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Major applications of electrochemical techniques at national metrology institutes

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Abstract

A review of the state of the art of electrochemical methods at the highest metrology level in national metrology institutes (NMIs) is given, with emphasis on standardization work (primary methods) in the fields of pH and electrolytic conductivity, as well as use of coulometry. Attention is also given to certain technical issues in the implementation of these methods.

1. Introduction

The best feature of electrochemical methods from the perspective of an analytical chemist is the direct conversion of chemical information into electrical signals such as current, potential and charge. Electroanalytical techniques are widely used to control water and food quality and safety as well as to monitor the environment, industrial processes, health care and production of advanced materials. Confidence in the reliability of the results requires complete knowledge of the chain of traceability linking the measured value of the quantity in the sample to a unit in the *Système International d'Unités* (SI), or, where this is not possible, to internationally agreed and stated references. This review considers the literature in the relevant areas through April 2007.

The Consultative Committee on Metrology in Chemistry (CCQM) Electrochemical Analysis Working Group (EAWG) started in 1998. Initially focused on pH metrology, the EAWG has since expanded to include electrolytic conductivity and coulometry. One of the main objectives of the EAWG is to develop and improve electrochemical techniques as primary methods and as high-level methods linked to primary ones. The terms of reference, especially in coulometry, include the interest of the Inorganic Working Group. Joint meetings proved to be a useful discussion board for interdisciplinary problems.

The importance of international assessment of measurement capability, including a unified approach to uncertainty, has increased considerably with the adoption of the Mutual

Recognition Arrangement [1], which facilitates the international recognition of certified reference materials (CRMs) issued by NMIs. For analytical data and CRMs to be internationally accepted, it is further necessary to demonstrate the equivalence of the national traceability structures, including the national measurement standards. The main mechanism to achieve this goal at the CCQM level consists of key comparisons (KCs) and pilot studies.

Table 1 lists the KCs and pilot studies organized by the EAWG to date, with the participating NMIs.

Traceable pH measurements are needed in many areas and are of high economic and scientific importance.

In health care, safety, biochemistry and environmental monitoring, pH is among the most frequently measured physicochemical properties [5]. Although pH is one of the most frequently measured quantities in the field and in industry, the problems involved in the traceability of pH are not well known to these users. Recent research in environmental science and biochemistry has revealed that the measurement uncertainty in pH makes a major contribution to the uncertainty of thermodynamic data and geochemical transport models [6].

One characteristic of pH measurements is that their traceability does not extend to the SI at the uncertainty level necessary for measurements by the end user. Internationally recognized primary pH reference buffer solutions, related as closely as possible to the thermodynamic definition of pH, and provisions for secondary measurements of pH to be traceable to the primary references are each urgently needed [7]. The present review summarizes both the primary method for pH and the dissemination of traceability to the field.

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Table 1. NMIs participating [2] in EAWG KCs and pilot studies by regional metrology organization and field.

CCQM-organized key comparisons (K) or pilot studies (P)			K9 + K9.1 ^a P37	K34 + K34.1 ^a	K36.a K36.b
Total KCs/Pilot Studies			4/3	1/3	2/2
Participant (NMI) ^c	Country ^d	RMO ^e	pH	Coulometry	Conductivity
BAM	DE	E		1/3	
CENAM	MX	S	4/2	0/1 ^f	2/1
CMI	CZ	E	3/3		2/2
DPL/DFM	DK	E	4/2	0/1	2/2
GUM	PL	E	4/1	0/2 ^f	2/2
IEN	IT	E	0/1		2/2
INMETRO	BR	S	2/2		2/1
INPL	IL	—	1/3	0/1 ^f	0/2
KRISS	KR	A	3/2	1/2	
LNE	FR	E	1/1	0/1 ^f	
NCM	BG	E	2/2		0/1
NIM	CN	A	3/1	1/3	
NIST	US	S	4/1	1/3	2/2
NMi	NL	E			0/2
NMIJ	JP	A	4/1	1/2	
NPL	UK	E		0/1 ^f	0/2
OMH	HU	E	1/1		2/2
PTB	DE	E	4/3	0/1	2/2
SMU	SK	E	4/2	1/3	2/2
SP	SE	E			2/1
UMTS	UA	C	1/0		2/2
VNIIFTRI, UNIIM, VNIIM	RU	C	3/0	1/2	2/2

^a K9.1 and K34.1 bilateral with K9 and K34, respectively.

^b P82 and K19 run in parallel.

^c See [3] for full NMI names.

^d Country designations conform to ISO 3166-1 [4].

^e Regional Metrology Organization (RMO): E—EUROMET; S—SIM, A—APMP, C—COOMET.

^f Participant used titrimetry in CCQM-P19/19.1.

The 2002 International Union of Pure and Applied Chemistry (IUPAC) recommendation on the measurement of pH [8] defines traceability for primary pH values to the SI and to a conventional reference frame which is recognized worldwide. This document also includes estimates of the uncertainties for representative lower-level measurements. This information permits linking field-level measurements to the primary standards by an unbroken chain of comparisons. A rational choice can be made by the analyst of the appropriate procedure to adopt to achieve the target uncertainty of sample pH [9].

Coulometric methods are capable of high precision and accuracy and are fully described by Faraday's Law. Coulometry is classified as a potential primary direct method for the amount of substance [10]. The coulometric determination of the amount of substance is directly linked with the mole, a base unit of the SI. Hence, coulometry requires no reference for comparative evaluation and traceability. The Faraday constant is one of the fundamental constants [11] and has been proposed as an ultimate standard in chemistry [12, 13], providing an alternative source for measurement traceability [14, 15] compared with the traditional approaches [16]. The main use of coulometry is in the certification of primary reference materials that can be subsequently used to disseminate traceability to chemical measurements, e.g.

titrimetry and methods that require calibration standards. In most cases, coulometry is suitable only for analyses of relatively pure substances or solutions, as information on the sample is needed for minor corrections. This characteristic is in line with its use at the higher metrological levels. If the contribution of co-titrated impurities is not known, the expression of the measurand must take this fact into account, stating what is actually determined. Examples are given in section 3.

The measurement of electrolytic conductivity is a functional analytical tool applied in various fields of science and technology. Although it is a non-specific sum parameter, conductivity measurements yield an estimate of the total concentration of ionized substances in a liquid sample. Under given conditions, conductivity is a useful and accessible quantitative measure of purity, replacing laborious and expensive chemical analyses. Important applications are in water purity assessment, according to normative standards; and in pharmaceuticals, drinking water, the food industry, health care, and environmental monitoring.

Electrolytic conductivity, κ , is the most widely used parameter for monitoring the ionic purity of water. To ensure data reliability and to comply with quality requirements, especially in the pharmaceutical industry [17], periodic calibration of the measuring instrumentation using reference

materials traceable to the SI must be performed. Although traceable reference materials and methods exist for calibrations of conductivity measurements at high κ values [18], stable reference materials are not available at low κ values ($\kappa < 10 \text{ mS m}^{-1}$ at 25.0°C). Improvement is expected from new approaches to afford calibration, traceable to the SI, of conductivity meters used in the ultra pure water range [19].

Possible future issues of great interest to the EAWG are the measurement of ion activity by ion-selective electrodes, the determination of salinity and the measurement of dissolved oxygen concentration. These measurement methods are presently applied at the field level on a large scale, without traceability to internationally recognized references, where such references currently even exist.

2. pH

2.1. Definition of pH

The pH value, expressing the acidity of the solution, was originally defined in terms of hydrogen ion concentration [20]. The current IUPAC recommendation [8] is now based on the thermodynamic definition, the negative decadic logarithm of the relative activity of the solvated hydrogen ion, a_{H^+} [21]. As single ion activities are not accessible by measurement [22–24], an extra-thermodynamic convention is introduced to approximate this thermodynamic definition.

2.2. Primary measurement method for pH

NMIs use the primary method for pH [8] to assign pH values to reference buffer solutions at the top of the national traceability chains. The primary method is based on the measurement of the potential difference of cell I [5, 8, 24, 25] without transference, often called the Harned cell [26]⁵:



The primary measurement *per se* yields a quantity known as the ‘acidity function’, $pa = -\log(a_{\text{H}^+}\gamma_{\text{Cl}^-})$ [8, 27, 28], where γ_{Cl^-} is the activity coefficient of the Cl^- ion at its molality, m_{Cl^-} . This pa measurement must be performed at a minimum of three m_{Cl^-} values.

To obtain the pH from the measured pa values, two steps are necessary [8]. First, the pa values are linearly extrapolated to $m_{\text{Cl}^-} \rightarrow 0 \text{ mol kg}^{-1}$, yielding pa^0 , the value of pa corresponding to zero chloride molality. Second, the value of the limiting (trace) activity coefficient of Cl^- , $\gamma_{\text{Cl}^-}^0$, at the ionic strength of the buffer with no added chloride is evaluated, using the Debye–Hückel equation [29] and the Bates–Guggenheim convention [30]. The pH may then be calculated from equation (1):

$$\text{pH} = pa^0 + \log \gamma_{\text{Cl}^-}^0. \quad (1)$$

The procedure outlined above establishes traceability to the SI if the expanded uncertainty attributable to the Bates–Guggenheim convention, estimated as 0.01 (95% confidence

interval) [8], is included in the uncertainty budget. This is already practised by some NMIs in certification of CRMs. Values of pH that include all sources of uncertainty *excepting* that of the Bates–Guggenheim convention, i.e. $u(\text{pH}) = u(pa^0)$, as is the common practice, are considered conventional pH values, which suffice for most uses [31].

The primary buffer solutions recommended by IUPAC today are based on the so-called multipoint pH protocol developed by Bates and co-workers at the National Bureau of Standards (US), now the National Institute of Standards and Technology (NIST) [23, 24]. Each primary buffer is a dilute aqueous solution between pH 3 and pH 10 and is certified in a temperature range from 5°C to 50°C . Criteria for the selection of primary buffers are given in [8]. The reagents used to produce the primary buffers must also be free from contaminant halides, to ensure linearity [32] in the extrapolation of pa to obtain pa^0 . An alkali chloride of certified high purity and low Br^- impurity [33] is used for the addition of Cl^- to the buffer. NaCl is usually preferred over KCl, owing to its typically lower Br^- impurity level.

2.3. State of the art

Approximately 20 NMIs (and their number is increasing, e.g. [34]) are currently equipped to make primary pH measurements in the Harned cell. Some systems have been described in various publications [25, 35–40]. Harned cells must fulfil several criteria. The H_2 stream that enters the Pt| H_2 half-cell must be saturated with water vapour at each measurement temperature. The anode and cathode chambers of the electrochemical cell must be separated with restricted mixing. The design of the Pt| H_2 half cell should efficiently exclude atmospheric O_2 .

