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STATUS OF THE FARADAY CONSTANT AS AN ANALYTICAL STANDARD

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INTRODUCTION

At the 1953 Conference of IUPAC, the late Professor P.S. Tutundžić proposed the adoption of the Faraday constant as an international standard for chemical application through the medium of coulometry,[1] and the suggestion was passed to the President of the, then, Analytical Chemistry Section for further study. The proposal was referred to the, then, Commission VI on Electrochemical Data, and a panel under the Chairmanship of Professor H. A. Laitinen was set up to examine it. The Panel took the opinions of some 50 eminent electrochemists, and digested the replies into the "Laitinen Report" which was presented to the Commission at the 1957 Conference.[2] Commission and Section approved the Report. The Report indicated, in brief, that the proposal was at least premature, and that adequate data of sufficient accuracy were not yet available for comparison with the best volumetric work. The Report added that, as a matter of principle, the adoption of a coulomb (meaning the Faraday constant; the coulomb is a defined unit) standard is equivalent to reference to pure silver by electrochemical rather than chemical means, and that, at best, the coulomb could only be considered as a secondary standard.

This conclusion was a true reflection of the state of the art at the time. However, even as the Report was being written, the first major breakthrough in instrumentation occurred with the introduction of operational amplifiers into potentiostat design.[3,4] At the same time, moreover, the work on high precision coulometry at the US National Bureau of Standards was gaining impetus under Dr. J. K. Taylor.[5,6] Tutundžić continued to advocate his proposal in his later publications, and the proposal has been renewed from time to time,[7] with increasing frequency as high precision results appeared. Although experimental techniques made such great strides in the 15 yr following the Laitinen Report as to supply the adequacy of data called for, yet one thing remained lacking. The subject of coulometry and current efficiencies remained to be rationalised; until all influential parameters had been identified, their effects examined, and a working theory developed from which predictions could be made of the experimental conditions required to meet a selected current efficiency, the proposal remained empirical and could not be accepted.

When the rationalisation was well advanced, Bishop renewed the proposal in respect of the Faraday constant

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at the 1967 Conference to the present Commission V.5, and was charged with a reappraisal of the Laitinen Report. The final stages of rationalisation were completed in 1969, and a preliminary Report was presented to Commission V.5 at the 1969 Conference. This Report summarised the high precision work achieved, stated the conclusions of the theoretical work, and examined certain fundamental matters of principle involved. It had been intended, before presenting a final report, to repeat the canvass of opinion on which the Laitinen Report was based, but the Commission deemed this now to be unnecessary, accepted the proposal in principle, and instructed the author to proceed to a final report. Such a report was completed early in 1970, but proved impossible to reproduce: the highly abbreviated report which follows has therefore been substituted.

REQUIREMENTS

The proper evaluation and validation of the proposal, granting that Faraday's Laws[8] are not in dispute, depends on three things. First, the value of the Faraday constant must be known to a precision and accuracy commensurate with its applications, at present 10–20 ppm. Second, conditions must be established for the electrochemical process which allow unequivocal interpretation, particularly of current efficiency, and this requires rationalisation of the processes (see Appendix). Third, as a corollary to the second point, it must be shown that coulometric determinations can be carried out experimentally with a precision and accuracy at least as good as those of classical chemical determinations.

1. THE FARADAY CONSTANT

The Faraday constant could be defined fundamentally in terms of the Avogadro constant and the protic (electronic) charge as the charge associated with the passage of one mole of electrons. It may alternatively be determined experimentally by either electrochemical or physical means. Many electrochemical determinations have been made, and perhaps the best electrochemical value up to the present time is that determined by the stripping of silver anodes into perchloric acid:[9] this value expressed in terms of the relative atomic mass of the carbon-12 isotope of 12 exactly is 96 487·2 A s mol⁻¹, with an uncertainty of about 18 ppm. The mean value quoted itself falls within the uncertainty of the presently accepted value determined by physical means, but the relative standard deviation of the electrochemical value is greater than the relative standard deviations of the Avogadro constant and the protic charge, which would suggest that the fundamental definition is to be preferred to the electrochemical experimental measurement. Independent physical methods have been used for the determination of the Faraday constant and gave values[10,11] in good agreement with the electrochemical values. The presently accepted value[12,13] of 96 486·7 ± 0·5 A s mol⁻¹ has been

determined by physical means, and is likely to be further refined, for example, by measurement of the product of the gyro-magnetic ratio, the mass and the magnetic moment of the proton. The uncertainty of the value just quoted is about 5 ppm, and is about 5 ppm better than the uncertainty in the relative atomic mass of silver, which is the present working chemical and electrochemical standard. Variation in the natural isotopic abundances of silver has not been entirely dismissed,[14] and this may derate the present standard a little.

