



# The physical chemistry primary traceability at CMI

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## Abstract

This article describes the actual achievements in the field of physical chemistry and introduces the methods of traceability used in the Department of Primary Metrology of Physical Chemistry in the fields of electrolytic conductivity, pH and coulometry.

The Department of Primary Metrology of Physical Chemistry is located in Brno, the second largest city of the Czech Republic.

The basic theory and the construction of the primary measurement standard of electrolytic conductivity is described. The primary conductometric cell consists of three parts. The length parameters of the most important middle part are precisely measured. The original conductometric cell was modified to reduce the volume of the measured liquid. The measurement standard participated in key comparisons with further publishing results in KCDB and in 2018 it was established as the state measurement standard of electrolytic conductivity in the range (0.005–10) S·m<sup>-1</sup>.

In 1999, the construction of the primary pH measurement standard began. The primary measurement standard consisted of five Harned cells without transfer. The challenge was the design of Harned cells. In 2005, a new, simpler design of Harned cells was used. After determining the standard potential of the five reference electrodes, the acidity function of the buffer is determined. The measurement standard participated in key comparisons with further publishing results in KCDB and in 2014 it was established as the state pH measurement standard.

The Czech Metrology Institute is also a producer of certified reference materials for pH and electrolytic conductivity. It was accredited by the Czech Institute for Accreditation according to the EN/ISO 17034 standard in 2015.

In 2015, the new primary measurement standard for substance quantities was put into operation. Coulometry as a primary method is used to realise and transfer the unit of substance through primary reference materials. In 2019, it successfully participated in the key comparison CCQM-K73.2018. It is planned to establish the primary measurement standard for the quantity of substances as a state measurement standard in the near future.

**Keywords:** primary traceability; physical chemistry; electrolytic conductivity; pH; coulometry.

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## 1. The state measurement standard of electrolytic conductivity in the range (0.005–10) S·m<sup>-1</sup>

Measurement of electrolytic conductivity of liquids is important in wide range of industrial sectors (energetic industry, waterworks industry, food industry, chemical industry, health service and pharmaceutical industry).

### 1.1. Basic theory of measurement of electrolytic conductivity

Electrolytic conductivity of liquids is ability of solution to conduct electric current. The magnitude of electric current is directly proportional to the quantity of ions present in conductive solution; therefore,

measurement of conductivity is in many cases informative about concentration of ions in the solution. In water solutions, the value of measurable conductivity is ranging from the lowest values in ultra-pure water (0.055 μS·cm<sup>-1</sup>) to the highest values in concentrated chemical samples (200 mS·cm<sup>-1</sup>). Value of conductance of electrolytes depends on migration of ions present in the solution to electrodes (mobility of ions), further on number of ions and their charge, and also on the temperature of the solution. Electrolytic conductivity is usually denoted using the symbol  $\kappa$  (small kappa). The unit of conductivity  $\kappa$  is S·m<sup>-1</sup>, in practice the most used units are mS·cm<sup>-1</sup> (1 mS·cm<sup>-1</sup> = 0.1 S·m<sup>-1</sup>) and μS·cm<sup>-1</sup> (1 μS·cm<sup>-1</sup> = 10<sup>-4</sup> S·m<sup>-1</sup>). Conductivity can

be expressed as reversed value of resistivity  $\rho$  (measurable resistance), i.e.  $\kappa = 1/\rho$ . Some devices, especially those for measuring very low conductance, display resistivity. Its basic unit is  $\Omega\cdot\text{m}$ ; frequently used unit is  $1\text{ M}\Omega\cdot\text{cm} = 10^4\ \Omega\cdot\text{m}$  which corresponds to conductivity  $1\ \mu\text{S}\cdot\text{cm}^{-1}$ .