NMIs use several different designs of Harned cells. The most widespread is the cell developed at NIST [25], but other cell designs have been developed independently and are being successfully used [39]. Results obtained with the different cell designs are equivalent. Differences mostly pertain to the ease of handling, stabilization time and the maximum time of a run before changes in solution composition become significant. The NIST design enables runs that last for many hours and uses no frits, which can be difficult to clean. The SMU cells [39] minimize dead volume (yielding rapid equilibration times) and simplify cell handling.

Four KCs for pH have been organized by the EAWG [41–45]. The agreement between the results and key comparison reference value (KCRV) expressed as a standard deviation is about 0.003 for experienced laboratories and about 0.007 for all laboratories, including newcomers. Participating NMIs in the pH KCs have observed a number of instrumental and methodological problems. Pilot studies present an opportunity to investigate issues, such as the stabilization time of Ag/AgCl electrodes [46], that have caused problems in KCs. Pilot studies are also used by newcomers to test their measurement capabilities.

Two routes are used to disseminate pH measurement traceability to users: liquid buffer solutions and solid materials. Stability and shelf life are problem points for the buffer

⁵ The Cl^- must be added to the buffer to poise (stabilize) the Ag|AgCl electrode in cell I.

Table 2. Change yielding $\Delta\text{pH} = 0.001$ in primary pH measurement.

Source	Change yielding $\Delta\text{pH} = 0.001$
<i>Measurement of E°</i>	
Voltage (measurement + stability), E	59 μV
Temperature, T	0.07 K
Molality of HCl, m_{HCl} (relative change)	0.11%
Activity coefficient, $\gamma_{\pm\text{HCl}}$	0.001
Pressure of H_2 , p_{H_2} (measurement + corrections)	~ 400 Pa
<i>Measurement of pH</i>	
Voltage (measurement + stability), E	59 μV
Temperature, T	0.02 K to 0.05 K
Chloride molality, m_{Cl^-} (relative change)	0.23%
Ionic strength	0.0016 mol kg^{-1}
Debye–Hückel coefficient [29]	0.005 $\text{kg}^{3/2} \text{mol}^{-1/2}$
Pressure of H_2 , p_{H_2} (measurement + corrections)	~ 400 Pa
Extrapolation of $\text{p}a$ to yield $\text{p}a^0$ (intercept)	0.001

solutions (especially the alkaline buffers), but the CRM is directly usable in the field. Solids CRMs require the user to prepare the solution with low uncertainty, without verification of the preparation by the NMI. However, solid CRMs have a much longer shelf life (> 10 yr). Homogeneity of the CRM must be assessed with either approach. Different approaches are used in different countries, depending on history, existence of an intermediate level (calibration laboratories) and size of the country. The three most used approaches are production of primary and secondary buffers at the NMI (SMU), calibration of secondary buffers at accredited calibration laboratories (PTB [36]) and direct distribution of solid materials certified by the primary pH measurement (NIST [25]).

Several technical reports have appeared in *Pure and Applied Chemistry* related to non/aqueous and mixed solvents [47–49], seawater [50], acid rain [51] and pH in D_2O solutions [52]. Different aspects of pH measurement and application were presented in two PTB seminars [53, 54]. Selected papers were published [55] in a special issue of *Analytical and Bioanalytical Chemistry*.

2.4. Uncertainty

Sample uncertainty budgets have been published [8, 56]. The combined standard uncertainty of $\text{p}a^0$ (i.e. exclusive of the Bates–Guggenheim convention) can be better than 0.002. The impact of the influence quantities on the final uncertainties can be easily visualized from table 2.

Experience shows that although the list of sources shown here is fairly complete, they themselves contain several contributions, which are not always taken into account [57] in estimating the uncertainties. A test of the reproducibility of E for HCl, or of a buffer with the same m_{Cl^-} , in several cells can reveal such unsuspected contributions. The spread should be less than 200 μV , but it may be as great as 1 mV, which cannot be explained by the measurement of the quantities alone. Possible causes are incomplete saturation of the cells with H_2 , diffusion of O_2 into the Pt| H_2 half-cell, contact problems with the electrodes, preparation of solutions and contamination during the filling of the cells (especially with alkaline buffers).

The primary pH procedure depends on a precise value for m_{HCl} of the HCl solution used in the determination of standard

potential, E° , of the Ag|AgCl electrode in cell I. This source of uncertainty is usually among the most significant. The method of choice for the assay at most NMIs is constant-current coulometry [58]. In some cases a HCl solution with higher molality (0.1 mol kg^{-1} to 1 mol kg^{-1}) is assayed. This solution is subsequently diluted by mass to obtain exactly the desired molality. If titrimetric standardization is used, the assay of Cl^- by precipitation titration (AgCl) is easier than acidimetric assay (of H^+), since the CO_2 interference in acid–base titration affects the results.

2.5. Secondary reference solutions and secondary measurement procedures

Secondary pH reference solutions can be derived by different measurement procedures. Using evaluated uncertainties, it is possible to rank primary and secondary reference buffers in terms of the methods used for their pH determination. The choice between the methods should be made according to the uncertainty required for the application [5].

For the highest metrological quality, it is strongly recommended to derive secondary standards from primary standards of nominally the same chemical composition. Liquid junction (diffusion) potentials are largely minimized when buffer solutions of nominally the same chemical composition are separated from each other in a strictly isothermal cell [59] containing two Pt| H_2 half-cells at identical p_{H_2} :



(cell II)

The primary and the secondary buffers are separated by a liquid junction device, || in cell II, preferably a glass disc of fine porosity. Under these conditions, the contribution of the liquid junction potential to the cell voltage, and therefore the increase in uncertainty above that of the primary pH measurement, is very small for $\Delta\text{pH} \leq 0.02$.

2.6. Secondary pH reference solutions derived from measurements in the Harned cell

Buffer materials that do not fulfil all the criteria for primary pH reference solutions, but to which pH values

can be assigned using Harned cell measurements, are also considered to be secondary reference solutions. An example is ethanoic (acetic) acid, for which it is difficult to achieve consistent chemical quality. Also the zwitterionic buffers [60,61] and nitrogen bases of the type BH^+ [e.g. tris-(hydroxymethyl)aminomethane, $(\text{HOCH}_2)_3\text{CNH}_2$, Tris] are not considered primary pH reference materials, either because the Bates–Guggenheim convention is not applicable (as the buffers contain Cl^-) or because the liquid junction potentials are high (Tris). It is possible to link the secondary pH values to the primary pH standards by comparison measurements using a cell with two free diffusion liquid junctions [62], but this cell is hard to realize. It will be a future task to link these standards to the primary ones with low uncertainty.

The Bates–Guggenheim convention is only valid at ionic strengths up to 0.1 mol kg^{-1} . For applications in clinical chemistry and in environmental samples (e.g. seawater), traceable pH reference solutions with ionic strengths more similar to these samples are expected to have lower liquid junction potentials in practical measurements, yielding improved comparability of measurement results. Further investigations into solution theory and into the concept of single-ion activity are necessary to overcome the present limitations for the primary pH standards and to extend traceability to standards to higher ionic strength. One approach is the Pitzer model of electrolytes [63], which uses a virial equation approach to provide an improvement in the primary method. The uncertainty of all components must also be estimated for this approach to afford traceability to the SI.

New developments are expected in the framework of IUPAC for improving the scientific basis and broadening the applicability of pH measurement [64].

3. Coulometry

3.1. Fundamentals

NMIs increasingly use constant-current coulometry for assays of primary reference materials at the top of the national traceability chains. From the chemical point of view, coulometric titrations are closely related to titrimetry. They enable the attainment of high precision and accuracy and are independent of the molar masses of elements in the sample. Their drawback is lower selectivity, a feature common to titrimetric methods. This makes coulometry especially suitable for determination of relatively pure substances used as standards by other (relative) methods.

Coulometry is based on direct or indirect electrochemical transformation of the determined substance. For a complete electrochemical transformation of a given amount of substance of the measurand, the electric charge needed is quantitatively described by Faraday's Law:

$$n = \frac{Q}{zF} = \frac{\int I dt}{zF}, \quad (2)$$

where n is the amount of substance, Q is electric charge, I is electric current, t is electrolysis time, z is the charge number of the reaction and F is the Faraday constant.

Two main modes are used in coulometry, depending on the function of I with t : constant-potential, in which I decreases exponentially with t ; and constant-current, in which I is constant. Intermediate modes are also known. Constant-potential coulometry is used for determinations of certain elements in solutions (e.g. precious metals, actinides, etc [65–67]) and provides advantages of higher selectivity and applicability to metals that are difficult to determine. Its use is very popular in detectors for chromatography, as the combination of the two techniques eliminates the problem of lower selectivity by exploiting the previous chromatographic separation, while retaining the facility for absolute quantitation of the analyte eluting from the column [68].

Constant-current coulometry is capable of providing results with smaller uncertainty and is implemented in a larger number of NMIs than is constant-potential coulometry. Therefore, constant-current techniques will be discussed in detail in this review.

The main use of coulometry at NMIs is the certification of primary reference materials of composition with a directly determined main component. As the selectivity is usually not high, information on interfering impurities (e.g. Br in KCl) is needed for direct assays of specific compounds (e.g. NaCl or KCl by argentimetric titration). Otherwise, the definition of 'measurand' should include the possibility for impurities (e.g. amount or content of 'acid expressed as $\text{KHC}_8\text{H}_4\text{O}_4$ ' for potassium hydrogen phthalate (KHP) or of 'oxidation capacity expressed as amount content of $\text{K}_2\text{Cr}_2\text{O}_7$ ' for potassium dichromate). One important point is the effect of water, usually the major impurity in different salts. Variations in the drying procedure can significantly affect the measurement results. The residual moisture content may vary with different procedures [69]. Drying at 120°C is not effective in removing occluded mother liquor from KCl or NaCl crystals; differences of 0.1% have been observed [70]. The drying protocol must therefore be stated when a result is reported on the assay of solid compounds and in CRM certificates.

Coulometry can also be used at a lower metrological level (e.g. Cl^- in serum [71]) to provide traceability of measurement results to the SI.

3.2. Applications

Two monographs treat constant-current coulometry through 1970 [72] and 1986 [73]. Since then, several NMIs [14, 74–77] have described state-of-the-art systems. Table 3 presents a summary of constant-current coulometric analyses implemented at NMIs, classified by analyte and titrant. Comparisons of CRMs and relevant CCQM KCs and pilot studies are also noted.