It may be concluded that the Faraday constant is at least as good an experimental standard as silver, and it is a much more useful and practical one. It is, furthermore, known to a better precision than are many relative atomic masses.[15] The report of Commission II.1 on atomic weights[16-18] shows 23 elements for which relative atomic masses are known to a better precision than that for silver, and of these seven are given to a precision better than one part per million, including that for iodine. The remainder of the 23, except arsenic, are not particularly useful for coulometry or for the evaluation of the Faraday constant. The precision of the value of the Faraday constant is better, or considerably better, than the precision of the relative atomic masses of the other 70 elements. Indeed, for 36 elements, the precision of the relative atomic mass is worse than 0·01%, and for eleven of these it is not better than 0·1%. Despite the uncertainty in the measurement of current in terms of a voltage drop across a standard resistor (see below), the Faraday constant is already a better working standard than such materials as sodium carbonate, sulphamic acid, benzoic acid, potassium dichromate, metallic zinc, copper and mercury, and other familiar chemical standards. Marinenko[15] has stated that with the advent of such high precision methods as absolute coulometry, with which relative standard deviations better than 10 ppm are accessible, more precise values of relative atomic masses have become an imperative need.

Clearly on experimental grounds alone, the Faraday constant is a viable analytical standard, of a status better than, and a usefulness much greater than, the relative atomic mass of silver.

Practical aspects of measurement

The value of the Faraday constant is given in terms of the unit of electric charge, the coulomb, which is a derived SI unit, being the product of the ampere and the second, both of which are defined SI base units. The second is defined in terms of an electronic transition in the isotope caesium-133 to a precision of 1 part in 10^{11}: it is probable that this definition will be amended to one of a precision approaching 1 part in 10^{13}. This standard is experimentally accessible, and electronic time measurement to a precision of 1 part in 10^9 is routinely practicable. Time measurement therefore places no restraint on the accuracy of the measurement and application of the Faraday constant. The ampere, however, is defined in an idealistic way that is not directly accessible experimentally. The high precision measurement of current is realised by the current balance, and calls for the evaluation of and correction for a number of factors. This involves measurement of distance to the same precision as the defined metre, based presently on an electronic transition in the krypton-86 atom. By such means, current and time can be measured to about the same precision. Current balances of this kind, with associated laser equipment, are not commonly available, so the experi-

mental measurement of current is almost invariably done by measurement of the voltage drop across a standard resistor through which the current is flowing. This shifts the measurement from a single base SI unit to two derived units: the ohm (dimensions $kg\, m^2\, s^{-3}\, A^{-2} = V\, A^{-1}$) and the volt ($kg\, m^2\, s^{-3}\, A^{-1} = J\, A^{-1}\, s^{-1}$): and in practice to reference to the working standard of voltage, the Weston cadmium cell. The common measurement of a quantity of electricity is therefore limited in its accuracy by the uncertainty in the practical values of the volt and the ohm, which amounts to several parts per million.[7] The present state of the art in constant current supplies touches the same level of accuracy, and in the foreseeable future the constancy of current sources and the accuracy of measurement will have to be refined by an order of magnitude in order to realise the full potential of high precision coulometry.