In standard practice there are different types of conductometers used for measuring electrolytic conductivity, which measure resistance of liquid in between electrodes of conductivity probe submerged in measured liquid. The majority of conductometers have the option of temperature compensation, i.e. they can recalculate current value of measured conductance of given solution to conductance at reference temperature  $25\ ^\circ\text{C}$ , alternatively  $20\ ^\circ\text{C}$ . Alternating current is used for measurement to prevent polarization of electrodes. Historically, the measurement of conductivity was carried out between two platinum boards (the size of  $1\times 1\text{ cm}$ ) placed  $1\text{ cm}$  far from each other. If the electric conductivity  $G$  of substance is known, then conductivity can be calculated using the relation (1), where  $l$  is the distance between electrodes in  $\text{cm}$  and  $S$  is the area of boards of electrodes in  $\text{cm}^2$

$$\kappa = G \cdot \left(\frac{l}{S}\right) = \left(\frac{1}{R}\right) \cdot \left(\frac{l}{S}\right). \quad (1)$$

### 1.2. The primary measurement standard

The purpose of metrology of electrolytic conductivity is to ensure the unit of electrolytic conductivity with traceability to units of SI and transfer it to primary certified reference materials, secondary measurement standard, secondary certified reference materials, working standards and working measuring instruments, in the range  $(0.0050\text{--}10)\ \text{S}\cdot\text{m}^{-1}$  and accuracy according to the needs of industry and other users in the Czech Republic [1–2].

The development of the primary measurement standard of electrolytic conductivity began in 1999. In the following years progressive enhancements were

performed, which enabled CMI to declare it as the national measurement standard in 2018.

The traceability of the primary measurement standard of electrolytic conductivity to units of SI is ensured via unit of length and unit of resistance.

The basis of the primary measurement standard of electrolytic conductivity in the range  $(0.005\text{--}10)\ \text{S}\cdot\text{m}^{-1}$  is the glass conductometry cell (Fig. 1) made in the Czech Republic – in the Institute of plasma physics of Czech Academy of Sciences Prague, located in Turnov, Developmental optical workroom. The cell consists of three parts. In the two edge parts there are platinum electrodes built-in, which are charged with alternating voltage. The middle part has got precisely measured length parameters (inner diameter  $d$  and length of cylinder  $l$ ). Based on these length parameters the constant of middle part is calculated by equation (2)

$$K = l/S = l/(\pi d^2/4), \quad (2)$$

where  $l$  is the length of middle part of the primary cell, calibrated, in  $\text{m}$ ;  $S$  is the area of cross section of middle part of the primary cell, in  $\text{m}^2$ ;  $d$  is the diameter of middle part of the primary cell, calibrated, in  $\text{m}$  [3–4].

The principle of the measurement standard is based on measurement of impedance of reference materials with different concentrations of potassium chloride in two positions – measurement with the middle part and measurement of the same solution without the middle part. Electrolytic conductivity is calculated from subtraction of impedances ( $Z_2 - Z_1$ ), which are measured in these two positions of cell and ratio of length of the middle part of cell to its area (constant of cell  $K$ ). Parasitic phenomenon emerging on platinum electrodes is being eliminated this way, because it contributes the same amount to conductance of cell both with and without the middle part. So, the