An important application is the coulometric Karl Fischer determination of water, which is used at some NMIs as a primary method for determination of water in materials. However, this method is restricted to samples with the absence of interfering substances [110], so in many cases the instruments are calibrated using reference materials (e.g. water-saturated octanol).

Coulometry is widely used in clinical chemistry as a reference method to determine Cl^- in human serum

Table 3. Constant-current coulometry at NMIs and in CCQM KCs (K) and pilot studies (P).

Analyte	Titrant	NMI ^a [ref]; KC or pilot study [ref]	Comments ^c
HCl	OH ⁻	BAM [78], NIST [76, 79], SMU [80]; P19/19.1 [58] (0.01 mol kg ⁻¹)	For back-titns [76, 80] and in E° determination for pH [58]
KHP	OH ⁻	ASMW ^b [81], BAM [78], NIST [79], NITE [82], SMU [14], UNIIM [83]; K34 [84], K34.1 [85], P36 [86]	CO ₂ bias: KHP > NH ₂ SO ₃ H [82] CRM comparisons (comp) [82]
C ₆ H ₅ COOH	OH ⁻	ASMW [81], BAM [78], NIST [76, 87]	
H ₂ C ₂ O ₄	OH ⁻	NIST [87]	
NH ₂ SO ₃ H	OH ⁻	NITE [82, 89], NMIJ [88], SMU [14, 80]	CRM comp [82]
H ₃ BO ₃	OH ⁻	NIST [90, 91]	
Tris ^d	OH ⁻	BAM [78], NIST [76], SMU [80]	Back-titn, excess added HCl
Na ₂ CO ₃	OH ⁻	NIST [76]	Back-titn, excess added HCl
Na ₂ CO ₃	H ⁺	ASMW [81], NIST [79]	
K ₂ Cr ₂ O ₇	Fe ²⁺	NIST [75, 92, 93], NITE [94], SMU [14, 80]; P7 [70]	CRM comp [93, 94]; comps versus CRM As ₂ O ₃ [93], KIO ₃ [94] and Na ₂ C ₂ O ₄ [94] by titrimetry
Sb(III)	Br ₂	NMIJ [95]	No IC; diffusion losses noted
NH ₃ , NH ₄ ⁺	OBr ⁻	NMIJ [96]	No IC; diffusion losses noted
U	Ti(III)	NIST [97, 98]	
U	Ce(IV)	IRMM [77]	Fe(III) secondary oxidant
As ₂ O ₃	I ₃ ⁻	BAM [78], NIST [93, 99], SMU [14, 80]	CRM comp [93]
GaAs (As)	I ₃ ⁻	NIST [100]	
KIO ₃	I ₂	NIM [101]	Back-titn of excess S ₂ O ₃ ²⁻
Na ₂ C ₂ O ₄	MnO ₄ ⁻ , Fe ²⁺	ASMW [102]	Back-titn of electrogenerated excess MnO ₄ ⁻
KCl	Ag ⁺	ASMW [103], SMU [14]; P7 [70]	
NaCl	Ag ⁺	ASMW [103], BAM [78], NIST [104], SMU [14, 105], UNIIM [103], NITE [106]; P7 [70]	
HCl	Ag ⁺	BAM [78], P19/19.1 [58]	Assay of Cl ⁻ in HCl
NaBr, KI	Ag ⁺	NIST [104]	
GaAs	Zn ²⁺ (EDTA ^e)	NIST [100]	Ga : As ratio, A _{Ga} . Back-titn
EDTA	Zn ²⁺	BAM [78]	
Ag (anode)	Ag ⁺	NIST [107]	Determination of F
Zn (anode)	Zn ²⁺	NIST [108, 109]	Determination of A _{Zn}

^a See table 1 for NMI-country affiliations.

^b ASMW = Amt für Standardisierung, Meßwesen und Warenprüfung (NMI of the former German Democratic Republic).

^c Abbreviations: diff = diffusion; IC = intermediate (cell) compartment; titn = titration.

^d Tris(hydroxymethyl)aminomethane, (CH₂OH)₃CNH₂.

^e Ethylenediaminetetraacetic acid.

[71]. It can also be applied in the field of gas metrology where acidic gases (CO₂, SO₂) may be determined in gas mixtures [111, 112]. Possible problems in this approach were pinpointed [113]. Closely related to these is the method for coulometric measurements of total CO₂ concentration in seawater, after stripping with an inert gas stream from acidified solution [114].

3.3. Procedure

In high-precision constant-current coulometry, charge is added in three stages. In the initial titration (pretitration), a small amount of analyte (spike) is added, and small charge increments at low current are used to locate the 'initial' end-point (EP) for the added spike. The EP can be the inflexion point on the titration curve, a fixed value of the indication signal, intersection of two linear parts (amperometric detection), etc. In this way, the effect of impurities potentially present in the working electrolyte is eliminated. The sample is typically introduced after the conclusion of the initial titration. After the addition of the sample, the main part (99.8% to 99.95%) of the required charge

is added at high current in a single step, the 'main titration'. Pregeneration of titrant [92, 99, 115] has also been used, with the sample being introduced after a similar fraction of the titrant is regenerated. Following the main titration, the EP for the titration of the sample is determined, in the 'final titration', in the same manner as in the initial titration. By Faraday's Law, the charge consumed between the two EPs is equivalent to the amount of sample. The current is usually measured as the voltage drop across a standard resistor. The measurement equation is written as

$$v = \frac{1}{zFm} \left(\frac{E_1}{R_1} (t_1 - \text{corr}_1) + \frac{E_{\text{main}}}{R_{\text{main}}} t_{\text{main}} + \frac{E_2}{R_1} (t_2 + \text{corr}_2) \right), \quad (3)$$

where v is the amount-of-substance content of analyte in the sample, m is the sample mass, t_1 is the current generation time in the initial titration from the EP up to the end of the initial titration (this quantity takes into account the charge necessarily added after the EP in the course of its determination), t_{main} is the current generation time of the main titration, t_2 is the current generation time in the final titration up to the EP, R_1 and R_{main} are the resistances of the standard resistors used for low and

high current measurement; if only one resistor is used then R_1 equals R_{main} . E_1 is the voltage drop across R_1 during initial titration, E_{main} is the voltage drop across R_{main} during main titration, E_2 is the voltage drop across R_1 during final titration, and corr_1 and corr_2 are corrections to filling the intermediate compartment(s) (IC) not exactly at the EP and for change in indication signal from final rinse of IC and/or cell walls.

Equation (3) shows that the direct result of the coulometric measurement is ν of the analyte. As ν is independent of the atomic weights, A_E , of the element(s) comprising the analyte, $u(A_E)$ does not contribute to the uncertainty of the coulometric method. However, if the mass fraction of analyte is the required quantity, it must be calculated from ν . Since this calculation necessarily involves the molar mass, a coulometric result expressed as the mass fraction of the analyte must include the $u(A_E)$ in the combined standard uncertainty of this mass fraction.

3.4. System design

The high-accuracy constant-current systems all follow the same general plan. The current generated by the constant-current source is measured and regulated as the voltage drop across a standard resistor(s), a precision timer is used to measure the generation time and an indicating circuit is used to follow the reaction in the cell. A variety of commercially available instruments can be used to assemble a high-accuracy coulometric system. The new systems are now computer-controlled [14, 75, 89, 94, 105]. The workload on the operator is thus significantly reduced, and the quality of the results is improved [14, 76] by eliminating the subjective judgement of the operator.

The coulometric cells constitute the heart of the whole system. Their construction must fulfil several criteria: the volume has to be adequate for accommodation of electrodes for the required current; the working compartment must be isolated from the counter electrode compartment; losses of generated titrant or analyte by diffusion, migration or convection should be minimized; and contamination of the working compartment with undesired substances from the counter electrode compartment or surroundings (e.g. CO_2 in acidimetry, O_2 in most redox titrations) should be eliminated. Temperature, T , control is advantageous if the cell temperature changes significantly. Although F and Faraday's Law are T -independent, most indicating electrode systems (e.g. pH electrodes, other potentiometric and amperometric systems) display a T dependence.

Vertical [14, 74, 78] or horizontal [75, 79, 89] cell configurations are used. Horizontal cells are easier to construct, have a smaller cell volume (hence, more sensitive EP indication), and simplify sample introduction. Cleaning of the frits is easier in vertical cells, they are easier to thermostat and solution handling is more easily automated.

Losses of analyte or titrant to the IC(s) must also be considered. Theoretical calculations indicate that loss via diffusion into the ICs is negligible in horizontal cell design [116, 117]. In practice, migration occurs in some titrations (e.g. KHP and $\text{K}_2\text{Cr}_2\text{O}_7$). Also, heating of electrolyte in the

frits can induce thermal convection in the IC(s). Hence analyte or titrant losses are greater than values predicted for diffusion alone. Investigations with a horizontal cell [118] indicate that $\approx 80\%$ of the mass transport of $\text{Cr}_2\text{O}_7^{2-}$ to the ICs derives from migration.

The counter-current principle (electrolyte flowing in the opposite direction to diffusion) has been used for a long time in vertical cells [115, 119]. However, this approach has the disadvantage of constant dilution during the main titration. It is preferential to use solution withdrawn from the cell, which is returned during the course of the main titration [14]. In this way, the composition of the solution can be exactly known, and the cell volume in the initial and final titrations remains nominally unchanged. Comparable results are obtained with horizontal and vertical cells in titrations of $\text{K}_2\text{Cr}_2\text{O}_7$ [70, 115], KCl [70] and NaCl [70].

Errors in the range of several per cent are possible if the cell design is deficient or other factors (e.g. excessive current density yielding a current efficiency below 100% at the generating electrode) are neglected. In establishing a coulometric system, testing with CRMs is therefore an indispensable part of the validation procedure.

3.5. Indicating systems

The requirements for the indication system are sufficient sensitivity and coincidence of EP with the equivalence point. Amperometric or potentiometric methods are used almost exclusively, although others (e.g. spectrophotometry) are, in principle, feasible. Evaluation of the indication system is preferably performed using a regression of the titration curve near the EP, as the result is less affected by the noise in the indication signal than using incremental derivatives. For evaluation of potentiometric titrations, curve fitting using a third-order polynomial [120] is readily implemented. A 'W-function' [121],

$$y_i = \frac{\beta_0}{1 + \exp[\beta_1(\beta_2 - x_i + x_0)]} + \beta_3(x_i - x_0) + \beta_4, \quad (4)$$

where x_i is the increment of added titrant, y_i the indication signal and β_0 through β_4 are adjusted (fitted) empirical constants, can also be used; it is often more robust than the third-order polynomial, but good estimates of the initial values are necessary for nonlinear regression.