2. HIGH PRECISION COULOMETRIC DETERMINATIONS

The value of the Faraday constant will need refinement by an order of magnitude in accuracy in the next decade, but the principle of its use is not in doubt. Its application is another matter entirely. It must be shown experimentally that determinations can be made with a precision and accuracy at least as good as those attained by classical methods using chemical standards. Evaluations of the Faraday constant are high precision coulometric operations,[9] but are excluded from this survey. Following up work on the coulometric coulometer Taylor and Smith[5] at the U.S. National Bureau of standards achieved relative standard deviations of 30–100 ppm in coulometric assays of sodium carbonate, hydrochloric, adipic and benzoic acids and potassium hydrogen phthalate.[6] Marinenko and Taylor[19] attained relative standard deviations of 70–90 ppm in the assay of halides with anodically stripped silver ion. Later[20] they assayed potassium dichromate by generation of iron(II) with an overall relative standard deviation of 29 ppm: four sets of these assays yielded relative standard deviations of less than 10 ppm. Their work continued with the generation of iodine with a current efficiency loss of less than 1 ppm, and the assay of arsenic (III) with a relative standard deviation of 30 ppm.[21] Assays of benzoic and oxalic acids gave relative standard deviations of 25 and 34 ppm respectively.[22] Marinenko has used high precision coulometric titration of boric acid in mannitol solutions to test the Roller equations for the difference between equivalence and potentiometric inflection points.[23] Coulometry has also been used by Marinenko at the National Bureau of Standards for the assay of highly purified potassium chloride and single crystal gallium arsenide, in a recent OECD materials characterisation programme.[24] Assay of the potassium chloride by coulometrically generated silver ion was accomplished with a relative standard deviation of a single determination of 22 ppm. For the second material, gallium was determined by ethylenediaminetetraacetate, which was, in turn, standardised by coulometrically generated zinc, while the arsenic was determined by coulometric iodimetry. Relative standard deviations of 50 and 40 ppm, respectively, were achieved. The gallium/arsenic ratio was found to be 0·999 994 with a standard deviation of 0·000 065. The high precision coulometry unit in these laboratories is now well established. Work is also in progress at the National Physical Laboratory in the United Kingdom.[13] Other laboratories, both industrial and academic, have also made contributions. In the Imperial Chemical Industries

Standards Laboratory, Cooper and Quayle[7,25] attained a relative standard deviation of 30 ppm in the assay of sodium carbonate. This sample had been collaboratively assayed against atomic mass grade silver by the Analytical Standards Committee of the Society for Analytical Chemistry (U.K.) by a weight titrimetric method, with a relative standard deviation of 29 ppm. Coulometric and weight titrimetric results agreed to within 10 ppm. Eckfeldt and Shaffer[26] at Leeds and Northrup have assayed constant boiling hydrochloric acid and potassium hydrogen phthalate. Goode and Herrington[27] determined uranium with a relative standard deviation of 90 ppm by a differential method like that of Rechnitz.[28] Later, Goode, Herrington and Jones[29] achieved a relative standard deviation of 40 ppm in a cerimetric finish for the determination of uranium. Goode and Jones[30] also made compleximetric determinations of thorium with a relative standard deviation of 200 ppm. This work has been done at Atomic Weapons Research Establishment, Aldermaston (U.K.) and similar work has been done at EURATOM, Geel. Sulphamic acid from the Standards Committee has been assayed in Bishop's laboratory with a relative standard deviation of 90 ppm, of which at least 50 ppm can be ascribed to inadequate potential measuring equipment.[31-34] Other high precision work involving external generation has been reported.[35]

These are but a few examples, and may be capped by the statement by the National Bureau of Standards that the evaluation of pure individual elements or compounds as standard reference materials for issue would henceforth be done by coulometric methods.[36]

3. RATIONALISATION AND THE PREDICTION OF CURRENT EFFICIENCIES

The idelal requirements are (1) that the desired reaction should proceed (a) virtually to completion and (b) with 100% current efficiency, and (2) that no electroactive species should enter or leave the sample compartment of the electrolysis cell. Only one type of electrode process can possibly be of 100% current efficiency: the electrolysis of the solvent (which may be a fused salt) and its ions: and then only under ideal conditions meeting requirement (2) above. In all other cases, at least two reactions will be proceeding at the working electrode, no matter what its potential may be. The real requirement (1a) is that the reaction should proceed to a known, or regulated, extent, and (1b) that the desired reaction should proceed at a known current efficiency or that conditions should be regulated to yield a required, or a maximum, current efficiency.

The current efficiency

Let the current of the desired reaction be IS, the undesired currents due to impurities or other components in the system be, in sum, $IImp$, the current due to electrolysis of the substrate—solvent or molten salt and its ions—be IB, and when an intermediate is used as in amperostatic coulometry, the current due to the electrode reaction of this intermediate be II; then the total current $IT = IS + IImp + IB(+II)$. The current efficiency, Eff, in percentage, or the loss in current efficiency, $Loss$, in ppm (which is more appropriate to the context of standards work) are

$$Eff = \frac{100(IS(+II))}{IS + IImp + IB(+II)}$$

$$Loss = \left(1 - \frac{IS(+II)}{IS + IImp + IB(+II)}\right) \times 10^6. \quad (1)$$