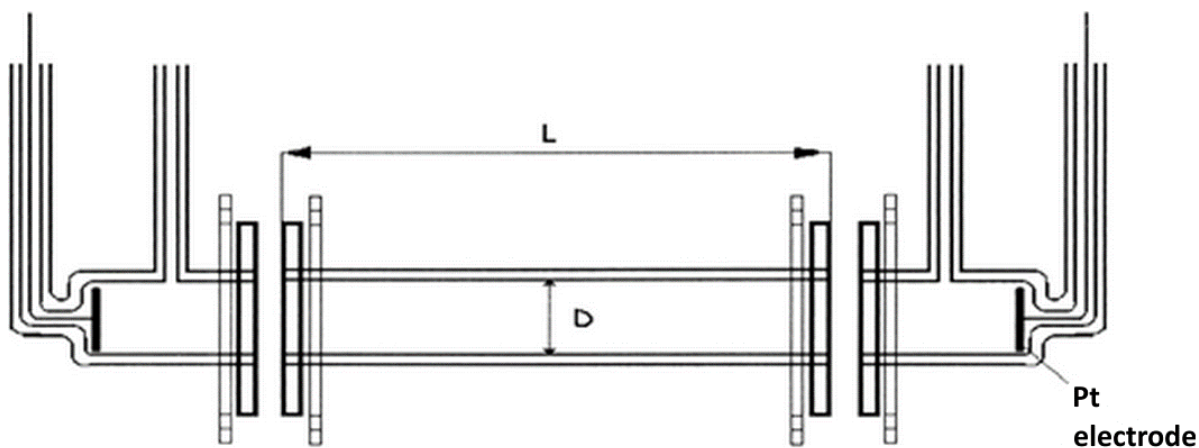


Fig. 1. The primary conductometry cell, schematic sketch

electrolyte resistance  $R_0$  can be calculated by simple subtraction:

$$R_0 = Z_2 - Z_1 = \Delta Z;$$

$$K = l/S;$$

$$\kappa = K/R_0,$$

where  $\kappa$  is electrolytic conductivity,  $S \cdot m^{-1}$ ;  $\Delta Z$  is the change of impedance corresponding the change of length of cell  $\Delta l$ ,  $\Omega$ ;  $K$  is constant of conductivity cell in  $m^{-1}$  and  $R_0$  is resistance of column of electrolyte of length  $l$ ,  $\Omega$ .

First, the measurement of electrolytic conductivity took place in oil bath Hart Scientific 7012 with thermostat regulating the temperature by  $\pm 0.005$  °C. In 2015 this bath was replaced with air thermostat TB4-LT, which reaches excellent value of stability ( $\pm 0.005$  °C) and homogeneity ( $\pm 0.01$  °C) of temperature and at the same time allows faster measurements and easier manipulation with the primary cell. Resistivity thermometer Pt 100 Tinsley 5187 SA and multimeter Keithley 2001 were replaced by resistivity thermometer Pt 25 Tinsley 5187 SA and converter Anton Paar MKT 50 in 2015. Other component of the primary measurement standard is accurate RLC bridge Agilent HP 4284A. For the construction of conductometry cell especially its plastic components 3D printer was used. Stand made by 3D printer specially tailored allows easier assemblage of the middle part of conductometry cell.

On the left there is bridge Agilent, on the right configuration of conductometry cell in the air thermostat (Fig. 2).



Fig. 2. Overall view of the configuration of the national measurement standard of electrolytic conductivity

### 1.3. Uncertainty budget for electrolytic conductivity

Table 1: Example of uncertainty  $u_B$  calculation for the primary method of electrolytic conductivity measurement of  $0.0050 S \cdot m^{-1}$ ; influence quantities:  $d$  – middle part diameter;  $l$  – middle part length;  $R_L$  – resistance with middle part;  $R_S$  – resistance without middle part;  $R_{L\infty}$  – extrapolation of  $R_L$  for  $f \rightarrow \infty$ ;  $R_{S\infty}$  – extrapolation of  $R_S$  for  $f \rightarrow \infty$ ;  $\Delta t$  – temperature stability;  $t$  – thermometer accuracy;  $x_{CO_2}$  –  $CO_2$  concentration.

### 1.4. Metrology characteristics of the primary measurement standard

The range of measurements with the primary measurement standard of electrolytic conductivity is given by the value of electrolytic conductivity of primary reference materials, which are measured on the primary measurement standard at the temperature of  $(25.000 \pm 0.005)$  °C (Table 2).

