calibrate microvolumetric apparatus such as burets, micropipets, and syringes. The apparatus to be calibrated is caused to deliver a solution of known concentration into an electrolysis cell where it is analyzed coulometrically. By the method described, volumes ranging from 300 μl to 1 μl have been calibrated with relative standard deviation of 0.03 to 3 percent, respectively.

Key Words: Constant-current coulometry, microburet calibrations, volume calibrations.

1. Introduction

Recent advances in the development of microvolumetric apparatus have benefited analysis in several ways. By use of solutions of ordinary analytical concentration and small volumes (10^{-3} to 10^{-6} ml), ultramicroanalysis of extremely small amounts of materials down to 10^{-12} g may be achieved [1, 2].[1] Furthermore, the use of concentrated reagents in microvolumetric amounts improves conventional titrimetric procedures by minimizing dilution effects on end-point determinations.

In order to conduct quantitative work with small volumes, however, it is necessary to have reliable methods for their calibration. Existing methods [2, 3] are essentially the same as have been used for macrovolumetric apparatus, for example, weighing the amount of a liquid of known density contained in or delivered by the apparatus. Unfortunately, this technique loses reliability when small volumes are concerned due to evaporative losses and liquid-transfer problems.

Titrimetric methods for calibration of small volumes have been suggested by Kirk [2]. However, he states that such procedures are inherently less accurate than weight calibration because all errors in the buret, in the end point, and in the concentration of the solution are included in the calibration.

The high precision of coulometric titrations [4, 5, 6] makes possible their use in volumetric calibrations. The method involves preparing a standard solution, dispensing a nominal volume of it with the volumetric apparatus to be tested, coulometrically determining the amount of reagent dispensed, and calculating the volume of reagent delivered.

2. Method

Primary standard potassium dichromate (NBS Standard Material 136b) is especially useful for the purpose of this method. It is stable in air, requires only superficial drying, and is highly soluble in water. Furthermore, it has been coulometrically assayed to a high degree of precision [6]. Accordingly, normal solutions can be readily prepared, corresponding to one microequivalent per microliter of solution.

The titration procedure is essentially that described in an earlier paper [6]. Briefly, it consists in the constant-current generation of Fe(II) at a platinum cathode in a solution 2 *M* in sulfuric acid and 0.5 *M* in ferric ammonium sulfate. The generated Fe(II) in turn reduces an equivalent amount of the dichromate. The end point is determined amperometrically (+0.85 V applied to a 1 cm^2 platinum indicator electrode, with reference to a saturated calomel electrode).

The coulometric cell used for high-precision calibrations consists of two electrode chambers separated by a two-compartment connecting tube. However, cells providing isolation of the anode in a glass tube whose bottom is a sintered-glass disk are satisfactory for the present purpose.

Polyethylene tubing drawn to a fine capillary opening is attached to the tips of the burets to be calibrated. Such tips provide a much smaller orifice than found on ordinary burets, thus minimizing interdiffusion of titrant with the solution when the tip is immersed, a procedure which is necessary for precise calibrations.

3. Results

The reliability of the coulometric method is illustrated with results obtained for the calibration of three typical volumetric instruments as follows:

A. An electrically driven positive-displacement buret (0.33 ml capacity) equipped with a revolution counter graduated to 0.01 microliter. The stainless

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[1] Figures in brackets indicate the literature references at the end of this paper.

steel piston has a nominal diameter of 0.099+in. The delivery tip is provided with a three-way stopcock so that the buret can be refilled in operating position.

B. A manual positive-displacement buret similar to the one described by Scholander [8]. The micrometer screw for volumetric read-out is subdivided in 0.2 μl intervals.

C. A 10 μl syringe subdivided in 0.1 μl intervals.

Results obtained for the calibration of buret A are given in table 1. The 300 μl graduation was also calibrated by the gravimetric method. Five determinations indicated the correction factor to be 1.0017, $s=0.0009$, which is in good agreement with the coulometrically determined value. Unfortunately, gravimetric calibrations are difficult if not impossible for samples much smaller than this.

TABLE 1. *Results for calibration of buret A*

Nominal volume delivered, μl	No. of determinations	Correction factor
		Volume, found/volume, nominal
300	3	1.0018, $s=0.0003$
100	8	1.0010, $s=$ .0015
50	3	1.0031, $s=$ .0021
20	3	1.0011, $s=$ .0013
10	3	1.005, $s=$ .002
5	5	1.008, $s=$ .003
1	7	1.002, $s=$ .034

An attempt was made to use buret A without immersing its tip but rather by collecting the fractional drop remaining on the tip by means of a glass rod. Results for 1- and 10-μl samples showed calibrations in agreement with those shown in table 1, but the standard deviations were about twice as large as those found with the immersion technique.

