Precise Coulometric Titration of the Potassium Hydrogen Phthalate (NBS-SRM 84d). The Use of the Faraday Constant as an International Standard†

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The purity of the potassium hydrogen phthalate (NBS SRM 84d) was determined by precise coulometric titration. The purity obtained was 99.995±0.002% (standard deviation: 0.003%), and was in excellent agreement with the purities of the same SRM determined already in three laboratories in U.S.A. These results support the recommendation on the use of the Faraday constant as an international standard for titrimetric analysis.

In 1974, the Commission V.5 of the Analytical Chemistry Division of IUPAC recommended the use of the Faraday constant as an international standard for chemical analysis.[1] This recommendation has been partly supported by Yoshimori.[2] He discussed on the relationship between the results of chemical analysis and the basic SI units, and pointed out that the Faraday constant should be used as the international standard for titrimetric analysis. The results of gravimetric analysis are obtainable as the mass fraction by using the masses of a sample and of a precipitate, and usually the atomic weights or the molar masses of the elements concerned should be used. Therefore, the results of gravimetric analysis can directly be referred to the system of SI units (including the values of international atomic weights). There is no opportunity to use the Faraday constant as the standard for gravimetry.

On the other hand, a standard solution in a titrimetric analysis plays only the role which relates the elementary entities in a weighed portion of a standard reference material (SRM) to those of the material to be determined in a sample. Actually, an SRM of 100% purity is not obtainable, and it is nearly impossible to weigh an SRM without any contamination.[2] Therefore, the concentration of a standard solution and the results obtained by using the solution always include, as a factor, the purity of the SRM which was utilized for the standardization.

The SRMs for titrimetric analysis are now produced and certified individually in many countries. Therefore, the results of titrimetric analysis are internationally not unified yet. Thus, the Faraday constant becomes an excellent standard when it is used as the standard for titrimetric analysis.[2] Since 1973, the Faraday constant has been defined as the electricity of one mole of electrons (or protons).[3] Therefore, the purities (as mass fraction) of the SRMs for titrimetric analysis determined by a precise coulometric titration are obtainable from both the values of molar masses and the physical measurements (weight of sample and electricity consumed), and provide the fundamentals of the system of the SI units. Thus, the results of the titrimetric analysis obtained by using the standard solutions which were standardized with such SRMs, may also be referred to the system of the SI units.

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In order to use the Faraday constant as an international standard for titrimetric analysis, the experimental proof is not enough to get the international concensus, though the opinion has theoretically excellent fundamentals. One of the methods to support the use of the constant is to determine the purity of the same and important SRM for titrimetric analysis in collaboration with many laboratories in various countries by the precise coulometry. This paper presents one of such results, namely, the purity of the potassium hydrogen phthalate given by the National Bureau of Standards (SRM 84d) which was already assayed in three laboratories in U.S.A. by the precise coulometric titration.

Experimental

The instruments for the constant-current coulometric generation of hydroxide ion were similar to those shown previously.[4,5] From the certified values of the measuring devices, it is expected that the standard deviation in the measurement of the generating current was not greater than 0.005%. A 50 Hz electronic oscillator based on the frequency of a quartz crystal and a cycle counter were used to measure the time interval of the electrolysis. All weights were corrected against absolute weights. The other apparatus and reagents were the same as those of the previous paper.[5]

The sample was gently crushed in an agate mortar to about 100 mesh, dried at 120 °C for 2 h and cooled in a desiccator containing magnesium perchlorate before weighing. The procedure for the coulometric titration was the same as that of the previous paper.[5] The following values

TABLE 1. RESULTS OF ASSAY OF NBS 84d POTASSIUM HYDROGEN PHTHALATE

Taken (mg)	Found (mg)	Purity (%)
453.385	453.351	99.993
444.449	444.406	99.990
479.025	479.005	99.996
516.018	516.013	99.999
483.945	483.936	99.998
438.308	438.284	99.995
526.112	526.086	99.995
538.650	538.615	99.994
		Mean=99.995±0.002%[a]
		s_R[b]=0.003%

a) The 95% confidence interval for the mean value.
b) Standard deviation calculated from the range.

Table 2. Summary of the results of assays of NBS 84d potassium hydrogen phthalate

Author	Purity	No. of detns.	Standard deviation (%)	Purity recalculated[a] (%)	Drying condition	Ref.
Bates and Wichers	99.987[b]	3	0.002	—	100 °C	(6)
Taylor and Smith	99.977	5	0.003	99.992	120 °C 2—3 h	(7)
Eckfeldt and Shaffer	99.999	10	0.003	100.002	120 °C 2 h	(8)
Knoeck and Diehl	99.991[c]	6	0.005	99.991	110 °C 24 h	(9)
This work		8	0.003	99.995	120 °C 2 h	

a) Purity recalculated on the basis of the values of the Faraday constant and the molar mass in this work. b) Titrimetric analysis. c) Coulometric titration with the external generation of titrant.

were used for calculating the results; Faraday constant: 96484.6 C mol^{-1}, molar mass of potassium hydrogen phthalate: 204.223 g mol^{-1}, density of the reagent: 1.64 g cm^{-3}.

Results and Discussion

The results obtained by this investigation on the NBS SRM-84d are given in Table 1. The SRM was first assayed in NBS in 1957[6] by titrimetry based on the purity of the single crystal of benzoic acid, then by the precise coulometric titration in 1959.[7] Eckfeldt and Shaffer[8] and more recently Knoeck and Diehl[9] also analyzed the same sample by the precise coulometry. These laboratories are in U.S.A. and based on the same system of prototypes and standards. Their results are summarized in Table 2 in comparison with the results given in Table 1. The purities shown previously were recalculated by using the latest values of the Faraday constant and the molar masses in 1977 (shown above). The recalculated results are in excellent agreement with the purity obtained by this investigation, though they were based on the different prototypes of weight and electricity between Japan and U.S.A. Therefore, the results in Table 2 can be the fundamental data which support the recommendation on the use of the Faraday constant as an international standard for titrimetric analysis.

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References

1) IUPAC Information Bulletin, Appendices on Provisional Nomenclature, Symbols, Units, and Standards—No. 35, "Status of the Faraday Constant as an Analytical Standard," (1974), IUPAC Oxford; *Pure Appl. Chem.*, **45**, 125 (1976).
2) T. Yoshimori, *Bunseki*, **1975**, 551; *Talanta*, **22**, 827 (1975); *Z. Chem. (Leipzig)*, **18**, 211, 251 (1978).
3) IUPAC, "Manual of Symbols and Terminology for Physicochemical Quantities and Units, 1973 ed."
4) T. Yoshimori and I. Hikawa, *Bunseki Kagaku*, **16**, 927 (1967).
5) T. Yoshimori and T. Tanaka, *Anal. Chim. Acta*, **66**, 85 (1973).
6) R. G. Bates and E. Wichers, *J. Res. Natl. Bur. Stand.*, **59**, 9 (1957).
7) J. K. Taylor and S. W. Smith, *J. Res. Natl. Bur. Stand.*, **63A**, 153 (1959).
8) E. L. Eckfeldt and E. W. Shaffer, Jr., *Anal. Chem.*, **37**, 1534 (1965).
9) J. Knoeck and H. Diehl, *Talanta*, **16**, 567 (1969).