Amperometric indicating systems can be advantageous in redox titrations that involve reactions with slow kinetics. In amperometric detection, a small excess of titrant is present throughout the EP determination. Depending on the redox mechanism, this small excess may accelerate the approach to equilibrium and speed up the EP determination.

In contrast, potentiometric EP detection is usually performed very close to and on either side of the equivalence point. A system with slow kinetics may reach equilibrium too slowly for effective use of the potentiometric method. In systems where potentiometric detection is feasible, it is generally less influenced by mass transport to the indicating electrode than the amperometric methods, which rely on mass-transport limited diffusion to the indicating electrode to

develop the response signal. Hence, potentiometric detection has less 'noise' that originates from hydrodynamic variations and from precipitate (e.g. AgCl) that adheres to the indicating electrode.

3.6. Evaluation of uncertainties

The evaluation of the sources of uncertainty associated with the measurement of physical quantities involved in the coulometric measurement equation does not present significant problems, as the influences have been known for decades. Relative uncertainties of measurement of the intervals t_1 , t_{main} and t_2 are negligible for good equipment. Relative uncertainties on the order of 0.0005% to 0.002% in m , R and E can be achieved [14], if stability and temperature effects are taken into account. With such a low instrumental uncertainty, other factors normally limit the achievable uncertainty, mainly those connected to the solution handling, chemical processes in the cell and the homogeneity of the material. These chemical sources usually represent the major contributions [14, 130].

The relative standard deviation of the measurement itself can be lower than 0.001% [84, 122, 123]. The following sources of uncertainty due to chemical sources have to be taken into account:

- Current efficiency: it must approach 100% and can be determined by various methods [72, 124, 125]. For the most frequently used systems the current efficiency exceeds 99.999%. For lower efficiencies, where a correction is made, the uncertainty of the correction must be taken into account. Hence, the range of analytes that can be determined with the highest accuracy (lowest uncertainty) is limited.
- Diffusion and migration losses: these are usually minimized by cell design and operation. There should be at least one IC between the working and counter electrode compartments, the contents of which can be rinsed back into the working compartment. Otherwise, the result will depend on the amount of sample, owing to losses into the counter electrode chamber.
- EP evaluation: the major part of uncertainty is reflected in the repeatability of the measurement. If the system behaves differently in the initial and final EP determinations (weak acid titrations, complexometric titrations), a bias can be introduced if the EP does not correspond to the equivalence point.
- Spray losses of analyte or titrant associated with bubbles from deaeration, gas evolution or solution handling.
- Effect of impurities in the inert gas used for deaeration, the electrolyte and/or the sample. The presence of CO₂ and O₂ can have a disastrous effect on acid–base and redox determinations, respectively, and their removal is never complete. In addition to systematic bias, reproducibility will usually be impaired.

Some of the contributions from the sources listed above are independent of the amount of sample and therefore limit the precision of assays of small samples [58]. Examples of uncertainty estimates for some materials can be found [14, 76]. The main problem associated with the above-mentioned

chemical sources of uncertainty is that they are much more difficult to estimate than the uncertainties corresponding to the physical quantities such as m , R , E , etc. Therefore, they are often omitted from uncertainty budgets [84, 101, 126], yielding underestimated uncertainties. A thorough understanding of the principles and experience with the method is necessary for qualified estimates of uncertainty from chemical sources.

3.7. Frequently encountered problems in coulometric measurements

Most NMIs initially implement coulometry as a primary method for acidimetric titrations. In coulometric acidimetry, the following problems are often observed:

- inefficient deaeration. This problem is most common. The efficiency can easily be checked by following the pH change during deaeration of a KCl solution, slightly acidified such that the final pH is about 6. The drift rate (dpH/dt) should preferably decrease by a factor of ten after 10 min of deaeration, and the pH should finally reach a stable value. Inefficient deaeration can easily lead to errors as high as 2%. Particular difficulty occurs in titrations of weak acids (e.g. KHP [127]), as the alkaline EP promotes the absorption of CO₂, yielding a positive systematic bias. The reproducibility is also often impaired.
- Connected with deaeration is the use of tubing with high gas permeability. CO₂ diffuses through the tubing into the inert gas, and its presence in the gas will be manifested by a negative drift in the measured pH value in the alkaline pH range.
- In analysis of solutions, CO₂ present in the sample must be eliminated before the final titration [58].
- The use of overly small increments leads to noisy curves in the EP determination, owing to limits in indication signal resolution.
- Current efficiency can be lowered by diffusion of Ag⁺ from the anode compartment, from the reference junction of the pH electrode or by the presence of reducible impurities in the electrolyte reagents (0.0001% of Pb in KCl used to prepare the electrolyte can cause an error of 1% in the titration of 2 mL of a HCl solution of molality 0.01 mol kg⁻¹).
- Assays should be performed on larger samples. The use of small samples (100 to 1000 times smaller than the usual 1 mmol to 5 mmol) is recommended only for method development and for checking of the system. If a constant systematic bias is present, the results will depend linearly on the reciprocal of sample amount. A constant bias will have a proportionally greater effect on the smaller sample.
- Impurities in HCl may cause significant positive errors in back-titrations if the EP pH values differ significantly. In the Tris determination, a bias on the order of 0.009% has been observed by the authors [128].
- EP evaluation. In titrations where a difference exists between the initial and final titration, a bias can be introduced if the EP does not correspond to the equivalence point (Roller effect [129]). Coulometric

titrimetry has verified this effect experimentally [91] using titrations of H_3BO_3 in varying concentrations of added mannitol.

- Glass electrode kinetics. In unbuffered solutions near neutrality ($\text{pH} \approx 6$ to $\text{pH} \approx 8$), glass electrodes respond slowly to incremental additions of H^+ or OH^- , approaching the new pH value asymptotically. Hence, pH data should be recorded only after the pH reading changes at a rate below a stated threshold (e.g. 0.01 pH min^{-1}).

Some other problems which affect the specified coulometric titrations are the following:

- Current loops (interfering leakage current) between the generation and indication circuits must be meticulously avoided in all titrations. Circuits for avoiding them have been published [75].
- In redox titrations, deaeration is necessary to protect reagent or analyte from air oxidation. A systematic bias on the order of 0.1% is possible. The influence of O_2 can be checked by analysis with and without deaeration. It may be dependent on the state of Pt (or other) generating electrode.
- Interfering substances in supporting electrolyte (e.g. hydrocarbons in dichromate titrations) react slowly and are not eliminated by initial titration. Such substances should be eliminated by adequate treatment of the electrolyte [92, 130]. The treatment protocol should be validated.
- In complexometry, deaeration is critical for the Zn amalgam electrode owing to air oxidation. The location of the EP may be difficult in amperometric titration curves rounded in the region of the EP if weaker complexing agents, such as nitrilotriacetic acid, are present as impurities in EDTA.
- Ag^+ titrations are sensitive to light [131].

The precautions mentioned here must be observed for coulometry to be accepted as a primary method for amount-of-substance content at an NMI.

3.8. Evaluation of the state of the art

The state of the art of coulometric analysis has been assessed in one KC, a bilateral KC, and three pilot studies (see table 2). Results generally agreed to better than 0.01% for solid samples and 0.1% for the 0.01 mol kg^{-1} HCl solution. The recent CCQM-K34 and CCQM-K34.1 [84, 85] assessed the state of the art of acidimetric coulometry in the measurement of assay of KHP. All participants used constant-current coulometry at different levels of sophistication. Impurities in the sample were also determined. The main difficulties included significant interference of CO_2 and the possibility of electrochemical reduction of KHP yielding low results. In general, very good agreement of the results was observed: the range of results of 5 out of 7 participants was less than 0.01%; the expanded uncertainties stated ranged from 0.006% to 0.031%. The KCRV, expressed as mass fraction of KHP, was 99.919%. The recalculated assay based on impurity determination was 100.008%. This demonstrates that great care must be taken if

the assay of compounds is based only on the 100%-impurities concept [70], as even the most significant impurities, such as potassium phthalate and water, may remain undetected.

4. Electrolytic conductivity

4.1. Fundamentals

The electrolytic conductivity, κ , defined as the ratio of the ionic current density to the applied electric field, is the fundamental measure of the transport of charge through an electrolyte. A reciprocal relationship exists between κ (units of S m^{-1}) and the resistivity, ρ (units of $\Omega \text{ m}$).

In principle, κ is obtained from a measurement of the solution resistance, R_s , of a homogeneous, isotropic electrolyte placed between electrodes in a conductivity cell ('cell') under specified conditions. The fundamental relationship between R_s and ρ is given by equation (5):

$$R_s = \rho K_{\text{cell}}. \quad (5)$$

The cell constant, K_{cell} (units m^{-1}), is nominally constant for a given cell of fixed dimensions. Substituting $1/\kappa$ for ρ in equation (5) and solving for κ yields equation (6), the fundamental relationship between κ , R_s and K_{cell} :

$$\kappa = \frac{K_{\text{cell}}}{R_s}. \quad (6)$$

In a cell with parallel, planar electrodes of area A , spaced a distance l apart, in which fringe effects are absent and in which the electric field between the electrodes is strictly homogeneous, K_{cell} equals l/A . In most cells, these conditions are not fulfilled. Hence, in general, K_{cell} cannot be directly calculated from l and A .

4.2. Primary measurement of κ

Cells that are specially constructed to maximize homogeneity of the electrical field and to minimize fringe effects are referred to as primary cells. In primary cells, K_{cell} is obtained from physical measurements of the relevant geometric quantities. Provided that the measurement of R_s is traceable to the SI (see below), such cells yield a measurement that is traceable to the SI.

A recent review of primary methods for the measurement of κ [18] describes the state of the art of primary measurements of electrolytic conductivity at a number of NMIs. Principal approaches include a removable centre section of accurately known A and l in a Jones-style [132] cell, movable piston cell with cross-sectional area A and micrometre positioning of l and four-electrode cells. Detailed descriptions are presented here only where relevant to the present review.