Table 1

Example of uncertainty  $u_B$  calculation for the primary method of electrolytic conductivity measurement of  $0.0050 S \cdot m^{-1}$

Influence quantity Symbol	Unit	Value	Standard uncertainty, $u_i$	Sensitivity coefficient, $c_i$	Uncertainty contribution, $u_i, c_i$	%
$d$	mm	28.2154	0.0010 mm	$-3.6 \times 10^{-4} S \cdot m^{-1}/mm$	$3.6 \times 10^{-7} S \cdot m^{-1}$	0%
$l$	mm	44.0076	0.1000 mm	$1.2 \times 10^{-4} S \cdot m^{-1}/mm$	$1.2 \times 10^{-5} S \cdot m^{-1}$	13%
$R_L$	$\Omega$	41 431	12 $\Omega$	$-3.8 \times 10^{-7} S \cdot m^{-1}/\Omega$	$4.5 \times 10^{-6} S \cdot m^{-1}$	5%
$R_S$	$\Omega$	27 760	8 $\Omega$	$3.8 \times 10^{-7} S \cdot m^{-1}/\Omega$	$3.0 \times 10^{-6} S \cdot m^{-1}$	3%
$R_{L\infty}$	$\Omega$	41 431	60 $\Omega$	$-3.8 \times 10^{-7} S \cdot m^{-1}/\Omega$	$2.3 \times 10^{-5} S \cdot m^{-1}$	24%
$R_{S\infty}$	$\Omega$	27 760	40 $\Omega$	$3.8 \times 10^{-7} S \cdot m^{-1}/\Omega$	$1.5 \times 10^{-5} S \cdot m^{-1}$	16%
$\Delta t$	°C	25	0.006 °C	$1.0 \times 10^{-4} S \cdot m^{-1}/^{\circ}C$	$5.9 \times 10^{-7} S \cdot m^{-1}$	1%
$t$	°C	25	0.008 °C	$1.0 \times 10^{-4} S \cdot m^{-1}/^{\circ}C$	$7.7 \times 10^{-7} S \cdot m^{-1}$	1%
$x_{CO_2}$	ppm	418	289 ppm	$1.2 \times 10^{-7} S \cdot m^{-1}/ppm$	$3.5 \times 10^{-5} S \cdot m^{-1}$	37%
–	–	–	–	$u_B (k = 1)$	$4.6 \times 10^{-5} S \cdot m^{-1}$	–
–	–	–	–	$u_B (k = 2)$	$9.2 \times 10^{-5} S \cdot m^{-1}$	1.8%

Ensuring the unit  $S \cdot m^{-1}$  via primary reference materials

Electrolytic conductivity at alternating electric current	Range	(0.005–10) $S \cdot m^{-1}$
	Expanded uncertainty ( $k = 2$ )	(1.7–0.1)%

### 1.5. Overview and analysis of international comparisons and calibrations

In 2005 the measurement standard took part in comparison CCQM-K36 (0.5  $S \cdot m^{-1}$  and 0.005  $S \cdot m^{-1}$ ) with pilot laboratory DFM Denmark, in 2011 – in comparison CCQM-K92 (0.05  $S \cdot m^{-1}$  and 20  $S \cdot m^{-1}$ ) with pilot laboratory SMÚ Slovakia and in 2016 CCQM-K36.2016 (0.5  $S \cdot m^{-1}$  and 0.005  $S \cdot m^{-1}$ ) – with pilot laboratory PTB Germany.

In all comparisons the measurement standard has confirmed declared uncertainty.