Solution of either form of eqn (1) requires evaluation of the several currents under the experimental working conditions, that is, at a constant total current, IT, in amperostatic coulometry, or at a controlled working electrode potential in potentiostatic coulometry.[37-39]

Migration effects

Requirement (2) above has reference to the migration of species through the separator dividing the working compartment from the auxiliary compartment of a divided coulometric cell, or to the interaction of species consumed or produced at working and auxiliary electrodes in a cell without liquid junction. This may lead to a loss of sample species by migration out of the working compartment, or to a loss of current efficiency at the working electrode because of migration of electroactive species, either reactants or products, into the working compartment. It is possible to minimise transfer (thermal diffusion, convection and bulk transfer of electrolyte) of both ionic and neutral species by immobilising the liquid junction between the compartments by means of a gel, or by suitable cell design. The current for the coulometric reaction must, however, be transported through the separator by means of ions, and for every Faraday of charge transferred, one equivalent of ions must cross the separator. All the ions, including those of the sample, will contribute to this process in proportion to their sign and magnitude of charge, concentration and mobility. If the nature and concentration of all the species present in working and auxiliary electrolytes are known, together with their mobilities, then the transport number, t_S, of the sample species can be calculated, and as the sample species is consumed in the coulometric process the transport number will decrease in proportion to IS. Integration over the time of the reaction will then give the loss of sample, if any. Similar treatment of any deleterious reactant or product in the auxiliary compartment will give the integrated loss of charge due to electrolysis of the deleterious species in the working compartment. If the desired reaction at the working electrode is cathodic, and the sample species is, or can be made, cationic, then there will be no loss of sample; and likewise for anodic reactions of anionic samples. If it can be arranged that the components and reaction products in the auxiliary compartment are innocuous should they be transported into the working compartment, then no error will arise from migration into the working electrolyte. This is not always possible, and then corrections must be made by the integration outlined, or determined experimentally.[37-41] It is possible to write explicit integral equations and this has been done,[42] but there are many cases to be set out, and generalised equations are highly diffuse. It is better to take the particular set of experimental conditions and to write and solve the simple specific equations for them. In conclusion, the migration problem is soluble by classical transport theory.

4. CONCLUSION

Coulometry, particularly amperostatic coulometry, is a technique capable of giving results of a very high precision and accuracy, better in many cases than those of the relative atomic or molecular masses of the materials being analysed: in such circumstances the accuracy cannot be assessed, but the precision can be measured. By coulometry a great multiplicity of chemical standard substances, and the difficulties associated with preparing and handling them, are replaced by a single standard—the

Faraday constant—which will serve for all manner of reactions and samples, and a substantial simplification of manipulation results. Moreover, coulometry allows many determinations not possible by other means and permits the use of electrolytically generated reagents which are difficult or impossible otherwise to handle. The Faraday constant has a precision and accuracy better than those of the relative atomic mass of silver, and is a very much more useful standard. The processes of coulometry have been rationalised so that it is possible to predict conditions under which a reaction proceeds at maximum, or any selected, current efficiency, and errors arising from transport of electrolyte between compartments of divided cells can be minimised or evaluated. Precisions and accuracies at the parts per million level have been attained for all the principal types of reactions, but it still remains essential to evaluate each new reaction experimentally in order to validate the use of the Faraday constant in a specific determination.

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APPENDIX
EVALUATION OF CURRENTS AND CURRENT EFFICIENCIES

The problem is to evaluate the several currents for a given working electrode potential, and *vice versa*, at any stage in a coulometric determination.[37] A working theory has been developed,[37,38] and the influential parameters have been identified and examined.[39] A study of parameter variations has led to the development of Pattern Theory for oxidation–reduction[40] and solvent molecule and ion[41] reactions which explicitly and quantitatively demonstrates parameter effects. This study, moreover, produced a fast rigorous method for the measurement of the mass and charge transfer rate parameters. These have by far the greatest influence on current efficiencies, and it is necessary to be able to determine them under the actual conditions of a coulometric determination.[37,38] Methods of so doing have been reviewed,[43] and a number of systems has been investigated.[44] This work is being extended in respect of both methods of determination of kinetic parameters and the chemical systems involved. The experimental results obtained[44,45] attest the validity of the rationalisation,[37,38] and the determination of current efficiencies before, during and after coulometric determinations is now routinely possible. Parameters[39–41] under the control of the operator can now be so controlled as to produce the highest possible current efficiency.