In four-electrode cells, the current and potential leads are separated, as in a conventional four-terminal resistor. Measurements of κ in four-electrode cells can be performed using direct current (dc) or alternating current (ac). Measurements using dc require reversible electrodes (e.g. $\text{Ag}|\text{AgCl}$ in KCl solutions), in order to avoid electrolysis and polarization effects. The dc approach has been used at the

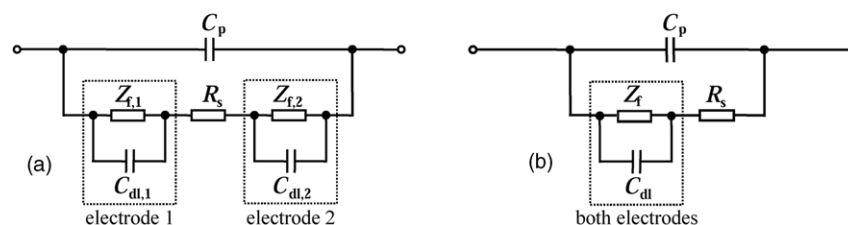


Figure 1. Equivalent circuits of two-electrode conductivity cell, with the electrode-related components (a) separated and (b) lumped⁶.

OMH [18] and NIST [133], and the ac approach at UkrCSM [18]. The chief advantage of the use of dc is that reactance effects are eliminated. Owing to the isolation of the potential leads from the current flow, dc and ac four-electrode methods both eliminate the effect of the lead resistance, R_{lead} , on the measurement.

The van der Pauw principle [134], originally developed for measurements of ρ of solid-state materials, has been investigated for use in primary measurements of κ of liquid samples [135, 136]. Four electrodes in the form of narrow lines or rods, or ‘virtual electrodes’, located in side-chambers connected via slits to the main portion of the cell, are placed at arbitrary points on the circumference of a cylinder or prism. The cell must have constant cross-section (of arbitrary shape) and constant thickness. The electrodes are used in a four-electrode ac protocol (current and potential electrode pairs separated). Measurements are cross-averaged, alternating the current and potential electrodes. The reported relative uncertainty is on the order of 0.3%, roughly 10 times greater than the uncertainty attained in conventional methods.

4.3. Secondary measurement of κ

Many NMIs use secondary measurements of κ in producing CRMs. This approach uses a primary calibrant to determine K_{cell} for a secondary (non-absolute) cell. The calibrated secondary cell is then used for performing the relevant measurement of κ for the CRM or other unknown solution. For calibrating cells with smaller values of K_{cell} , transfer (working) standards of intermediate κ are prepared. The value of κ for each transfer standard is determined in the cell calibrated with the primary standard, and the set of transfer standards is used to determine K_{cell} for the second cell. The concentration of the transfer standards need not be accurately known, but they must be equilibrated with atmospheric CO_2 to avoid bias in the measurement. At NIST, multiple ($n \geq 6$) primary standards are prepared independently to assess the reproducibility of preparation. If transfer standards are used, the remaining components of uncertainty (see below) are evaluated for each successive measurement. The combined standard uncertainty, $u_c(y)$, of the entire calibration process is expressed as $u_c(K_{\text{cell}})$ for the relevant calibration. The respective components of uncertainty for the κ measurement of the unknown must also be assessed and included in the final measurement. In the certification of CRMs with $\kappa \leq 10 \text{ mS m}^{-1}$, additional components of uncertainty (stability [137, 138] and CO_2 at the user’s laboratory) exceed $u_c(K_{\text{cell}})$ and govern the overall uncertainty of the CRM. In CRMs with higher κ values, $u_c(K_{\text{cell}})$ usually dominates.

Traceability for secondary measurements relies on the constancy of κ of the primary standard at the current preparation with respect to the time that the original primary measurement of κ was performed. Primary standards with defined molalities of KCl (1.0 mol kg^{-1} , 0.1 mol kg^{-1} and 0.01 mol kg^{-1}) [18, 133] are routinely used at NIST. The Organisation Internationale de Métrologie Légale (OIML)-R56 [139] standards, derived from classical measurements [140, 141], are also frequently used at NMIs.

The secondary method of calibration was used by Jones and Bradshaw [140] to obtain κ values for specified mass fractions [139, 140, 142] of KCl, w_{KCl} , nominally equal to the corresponding amount-of-substance concentration at 0°C , using the molar masses from 1933. Starting from metallic Hg (the then-current primary standard for the ohm), they proceeded via transfer measurements using concentrated H_2SO_4 and KCl solutions to obtain the reported κ values for the final aqueous KCl solutions. The estimated relative uncertainty of their solutions was on the order of 0.02%. Primary measurements of κ of KCl solutions with the same w_{KCl} as in [140] were obtained [143, 144] contemporaneously with the measurements of the molality-based standards [133]. The redetermined values agreed with [140] to within the uncertainties of the respective measurements [133], after the values in [140] had been corrected for historical changes in the respective units.

4.4. Traceable measurement of R_s

Measurements of κ are usually performed using ac at frequencies, f , in the audio range (20 Hz to 20 kHz). The use of ac eliminates net electrolysis of the sample and reduces polarization at the electrodes. Subtracting R_{lead} from the measured resistance yields the apparent cell resistance, R_{cell} . The value of R_{lead} is obtained by direct measurement (e.g. with an ohmmeter) of the relevant leads.

The quantity R_{cell} is the real component of the total cell impedance (Z), Z_{cell} . The imaginary component of Z_{cell} is a reactance (X), X_{cell} . The quantity R_s , which yields κ via equation (6), is obtained either by extrapolation or by circuit analysis, using a theoretical equivalent circuit (model) of the cell.

Figure 1 shows the classical equivalent circuit in two versions. In (a), the faradaic impedances, $Z_{f,1}$ and $Z_{f,2}$, and double-layer capacitances, $C_{dl,1}$ and $C_{dl,2}$, for each electrode

⁶ In figure 1(b), Z_f equals the vector sum of $Z_{f,1}$ and $Z_{f,2}$, and C_{dl} equals $C_{dl,1}C_{dl,2}/(C_{dl,1} + C_{dl,2})$, respectively. For identical electrodes, $Z_{f,1} = Z_{f,2}$, $C_{dl,1} = C_{dl,2}$, $Z_f = 2Z_{f,1}$ and $C_{dl} = C_{dl,1}/2$.

are depicted separately [19]. This presentation is useful in cases where the electrodes differ in area or are otherwise not identical. In (b), Z_f and C_{dl} represent the corresponding lumped quantities [145]. The quantity C_p is the parallel (or geometric) cell capacitance.

In the models of figure 1, R_s is ideal (f -independent). C_p and C_{dl} are each pure (ideal) capacitances.⁷ Each Z_f is the sum (series connection) of two components: the charge transfer (polarization) resistance, associated with reduction and oxidation at the electrode surface, and the Warburg impedance, associated with diffusion of electroactive species to the surface [146]. Each Warburg impedance, in turn, is equivalent to a resistance and a capacitive reactance of equal magnitude, proportional to \sqrt{f} , in series.

In the classical measurement, typically used for $\kappa > 1 \text{ mS m}^{-1}$, measurements of R_{cell} are obtained at multiple values of f . As $f \rightarrow \infty$, $X(C_{dl})$ approaches zero, and R_{cell} approaches R_s . The intercept of the linear extrapolation of R_{cell} as a function of $1/f$ is taken as R_s . Variations from linearity have been noted [145, 147], and the exact dependence of R_{cell} on f should be evaluated in each case.

The effect of C_p on the measurement must also be considered. Direct compensation for C_p is generally successful at audio frequencies for cells with $K_{cell} > 10 \text{ m}^{-1}$ and $\kappa > 1 \text{ mS m}^{-1}$ [147]. As K_{cell} and κ decrease, the influence of $X(C_p)$ on R_{cell} increasingly dominates over that of $X(C_{dl})$. Recent experimental data [19] demonstrate that the classical extrapolation of R_{cell} versus $1/f$ fails for high-purity water ($\kappa = 5.5 \mu\text{S m}^{-1}$) in a cell with $K_{cell} \approx 0.7 \text{ m}^{-1}$. Values of R_s obtained by extrapolation of R_{cell} to $f \rightarrow 0$ (i.e. $X(C_p) \rightarrow \infty$) and by calculation using a simplified theoretical model agree to 0.02% [19]. Modelling of conductivity cells [147], based on assumed values for the relevant quantities and using the principles of impedance spectroscopy [148], is valuable in evaluating candidate procedures for extracting R_s and predicting the optimum frequency range to be used for different K_{cell} and κ ranges.

An alternative approach to the use of frequency extrapolation is to use a four-electrode measurement, as described above.

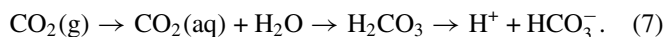
4.5. Measurements of κ of high-purity water: coaxial cells

A (probably the) major application for measurements of κ is in evaluation of the ionic purity of water. The non-specific character of κ is useful in this application, since it provides a sensitive gauge of the presence or absence of all ionic species⁸. To ensure the validity of the measured κ , the sample must be rigidly excluded from exposure to atmospheric CO_2 . Equilibration with atmospheric CO_2 (mole fraction, $x_{\text{CO}_2} = 380 \mu\text{mol mol}^{-1}$) raises the κ of a sample of pure water at 25°C from $5.5 \mu\text{S m}^{-1}$ ($\rho = 18.2 \text{ M}\Omega \text{ cm}$) to $110 \mu\text{S m}^{-1}$ ($\rho = 0.9 \text{ M}\Omega \text{ cm}$) [133]. The increase in κ results from

⁷ A constant-phase element model has also been used for C_{dl} [147].

⁸ As an example, a CO_2 -free aqueous solution with a mass fraction of NaCl equal to 21 ng g^{-1} (amount concentration $0.36 \mu\text{mol L}^{-1}$) has $\kappa = 0.0010 \mu\text{S m}^{-1}$ ($\rho = 10 \text{ M}\Omega \text{ cm}$). The sensitivity to different ions varies approximately proportionately to their limiting molar conductivities and their respective ionic charges. See [149].

dissolution of CO_2 in the water and subsequent dissociation to yield H^+ and HCO_3^- ions:



Issues relating to the traceability of measurements of κ of high-purity water are treated in [149]. The ubiquitous presence of CO_2 and the difficulty in avoiding leaching of any trace ions at the level of parts in 10^9 from containers preclude the use of CRMs as a vehicle for ensuring traceability in the field. As a substitute for CRMs, high-purity water in a closed loop system is used as a ‘transient’ reference material [149–153]. Commercial high-purity water systems typically measure κ at ambient temperature and correct the measured value to 25°C using a model equation for the κ as a function of temperature [149].

Coaxial cells are widely used in measurements of high-purity water, owing to four advantages. First, coaxial cells are suited to inline operation. Second, cells of this geometry are readily constructed with $K_{cell} \leq 10 \text{ m}^{-1}$, in the optimal range for measurements of κ for high-purity water. Third, the outer electrode may be earthed, serving simultaneously as an electromagnetic and CO_2 shield. Fourth, a thermistor, required for temperature measurement, is conveniently placed within the inner electrode of a coaxial cell.