### 2. pH national standard

The concept of pH is unique among the commonly encountered physicochemical quantities in terms of its definition. pH was originally defined by the Danish biochemist Søren Sørensen [5] in the 1909 in terms of the concentration of hydrogen ions as:

$$pH = -\log \frac{c_{H^+}}{c^0},$$

where  $c_{H^+}$  is the hydrogen ion concentration in  $mol \cdot dm^{-3}$  and  $c^0 = 1 mol \cdot dm^{-3}$  is the standard amount concentration. Later it has been accepted that it is more satisfactory to define pH in terms of the relative activity of hydrogen ions in the solution

$$pH = -\log a_{H^+} = -\log \left( m_{H^+} + \gamma_{H^+} / m^0 \right),$$

where  $a_{H^+}$  is the relative activity and  $\gamma_{H^+}$  is the molal activity coefficient of the hydrogen ion  $H^+$  at the molality  $m_{H^+}$ , and  $m^0$  is the standard molality. The activity of the hydrogen ion  $a_{H^+}$ , which is immeasurable by any thermodynamically valid method, requires a convention for its evaluation.

In chemistry, the pH quantity serves as a scale to specify how acidic and or basic a water-based solution is. pH scale is traceable to a set of the primary standard solutions (buffers) whose pH is established by international agreement [6]. The primary pH standard values are determined using the Harned cell, by measuring the potential difference between a hydrogen electrode and a silver/silver chloride electrode. These primary standards have good reproducibility and low uncertainty.

The main role of pH primary metrology is to provide pH quantity traceable to the SI units and to transfer it to the primary reference materials, secondary standard, secondary reference materials, reference materials used for the calibration of pH electrodes,

working standards and working instruments at the range between 1.67–12.81 pH units according to needs of industry and other users in Czech Republic. The design and realization of the CMI pH standard took place between 1999–2004. It played a role of a reference standard until the declaration as the national pH standard in 2014.

The principal parts of the pH national standard (Fig. 3) are 5 pieces of Harned cell, 5 hydrogen electrodes, 5 silver/silver chloride reference electrodes, digital multimeter Keithley with scan card, barometer and resistance thermometer ZPA Ecoreg Pt 100. As the auxiliary equipment serves the water bath with the thermostat, balances, hydrogen gas management, computer with the measuring software and GPIB converter. The glass cell used for measurement consists of two half-cells. The reference silver/silver chloride electrode is placed to the right half-cell. The platinum electrode covered with the platinum black is placed to the upper part of the left half-cell. The electrodes are situated in the measuring solution. The lower part of the left half-cell constitutes of 3 parts divided by the glass frit from each other. These 3 parts are also filled with the measuring solution and the hydrogen gas is moisturized and separated to the small bubbles by passing through glass frits. The hydrogen bubbles penetrate through the third frit to the measuring solution and adsorb to the platinum black of hydrogen electrode.

### The international comparison

The pH standard took part in international comparison CCQM K-17 pH determination of an unknown phthalate buffer by Harned-Cell measurements and also at projects CCQM P-37 “Fundamental studies of pH standards” and CCQM P-52 “Study on pH of carbonate buffer” before 2004.



Fig. 3. CMI national pH standard

Example of uncertainty  $u_B$  calculation for the pH primary method of measurement