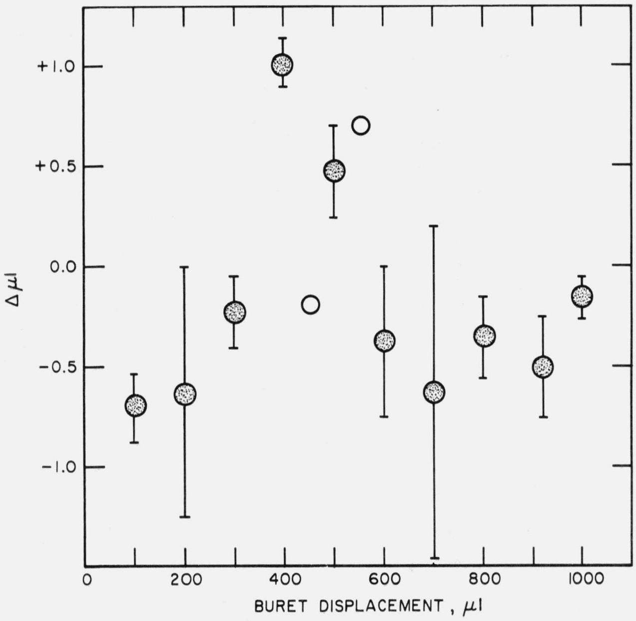

FIGURE 1. *Calibration of 100 μl aliquots delivered by different intervals of the piston displacement of buret B.*

○, Gravimetric values.
●, Coulometric values.
Average values are plotted. The vertical bars show the range of the individual measurements.

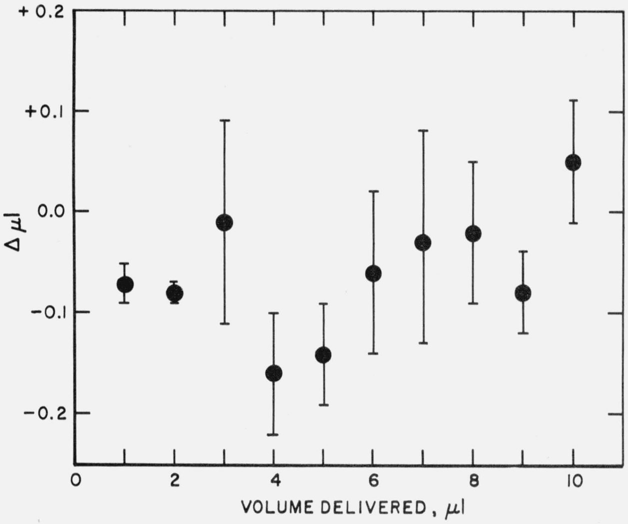

FIGURE 2. *Coulometric calibration of a 10-μl syringe.*
Average values are plotted. The vertical bars show the range of the individual measurements.

Results for the calibration of buret B at 100-μl intervals are shown in figure 1. The 0–100 μl interval was calibrated six times for which the correction −0.69 μl $s=0.17$ μl was found. Duplicate calibrations were made at all other intervals and the average values are plotted.

The open circles in the figure represent results of calibration of the 350 to 450 and the 450 to 550 μl intervals by a specially developed gravimetric procedure [9].

The results for duplicate calibrations of the 10-μl syringe, buret C, are shown in figure 2. In this case, the syringe was not mounted permanently in the cell. Rather, after adjusting to an initial reading, the needle was rinsed with distilled water, after which it was immersed in the cell for delivery of the volume indicated. The results no doubt indicate deviations from calibration as well as imprecision in delivering specified volumes with this type of equipment.

4. Discussion

The results of this investigation demonstrate the reliability of coulometric calibration of volumetric apparatus. For moderately small volumes (e.g., 300 μl), values comparable with gravimetric procedures are obtained. The coulometric method is specially useful for calibration of small volumes where weighing of calibrating liquids such as water and methylene iodide is impaired by evaporative losses and where weighing of mercury may be objectionable because of the drastically different physical properties of water and mercury.

The precision of the coulometric method appears to be limited by the sensitivity of the end-point determination. The present work was carried out with an 100-ml electrolytic cell, designed for high-precision measurements with amounts of 10 to 20 milliequivalent of materials [6]. In that application, an end-point uncertainty of about 0.01 microequivalent was noted which is comparable with the volumetric precision of the calibrations reported here. Some increase in precision of microcalibrations would undoubtedly be realized by the use of electrolysis cells of smaller capacity.

For work of the highest precision, the use of a standard such as potassium dichromate is preferred to establish the concentration of the calibrating solution. However, other solutions could be used provided that they were carefully standardized.

(Paper 70C1–165)

5. References

[1] I. P. Alimarin and M. N. Petrikova, Zavodsk. Lab. **24**, 29 (1958).

[2] P. L. Kirk, Quantitative Ultramicroanalysis (John Wiley & Sons, Inc., New York, N.Y., 1950).

[3] A. A. Benedetti-Pichler, Introduction to the Microtechnique of Inorganic Analysis (John Wiley & Sons, Inc., New York, N.Y., 1942).

[4] J. K. Taylor and S. W. Smith, J. Res. NBS **63A** (Phys and Chem), No. 2, 153 (1959).

[5] G. Marinenko and J. K. Taylor, J. Res. NBS **67A** (Phys and Chem), No. 1, 31 (1963).

[6] G. Marinenko and J. K. Taylor, J. Res. NBS **67A** (Phys and Chem), No. 5, 453 (1963).

[7] Handbook of Chemistry and Physics, 36th ed. (Chemical Rubber Publishing Co., Cleveland, Ohio, 1954–55).

[8] P. F. Scholander, Science **95**, 177 (1942).

[9] A. Johnson, NBS Metrology Division (212.31), private communication.