The equation for K_{cell} for a coaxial cell is given by equation (8), where d_o , d_i and l are the diameter of the outer and the inner cylindrical electrodes and the length, respectively:

$$K_{cell} = \frac{\ln\left(\frac{d_o}{d_i}\right)}{2\pi(l+a)} \quad (8)$$

The quantity a , with units of length, represents a correction for fringe effects [151, 153].

Two approaches are currently under investigation to eliminate a in equation (8), thereby attaining the possibility for a primary measurement. The first approach [152, 153] consists of a compound coaxial cell with two inner cylinders, A and B, of lengths l_A and l_B and identical d_i , each mounted coaxially inside a single outer cylinder of diameter d_o . The current passing through the two sub-cells A and B, each composed of the respective inner cylinder and the outer cylinder, is measured sequentially, with the complementary inner cylinder earthed. Subtracting the two currents cancels the respective fringe effects at the proximal and distal ends of the inner cylinders, assuming the corresponding fringe effects of sections A and B to be equal. The second approach is to use guard cylinders, first used in 1907 in an absolute capacitor for the measurement [154] of the permittivity of free space. In this approach, the inner cylinder is sectioned into a central, active section and two guard cylinders, one at each end. The sections are mounted coaxially with the outer cylinder, as in the compound cell. The current passing through the active portion of the inner cylinder is measured with the two guard sections earthed. Fringe effects at the gaps between the active section and the guards are reduced by minimizing the width of the gaps.

Table 4. CCQM-K36.a results [160]. Relative uncertainties, $u_c(\kappa)/\kappa$ and $u_i(\kappa)/\kappa$, are given as percentages.

NMI	Method	$\kappa/\text{S m}^{-1}$	$u_c(\kappa)/\kappa$	$u_i(\kappa)/\kappa$ values, in %, for stated source, i				
				K_{cell}	R_s	T	CO_2	$u_A(\kappa)$
CENAM	Movable piston cell	0.51097	0.102	0.031	0.030	0.021	—	0.090
CMI	Differential cell	0.51095	0.760	0.005	0.000	0.000	0.000	0.760
DFM	Differential cell	0.50708	0.023	0.018	0.009	0.010	0.001	0.001
GUM	CRM calibrant	0.50668	0.045	0.041	0.015	0.010	0.000	0.004
IEN	Differential cell	0.50677	0.073	0.001	0.045	0.012	0.001	0.057
INMETRO	CRM calibrant	0.50420	0.469	0.071	0.006	0.458	—	0.072
INPL	CRM calibrant	0.50700	0.069	0.040	0.004	0.054	0.002	0.013
NIST	IUPAC calibrant [133]	0.50714	0.021	0.017	0.006	0.009	0.006	0.004
OMH	OIML calibrant [139]	0.50689	0.020	0.017	0.011	0.003	—	—
PTB	Movable piston cell	0.50729	0.055	0.007	0.048	0.010	0.000	0.024
SMU	Kohlrausch curve	0.50684	0.043	0.036	0.020	0.012	—	0.004
SP	IUPAC calibrant [133]	0.50610	0.146	0.107	0.077	0.050	0.040	0.007
UkrCSM	Four-electrode ac cell	0.50697	0.022	0.014	0.013	0.010	0.004	—
VNIIFTRI	Primary cell	0.50273	0.012	0.004	0.010	0.006	—	—

4.6. Other techniques

A novel approach to calibrating conductivity cells, first described by Kohlrausch in 1906 [155], consists of determining K_{cell} from a capacitance measurement, with the cell filled with a fluid of known relative permittivity (dielectric constant), ϵ_r . This value of K_{cell} is subsequently used in the measurement of κ in the same cell filled with the conductivity sample. A fundamental requirement, closely approached in shielded coaxial cells, is that the electric field be identical in both measurements. The technique was later adapted to calibrate a coaxial cell for aviation fuels [156] ($1 \text{ pS m}^{-1} < \kappa < 1000 \text{ pS m}^{-1}$) and forms the basis of an ASTM standard [157] for this application. A separate measurement of the capacitance of the empty cell corrects for fringe effects in the capacitance measurement. The approach is best suited to cells used to measure $\kappa \leq 5.5 \mu\text{S m}^{-1}$, the κ of pure water.

A closed-flow system [158], based on continuous on-line dilution, has been developed for producing standards at $0.05 \text{ mS m}^{-1} \leq \kappa \leq 1 \text{ mS m}^{-1}$ from a concentrated electrolyte solution and CO_2 -free water. The technique is ideally suited to on-line production of low- κ standards to calibrate inline (flow-through) cells. The κ of the delivered solution can be determined either from a model for the κ -concentration relationship or via a ‘step-down’ approach, analogous to [140] but extending from a κ at which accurate CRMs are available down to the κ of high-purity water. Either approach minimizes the contribution from CO_2 to negligible proportions.

4.7. Temperature control, selection of thermostat fluid and cell layout

Control of the cell temperature, T , is critical if a low uncertainty in κ is required. The majority of strong electrolytes have relative temperature coefficients, $\alpha_\kappa = (d\kappa/dT)/\kappa$, on the order of 0.02 K^{-1} ($2\% \text{ K}^{-1}$) at 298 K (25°C), owing to the T dependence of the ionic mobility. Strong acids (e.g. HCl) have α_κ values on the order of 0.015 K^{-1} ($1.5\% \text{ K}^{-1}$) at 298 K [145]. Owing to the additional temperature dependence of the autoprotolysis constant, K_w , of water, α_κ for pure water is greater, 0.053 K^{-1} ($5.3\% \text{ K}^{-1}$) at 298 K [149]. Hence,

the uncertainty in the control and measurement of T must be less than 0.01 K for T to contribute less than roughly 0.02% (0.053% for pure water) to the uncertainty of the κ measurement.

The choice of thermostat fluid is also important. A fluid with a small κ (large ρ) and small ϵ_r maximizes the shunt impedance, Z_{shunt} , which arises from leakage paths through the thermostat fluid. The effect of Z_{shunt} on Z_{cell} increases as $Z_{\text{shunt}}/Z_{\text{cell}}$ decreases. Variations in K_{cell} as a function of κ are observed if Z_{shunt} includes a resistive component [132], R_{shunt} . Mineral oil is the most used thermostat fluid, with ρ about 10^5 times greater than water [159] and $\epsilon_r \approx 2.1$. Water, with its high specific heat, is better from the standpoint of control of T , but its ϵ_r (80) and ρ yield a lower Z_{shunt} with a significant R_{shunt} . Air (with $\epsilon_r \approx 1$) has been used to increase Z_{shunt} above values observed in oil, at the cost of increased equilibration time.

The value of Z_{shunt} increases with increasing separation of the cell lead and filling tube associated with one electrode from those for the other electrode. The ‘Jones cell’ design [132] maximizes Z_{shunt} in this manner.

4.8. Uncertainty and comparison of state-of-the-art methods

The state of the art of κ measurement was assessed in 2006 in CCQM-K36 [160]. Methods used included most of the primary and secondary methods outlined in [18] and the present review. Measurement agreement and uncertainty were assessed for two solutions: CCQM-K36.a, with a KCRV of $0.506992 \text{ S m}^{-1}$, $\nu_{\text{KCl}} \approx 0.0380 \text{ mol kg}^{-1}$, and CCQM-K36.b, with KCRV 5.1231 mS m^{-1} , $\nu_{\text{HCl}} \approx 1.21 \times 10^{-4} \text{ mol kg}^{-1}$.

Tables 4 and 5 summarize the results. The first column lists the participating NMIs. The second column lists the type of primary cell, or for secondary measurements, the source of traceability. The reported κ and the relative combined standard uncertainty, $u_c(\kappa)/\kappa$, are in the third and fourth columns, respectively. Subsequent columns list the components, $u_i(\kappa)$, of $u_c(\kappa)$ generated by the standard uncertainty, $u(x_i)$, of each input quantity, x_i , attributable to the respective sources, i . The $u(x_i)$, $u_i(\kappa)$ and $u_c(\kappa)$ are calculated according to the *Guide to the Expression of Uncertainty in Measurement* [161]. Tables 4 and 5 list the $u_i(\kappa)$ on a relative basis, $u_i(\kappa)/\kappa$, as percentages.

Table 5. CCQM-K36.b results [160]. Relative uncertainties, $u_c(\kappa)/\kappa$ and $u_i(\kappa)/\kappa$, are given as percentages.

NMI	Method	$\kappa/\text{mS m}^{-1}$	$u_c(\kappa)/\kappa$	$u_i(\kappa)/\kappa$ values, in %, for stated source, i				
				K_{cell}	R_s	T	CO_2	$u_A(\kappa)$
CENAM	Movable piston cell	5.040	0.408	0.030	0.074	0.010	—	0.400
CMI	Differential cell	5.019	1.634	0.007	0.008	0.013	0.008	1.634
DFM	Differential cell	5.1239	0.024	0.020	0.009	0.007	0.003	0.001
GUM	CRM calibrant	5.108	0.146	0.140	0.011	0.015	0.000	0.035
IEN	Differential cell	5.130	0.377	0.001	0.260	0.012	0.115	0.247
INMETRO	CRM calibrant	5.100	1.240	1.176	0.060	0.320	—	0.221
INPL	CRM calibrant	5.117	0.085	0.040	0.007	0.054	0.046	0.024
NIST	IUPAC calibrant [133]	5.1250	0.040	0.024	0.008	0.006	0.002	0.030
OMH	OIML calibrant [139]	5.0401	0.034	0.017	0.029	0.003	—	—
PTB	Movable piston cell	5.1136	0.125	0.006	0.060	0.100	0.020	0.040
SMU	Kohlrausch curve	5.1245	0.043	0.036	0.020	0.012	—	0.006
SP	Kohlrausch curve	5.155	0.349	0.132	0.194	0.049	0.233	0.101
UkrCSM	Four-electrode ac cell	5.1166	0.063	0.022	0.038	0.020	0.040	—
VNIIFTRI	Primary cell	4.981	0.027	0.026	0.007	0.005	—	—

The sources are those listed in the previous sections of this review: K_{cell} , from the physical measurement in primary cells or from the calibration of K_{cell} in secondary cells; R_s , including the measurement of R_{cell} and R_{lead} , and the extrapolation of R_{cell} to yield R_s ; T , including calibration of the thermometer, temperature stability and equilibration of the cell; CO_2 dissociation; and $u_A(\kappa)$, the Type A [161] measurement reproducibility. The largest source of uncertainty is typically the determination of K_{cell} .