	Influence quantity, $q_i$	Symbol	Unit	Values	Standard uncertainty, $u_i$	Sensitivity coefficient, $c_i$	Uncertainty contribution, $u_i, c_i$	%
E° measurement	Cell voltage	$U$	V	0.4646	$2.50 \times 10^{-6}$	16.9	$4.23 \times 10^{-5}$	0.08%
	Temperature	$T$	K	298.15	$1.15 \times 10^{-2}$	-0.014	$1.58 \times 10^{-4}$	0.05%
	HCl Molality	$b$	mol·kg <sup>-1</sup>	0.010	$1.90 \times 10^{-6}$	86.86	$1.65 \times 10^{-4}$	0.49%
	Partial pressure H <sub>2</sub>	$p$	Pa	97100	1.50	$-2.17 \cdot 10^{-6}$	$3.26 \times 10^{-6}$	0.01%
	Stability	-	V	0.2228	$8.00 \times 10^{-6}$	16.9	$1.35 \times 10^{-4}$	16.0%
	Activity coefficient	$\gamma_{\pm\text{HCl}}$	1	0.9042	$2.89 \times 10^{-4}$	0.961	$2.77 \times 10^{-4}$	0.15%
pH determination	Cell voltage	$U$	V	0.5750	$2.50 \times 10^{-6}$	16.9	$4.23 \times 10^{-5}$	0.08%
	Temperature	$T$	K	298.15	$1.15 \times 10^{-2}$	-0.020	$2.31 \times 10^{-4}$	0.12%
	Chloride molality	$b_{\text{KCl}}$	mol·kg <sup>-1</sup>	0.0149	$5.77 \times 10^{-6}$	29.2	$1.69 \times 10^{-4}$	0.06%
	Partial pressure H <sub>2</sub>	$p$	Pa	97100	1.50	$-2.17 \times 10^{-6}$	$3.26 \times 10^{-6}$	0.01%
	Intercept	AF	1	4.0973	$3.55 \times 10^{-3}$	1.00	$3.55 \times 10^{-3}$	82.9%
	DH coefficient A	$A_{\text{DH}}$	(kg/mol) <sup>1/2</sup>	0.5107	$2.89 \times 10^{-4}$	-0.172	$4.96 \times 10^{-5}$	0.00%
	Ionic strength $I$	$I$	mol·kg <sup>-1</sup>	0.0535	$2.89 \times 10^{-4}$	-0.609	$1.76 \times 10^{-4}$	0.06%
					$u_B$	<b>0.0036</b>		

Between 2004 and 2018 the national pH standard took part in international comparisons: APMP. QM K-91 “APMP comparison pH measurement of borate buffer”; CCQM K-18 “pH determination of an unknown carbonate buffer”; CCQM K-20 “pH determination of an unknown tetraoxalate buffer” and pilot study CCQM P-93 “Preparation pilot study for phosphate pH CRMs”. The international comparison on preparation of silver/silver chloride electrode used for the primary pH measurements took place in 2013 and the results are in more details described in [7].

Uncertainty budget for primary pH method of measurement described in Table 3.

### 3. Coulometry

Coulometry is based on the direct or indirect electrochemical change of an analyte. Electrode reaction on the working electrode must always be performed with 100% current efficiency, only one reaction may take place on the electrode. The value of needed  $Q$  is expressed by the Faraday's law (3) where  $z$  is charge number,  $F$  represents Faraday's constant.

$$Q = n \cdot z \cdot F. \quad (3)$$

The solution is electrolyzed at a constant current at amperostatic coulometry. The charge  $Q$  thus is

calculated as the product of average current and the time of electrolysis where  $Q$  is charge,  $I$  is current and  $t$  is time of electrolysis:

$$Q = I \cdot t = n \cdot z \cdot F.$$

The amount of substance determination is thus directly related to the base SI units and doesn't require comparison with any reference material. Faraday's constant  $F$  is one of the essential physical constants.

#### 3.1. Primary and secondary titrations

In practice, two types of coulometric titrations are used – primary and secondary coulometric titrations. At primary coulometric titration the analyte reacts electrochemically directly on the electrode surface. This type of titration is not very common. For secondary coulometric titration the analyte reacts with the reagent produced by electrochemical reaction at one of the electrodes from a suitable supporting electrolyte. This type of coulometric titration applies to all types of volumetric assays. A total of 60 titrating agents can thus be generated. Essential requirement is that the substance from which the reagent is formed, should be in the solution dissolved in the sufficient excess. Amperostatic coulometry is a method, that produces results with low uncertainty values and is implemented in a large number of national metrology institutes.

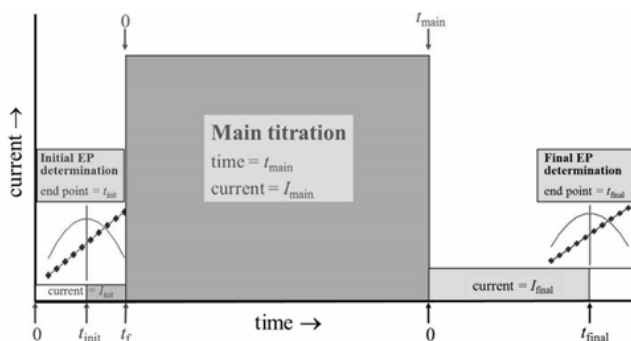


Fig. 4. Procedure of coulometric amperostatic titration [8]

General measuring procedure of amperostatic acid-base coulometric titration comprises following steps:

1. Pretitration of solution (initial endpoint determination). The current used for this step is low (on the order of mA). This step corresponds to the blank determination in classical titration.

2. Manually sample introduction directly to cathodic part of the cell.

3. Main titration of solution. The current used for this step reaches high value and more than 99.8% of sample content is titrated during this step.

4. Final titration of solution (final endpoint determination). The initial and final endpoint routines bracket the main titration and are identical.

5. Assay calculation with uncertainty analysis. Assay calculation is performed by controlling software using equation (4) after conclusion of the final endpoint determination.

The whole measuring procedure is graphically described in Fig. 4.

$$v = \frac{I_1 \cdot (t_1 - \text{kor}_1) + I_2 \cdot t_2 + I_3 \cdot (t_3 + \text{kor}_2)}{z \cdot F \cdot m' \cdot \text{kor}}, \quad (4)$$

where  $v$  – amount content of the analyte in the sample ( $\text{mol} \cdot \text{kg}^{-1}$ );  $z$  – charge number;  $F$  – Faraday's constant ( $96\,485.33212 \text{ C} \cdot \text{mol}^{-1}$ );  $m'$  – apparent mass of sample (kg);  $I_1$  – pretitration current (A);  $I_2$  – main electrolysis current (A);  $I_3$  – final titration current (A);  $t_1$  – total time of pretitration from pretitration end-point (s);  $t_2$  – main electrolysis time (s);  $t_3$  – total time of final titration until final titration endpoint (s);  $\text{kor}$  – correction to air buoyancy (1);  $\text{kor}_1$  – correction to difference between end-point and time of solution intake into the intermediate compartment (s);  $\text{kor}_2$  – correction to indication signal change after pushing solution from the intermediate compartment (s).

### 3.2. CMI coulometric standard

CMI starts to build coulometric standard in 2014. The high precision coulometry equipment was produced by Applied Precision, Slovakia. The coulometric device constitutes from the current source, the indication and valve units and from the additional devices (piston burette with accessories, exchange unit, magnetic stirrer, two coulometric cells for acid-base and other titrations, controlling computer with communication converters and controlling software). The picture of coulometric device is shown in Fig. 5.

CMI coulometric standard has successfully participated on the international key comparison CCQM K-73.2018 “Amount content of  $\text{H}^+$  in Hydrochloric Acid with nominal value  $\sim 0.1 \text{ mol} \cdot \text{kg}^{-1}$ ”. The precise determination of  $\text{H}^+$  amount content in HCl is essential for the primary pH measurement where HCl is used for the  $E^0$  determination of Ag/AgCl reference electrodes.

Uncertainty budget for coulometric titration is shown in Table 4.