References

- [1] CIPM Mutual Recognition Arrangement, information available at <http://www.bipm.fr/en/cipm-mra/>
- [2] Published Key Comparison reports available at <http://kcdb.bipm.org/AppendixD>
- [3] Full NMI names available at http://www.bipm.org/en/practical_info/useful_links/ under 'acronyms'
- [4] ISO 3166-1 codes available at http://www.iso.org/iso/en/prods-services/iso3166ma/02iso-3166-code-lists/iso_3166-1_decoding_table.html
- [5] Spitzer P and Werner B 2002 *Anal. Bioanal. Chem.* **374** 787–95
- [6] Meinrath G and Spitzer P 2000 *Microchim. Acta* **135** 155–68
- [7] Spitzer P 2001 *Accred. Qual. Assur.* **6** 55–60
- [8] Buck R P *et al* 2002 *Pure Appl. Chem.* **74** 2169–200
- [9] Baucke F G K 2002 *Anal. Bioanal. Chem.* **374** 772–7
- [10] Milton M J T and Quinn T J 2001 *Metrologia* **38** 289–96
- [11] Mohr P J and Taylor B N 2005 *Rev. Mod. Phys.* **77** 1–107, also available at [http://physics.nist.gov/cgi-bin/cuu/Value?f\[search_for\]=faraday](http://physics.nist.gov/cgi-bin/cuu/Value?f[search_for]=faraday)
- [12] Tutundzic P S 1953 *Anal. Chim. Acta* **8** 182–3
- [13] IUPAC Commission on Electroanalytical Chemistry 1976 *Pure Appl. Chem.* **45** 127–30
- [14] Máriássy M, Vyskočil L and Mathiasová A 2000 *Accred. Qual. Assur.* **5** 437–40
- [15] Pan X R 1997 *Metrologia* **34** 35–9
- [16] Kipphardt H, Matschat R, Rienitz O, Schiel D, Gernand W and Oeter D 2006 *Accred. Qual. Assur.* **10** 633–9
- [17] Spitzer P, Rossi B, Gaignet Y, Mabic S and Sudmeier U 2005 *Accred. Qual. Assur.* **10** 78–81
- [18] Brinkmann F *et al* 2003 *Accred. Qual. Assur.* **8** 346–53
- [19] Xiaoping S, Spitzer P and Sudmeier U 2007 *Accred. Qual. Assur.* **12** 351–5
- [20] Sørensen S P L 1909 *Biochem. Z.* **21** 131–200
- [21] Sørensen S P L 1909 *Biochem. Z.* **21** 201–304
- [22] Sørensen S P L, Linderstrøm-Lang K L 1924 *C. R. Trav. Lab. Carlsberg* **15** 1–40
- [22] Schwabe K 1976 *Fortschritte der pH-Messtechnik* 4th edn (Dresden, Germany: Verlag Theodor Steinkopff)
- [23] Bates R G 1981 *CRC Crit. Rev. Anal. Chem.* **10** 247–78
- [24] Bates R G 1973 *Determination of pH. Theory and Practice* 2nd edn (New York: Wiley)
- [25] Wu Y C, Koch W F and Durst R A 1988 *Standardization of pH Measurements (NBS Special Publication 260-53)* (Washington, DC: US Government Printing Office)
- [26] Harned H S and Owen B B 1958 *The Physical Chemistry of Electrolyte Solutions* (New York: Reinhold Scientific)
- [27] Hitchcock D I 1936 *J. Am. Chem. Soc.* **58** 855–6
- [28] Bates R G and Gary R 1961 *J. Res. Natl Bur. Stand. (US) A* **65** 495–505
- [29] Debye P and Hückel E 1923 *Phys. Z.* **24** 305–25
- [30] Bates R G and Guggenheim E A 1960 *Pure Appl. Chem.* **1** 163–8
- [31] Baucke F G K 2002 *Anal. Bioanal. Chem.* **374** 772–7
- [32] Camões M F and Lito M G 2002 *Anal. Bioanal. Chem.* **374** 806–12
- [33] Pinching G and Bates R G 1946 *J. Res. Natl Bur. Stand. (US)* **37** 311–19
- [34] Laongsri B, Boonyakong C, Tangpaisarnkul N and Cherdchu C 2007 *Accred. Qual. Assur.* **12** 194–200
- [35] Kristensen H B, Salomon A and Kokholm G 1991 *Anal. Chem.* **63** 885A–91A
- [36] Spitzer P, Eberhardt R, Schmidt I and Sudmeier U 1996 *Fresenius J. Anal. Chem.* **356** 178–81
- [37] Lee H, Kim M, Lee J and Oh S 1998 *J. Korean Chem. Soc.* **42** 432–42
- [38] Zdorikov N N *et al* 1998 *Meas. Tech.* **41** 499–503
- [39] Mathiasová A and Vyskočil L 2005 *Metrologia Skúšobníctvo* **10** 24–7
- [40] Masaki O 2005 *AIST Bull. Metrol.* **3** 657–66
- [41] Spitzer P *et al* 1999, 2001 CCQM-K9 *Final Report* available at <http://kcdb.bipm.org/AppendixD/>
- [42] Spitzer P 2001 CCQM-K9.1 *Final Report* available at <http://kcdb.bipm.org/AppendixD/> (phosphate PTB-SMU bilateral)
- [43] Spitzer P *et al* 2003 *Metrologia* **40** (Tech. Suppl.) 08006
- [44] Spitzer P *et al* 2006 *Metrologia* **43** (Tech. Suppl.) 08015
- [45] CCQM-K18, information available at <http://kcdb.bipm.org/AppendixD/> (carbonate)

- [46] Brown R J C and Milton M J T 2005 *Accred. Qual. Assur.* **10** 352–5
- [47] Rondinini S, Mussini P R and Mussini T 1987 *Pure Appl. Chem.* **59** 1549–60
- [48] Mussini T, Covington A K, Longhi P and Rondinini S 1985 *Pure Appl. Chem.* **57** 865–76
- [49] Rondinini S, Mussini P R, Mussini T and Vertova A 1998 *Pure Appl. Chem.* **70** 1419–22
- [50] Covington A K and Whitfield M 1988 *Pure Appl. Chem.* **60** 865–70
- [51] Durst R A, Davison W and Koch W F 1994 *Pure Appl. Chem.* **66** 649–58
- [52] Mussini P R, Mussini T and Rondinini S 1997 *Pure Appl. Chem.* **69** 1007–14
- [53] 1997 126. PTB Seminar PTB-W-68, Traceability of pH measurement (Braunschweig) ISBN 3-89-429-8
- [54] PTB-ThEx-25, Importance of traceable pH measurements in science and Technology 166th PTB-Seminar (Braunschweig) ISBN 3-89701-903-5
- [55] 2002 *Anal. Bioanal. Chem.* **374** 765–980
- [56] Milton M J T and Wielgosz R I 1999 New consensus on pH measurements and their traceability to the SI CCQM at its 5th Meeting (Sèvres) CCQM 99–07. Referenced in: Kadis R 2002 *Anal. Bioanal. Chem.* **374** 817–23
- [57] Damasceno J C, Borges R M H, Couto P R G, Ordine A P, Getrouw M A, Borges P P and Fraga I C S 2006 *Metrologia* **43** 306–10
- [58] CCQM-P19/P19.1 Assay of 0.01 mol kg⁻¹ hydrochloric acid Final Report
- [59] Baucke F G K 1994 *J. Electroanal. Chem.* **368** 67–75
- [60] Good N E et al 1966 *Biochem. J.* **5** 467–77
- [61] Feng D, Wu Y C and Koch W F 1989 *Anal. Chem.* **61** 1400–5
- [62] Covington A K and Rebelo M J F 1987 *Anal. Chim. Acta* **200** 245–60
- [63] Pitzer K S 1991 *Activity Coefficients in Electrolyte Solutions* (Boca Raton, FL: CRC Press)
- [64] IUPAC Project 2004-005-2-500: Comparable pH Measurements by metrological traceability: Part I—pH Measurements in water quality monitoring and assessment; Part II—pH Measurements of clinical and biochemical: To implement traceability chains for pH values in routine measurements in order to achieve target uncertainties for specific applications <http://www.iupac.org/web/ins/2004-005-2-500>
- [65] Harrar J E 1987 *Trends Anal. Chem.* **6** 152–7
- [66] Felber H, Weber M and Rivier C 2002 *Metrologia* **39** (Tech. Suppl.) 08002
- [67] Le Duigou Y, Leidert W and Bickel M 1995 *Fresenius J. Anal. Chem.* **351** 499–506
- [68] Schieffer G W 1985 *Anal. Chem.* **57** 968–71
- [69] Yoshimori T 1982 *Bunseki Kagaku* **31** E343–59
- [70] CCQM document WGIN99-01 1999 CCQM-P7 Determination of the purity of a pure compound using classical and/or instrumental methods Working Documents of the 5th Meeting (Sèvres)
- [71] Velapoldi R A, Paule R C, Schaffer R, Mandel J, Murphy T J and Gramlich J W 1979 *Standard Reference Materials: A Reference Method for the Determination of Chloride in Serum* (NBS Special Publication 260–67) (Washington, DC: US Government Printing Office)
- [72] Bishop E 1975 Coulometric analysis *Comprehensive Analytical Chemistry* ed C L Wilson and D W Wilson vol 2d (Amsterdam: Elsevier)
- [73] Berčík J 1986 *Coulometria* (Olomouc, Czechoslovakia: Vydavatelstvo ÚNM)
- [74] Breitenbach M, Eckardt E, Einert P, Jansky H-J and Moritz M 1985 *Metrologische Abh.* **5** 253–64
- [75] Pratt K W 1994 *Anal. Chim. Acta* **289** 125–34
- [76] Pratt K W 1994 *Anal. Chim. Acta* **289** 135–42
- [77] Finoly G, Leidert W, Stüber W, Le Duigou Y and Bickel M 1997 *Fresenius J. Anal. Chem.* **358** 728–35
- [78] Breitenbach M 2006 Precision Constant Coulometry System, available at http://www.bam.de/en/service/publikationen/publikationen_medien/unique_pruef/upe_101_en_1-1.pdf
- [79] Taylor J K and Smith S W 1959 *J. Res. Natl Bur. Stand. (US)* **A 63** 153–9
- [80] Berčík J, Čakrt M and Hladký Z 1979 *Conf. Coulometric Analysis—Mátrafüred* 1978 ed E Pungor and I Buzos (Budapest: Akadémiai Kiadó) pp 155–64
- [81] Breitenbach M, Eckhardt E, Jansky H-J and Schröder V 1988 *Metrologische Abh.* **8** 137–49
- [82] Asakai T, Murayama M and Tanaka T 2007 *Accred. Qual. Assur.* **12** 151–5
- [83] Malkova E M, Levchenko J N, Katyshev V N and Grishakova T E 1981 *Izmer. Tekh.* **4** 58–9
- Malkova E M, Levchenko J N, Katyshev V N and Grishakova T E 1981 *J. Meas. Sci. (USSR)* **24** 332–5 (transl.)
- [84] Máriássy M et al 2006 *Metrologia* **43** (Tech. Suppl.) 08008
- [85] CCQM-K34.1 Assay of potassium hydrogen phthalate Bilateral Comparison (BAM-SMU), Final Report
- [86] CCQM-P36 Assay of potassium hydrogen phthalate Final Report
- [87] Marinenko G and Taylor J K 1968 *Anal. Chem.* **40** 1645–51
- [88] Hioki A, Kokubun A and Kubota M 1994 *Analyst* **119** 1879–82
- [89] Asakai T, Minegishi R, Inaba N, Ishimura Y, Murayama M and Tanaka T 2006 *Anal. Sci.* **22** 461–3
- [90] Marinenko G and Champion C E 1971 *J. Res. Natl Bur. Stand. (US)* **A 75** 421–7
- [91] Marinenko G and Champion C E 1969 *Anal. Chem.* **41** 1208–11
- [92] Marinenko G and Taylor J K 1963 *J. Res. Natl Bur. Stand. (US)* **A 67** 453–9
- [93] Sappenfield S A, Marinenko G and Hague J L 1972 *Standard Reference Materials: Comparison of Redox Standards* (NBS Special Publication 260–24) (Washington, DC: US Government Printing Office)
- [94] Asakai T, Kakiyama Y, Kozuka Y, Hossaka S, Murayama M and Tanaka T 2006 *Anal. Chim. Acta* **567** 269–76
- [95] Hioki A, Kubota M and Kawase A 1992 *Analyst* **117** 997–1001
- [96] Hioki A, Kubota M and Kawase A 1991 *Talanta* **38** 397–404
- [97] Marinenko G, Koch W F and Etz E S 1983 *J. Res. Natl Bur. Stand. (US)* **88** 117–24
- [98] Tanaka T, Marinenko G and Koch W F 1985 *Talanta* **32** 525–30
- [99] Marinenko G and Taylor J K 1967 *Anal. Chem.* **39** 1568–71
- [100] Marinenko G 1977 *J. Res. Natl Bur. Stand. (US)* **A 81** 1–4
- [101] Ma L D 2002 *Accred. Qual. Assur.* **7** 163–7
- [102] Breitenbach M 1988 *Metrologische Abh.* **8** 335–42
- [103] Breitenbach M, Jansky H-J, Levchenko J N and Proskurnikow A A 1989 *Metrologische Abh.* **9** 197–204
- [104] Marinenko G and Taylor J K 1963 *J. Res. Natl Bur. Stand. (US)* **A 67** 31–5
- [105] Ostermann M, Berglund M, Taylor P D P and Máriássy M 2001 *Fresenius J. Anal. Chem.* **371** 721–5
- [106] Asakai T, Hara H, Murayama M and Tanaka T 2006 *Analyt. Sci.* **22** 1121–4
- [107] Bower V E and Davis R S 1980 *J. Res. Natl Bur. Stand. (US)* **85** 175–91
- [108] Marinenko G and Foley R T 1975 *J. Res. Natl Bur. Stand. (US)* **A 79** 737–45
- [109] Marinenko G and Foley R T 1975 *J. Res. Natl Bur. Stand. (US)* **A 79** 747–59
- [110] Margolis S A 1997 *Anal. Chem.* **69** 4864–71

- [111] Mitchell G D and Bell A A 1991 *J. Res. Natl Inst. Stand. Technol.* **96** 547–50
- [112] Mitchell G D and Bell A A 1991 *J. Res. Natl Inst. Stand. Technol.* **96** 541–6
- [113] Magonski J and Korzeniewski K 2002 *Chemia Analityczna* **47** 559–70
- [114] Johnson K M, Kortzinger A, Mintrop L, Duinker J C and Wallace D W R 1999 *Mar. Chem.* **67** 123–44
- [115] Knoeck J and Diehl H 1969 *Talanta* **16** 181–93
- [116] Claesson J and Lindberg J 1972 *J. Electroanal. Chem.* **40** 255–64
- [117] Claesson J and Lindberg J 1972 *J. Electroanal. Chem.* **40** 265–81
- [118] Pratt K W 1998 personal communication *CCQM IAWG Meeting (Sèvres, France, April 1998)*
- [119] Eckfeld E L and Schaffer E W 1965 *Anal. Chem.* **37** 1534–40
- [120] Koch W F, Poe D P and Diehl H 1975 *Talanta* **22** 609–11
- [121] Vyskočil L and Mathiasová A 1986 Approximation of the titration equivalent point location in the determination of major constituent in reference materials *Proc. 8th INSYMET '86 (Int. Symp. on Metrology) (Bratislava)* pp 128–32
- [122] Koch W F, Hoyle W C and Diehl H 1975 *Talanta* **22** 717–27
- [123] Hoyle W C, Koch W F and Diehl H 1975 *Talanta* **22** 649–53
- [124] Lingane J J, Langford C H and Anson F C 1957 *Anal. Chim. Acta* **16** 165–74
- [125] Lingane J J and Kennedy J H 1956 *Anal. Chim. Acta* **15** 465–72
- [126] CCQM document CCQM99-16 1999 CCQM Working document on coulometry *Working Documents of the 5th Meeting (Sèvres)*
- [127] Tang G, Lin D and Li Z 1985 *Acta Metrologica Sin.* **6** 50–4
- [128] Máriássy M and Pratt K W 1997 Personal communication, NIST
- [129] Roller P S 1932 *J. Am. Chem. Soc.* **54** 3485–99
- [130] Máriássy M 2000 Coulometry for purity determination *CCQM Primary Methods Symp. (Sèvres, France, 4–5 April 2000)*
- [131] Champion C E and Marinenko G 1969 *Anal. Chem.* **41** 205–7
- [132] Jones G and Bollinger G M 1931 *J. Am. Chem. Soc.* **53** 411–51
- [133] Pratt K W, Koch W F, Wu Y C and Berezansky P A 2001 *Pure Appl. Chem.* **73** 1784–93
- [134] Van der Pauw L J 1958 *Philips Res. Rep.* **13** 1–9
- [135] Moroń Z, Rucki Z and Szczepanik Z 1997 *IEEE Trans. Instrum. Meas.* **46** 1268–73
- [136] Moroń Z 2003 *Measurement* **33** 281–90
- [137] Schreiner R H 2002 *J. Res. Natl Inst. Stand. Technol.* **107** 393–9
- [138] Barron J J and Ashton C 2005 *Cal Lab* **12** 24–9
- [139] OIML 1981 *Standard Solutions Reproducing the Conductivity of Aqueous Electrolytes International Recommendation R56* (Geneva, Switzerland: Organisation Internationale de Métrologie Légale) available at <http://www.oiml.org/publications/R/R056-e81.pdf>
- [140] Jones G and Bradshaw B C 1933 *J. Am. Chem. Soc.* **55** 1780–800
- [141] Shedlovsky T 1932 *J. Am. Chem. Soc.* **54** 1411–28
- [142] Juhász E and Marsh K N 1981 *Pure Appl. Chem.* **53** 1841–5
- [143] Wu Y C, Koch W F, Feng D, Holland L A, Juhász E, Arvay E and Tomek A 1994 *J. Res. Natl Inst. Stand. Technol.* **99** 241–6
- [144] Wu Y C and Koch W F 1991 *J. Solut. Chem.* **20** 391–401
- [145] Robinson R A and Stokes R H 1959 *Electrolyte Solutions* 2nd edn (London: Butterworths) vol 87 pp 93–5
- [146] Bard A J and Faulkner L R 2001 *Electrochemical Methods: Fundamentals and Applications* 2nd edn (New York: Wiley) pp 376–80
- [147] Jensen H D 2005 Deriving the Conductivity Value presented at *CCQM EAWG Meeting, Bureau Int. des Poids et Mesures (Sèvres, France, 11 April 2005)*
- [148] Barsoukov E and Macdonald J R 2005 *Impedance Spectroscopy: Theory, Experiment, and Applications* 2nd edn (Hoboken, NJ: Wiley)
- [149] Clinical and Laboratory Standards Institute (formerly NCCLS) Miller W G (Chair) 2006 *Preparation and Testing of Reagent Water in the Clinical Laboratory; Approved Guideline—Fourth Edition* (Wayne, PA, USA: CLSI) Document C3-A4
- [150] Light T S, Licht S, Bevilacqua A C and Morash K R 2005 *Electrochem. Solid State* **8** E16–9
- [151] Thornton R D and Light T S 1989 *Ultrapure Water* **6** 14–21
- [152] Spitzer P, Rossi B, Gagniet Y, Mabic S and Sudmeier U 2005 *Accred. Qual. Assur.* **10** 78–81
- [153] Spitzer P 2006 *Springer Handbook of Materials Measurement Methods* H Czichos *et al* (Berlin: Springer) pp 444–52
- [154] Rosa E B and Dorsey N E 1907 *Bull. Bur. Stand.* **3** 433–604
- [155] Kohlrausch F 1906 *Verh. Deutsch. Phys. Ges.* **8** 151–4
- [156] Radius N and Douwes C 1970 Simple cell for rapid determination of electrical conductivity of low-conductivity liquids *Proc. 1st Int. Conf. on Static Electricity (Vienna)* (Koninklijke Shell-Laboratorium Amsterdam) pp 240–7
- [157] ASTM International 2000 *Standard Test Method for Electrical Conductivity of Liquid Hydrocarbons by Precision Meter* Standard D4308.85 (Reapproved 2000) (Conshohocken, PA, USA: ASTM International)
- [158] Haraldsson C, Magnusson B and Pyykkö R 2003 Calibration—low conductivity from ultra pure water to $10 \mu\text{S cm}^{-1}$ (1 mS m^{-1}) *CCQM EAWG Meeting (Sèvres, France, 8 April 2003)*
- [159] Farrington A M and Slater J M 1997 *Analyst* **122** 593–6
- [160] Jensen H D 2006 *Final Report of Key Comparison CCQM-K36* 15 August 2006, available online at http://kcdb.bipm.org/AppendixB/appbresults/ccqm-k36/ccqm-k36_final_report.pdf
- [161] 1993 *ISO Guide to the Expression of Uncertainty in Measurement* 1st edn ISBN 92-67-10188-9 (Geneva, Switzerland: International Organization for Standardization)