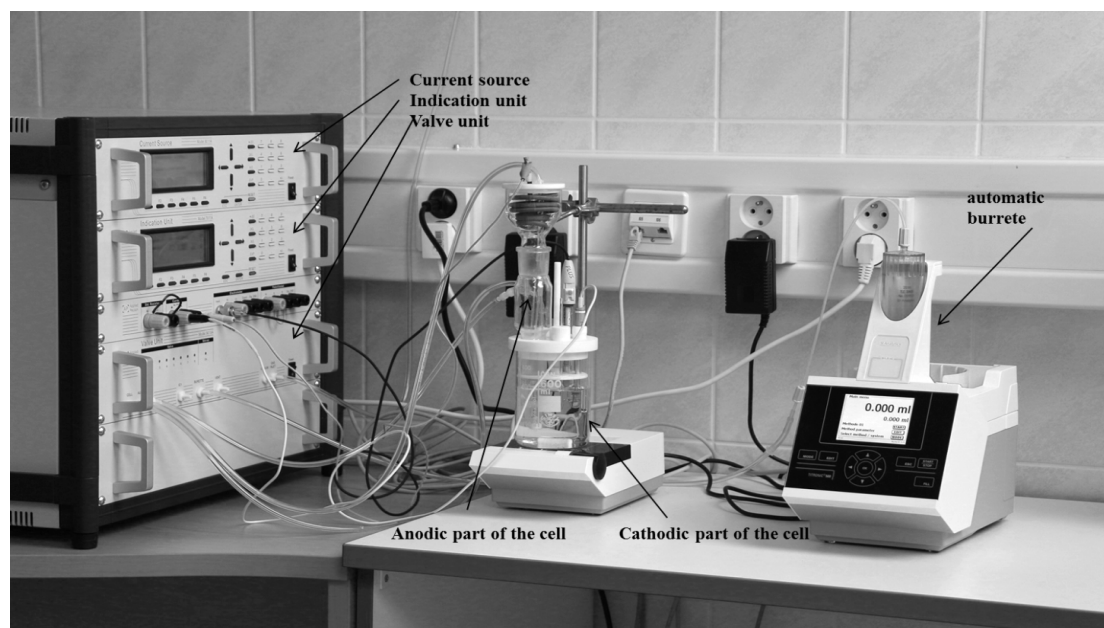


Fig. 5. Coulometric equipment

Example of uncertainty  $u_B$  calculation for the amperostatic coulometric titration of HCl with nominal value  $\sim 0.1 \text{ mol}\cdot\text{kg}^{-1}$ 

	Influence quantity, $q_i$	Symbol	Unit	Values	Standard uncertainty, $u_i$	Sensitivity coefficient, $c_i$	Uncertainty contribution, $u_i, c_i$	%
Physical part	Pretitration current	$I_1$	A	$2.0 \times 10^{-3}$	$2.04 \times 10^{-6}$	0.0197	$4.01 \times 10^{-8}$	0.00%
	Pretitration time	$t_1$	s	20	$3.01 \times 10^{-6}$	$2.07 \times 10^{-6}$	$6.23 \times 10^{-12}$	0.00%
	Correction 1	$cor_1$	s	1.00	$6.00 \times 10^{-2}$	$-2.07 \times 10^{-6}$	$-1.24 \times 10^{-7}$	0.03%
	Main titration current	$I_2$	A	0.2	$2.83 \times 10^{-6}$	$5.18 \times 10^{-1}$	$1.47 \times 10^{-6}$	4.79%
	Main titration time	$t_2$	s	500	$5.16 \times 10^{-6}$	$2.07 \times 10^{-4}$	$1.07 \times 10^{-9}$	0.00%
	Final titration current	$I_3$	A	$2.0 \times 10^{-3}$	$2.04 \times 10^{-6}$	$2.48 \times 10^{-2}$	$5.07 \times 10^{-8}$	0.01%
	Final titration time	$t_3$	A	24	$3.01 \times 10^{-6}$	$2.07 \times 10^{-6}$	$6.23 \times 10^{-12}$	0.00%
	Sample weight	m	kg	0.010	$3.10 \times 10^{-8}$	10	$3.10 \times 10^{-7}$	0.21%
	Correction	cor	1	1.001	$1.75 \times 10^{-6}$	$-1.04 \times 10^{-1}$	$-1.81 \times 10^{-7}$	0.07%
Chemical part	Aerosol losses				$4.00 \times 10^{-7}$	0.10	$4.00 \times 10^{-8}$	0.00%
	Current efficiency				$1.30 \times 10^{-7}$	0.10	$1.30 \times 10^{-8}$	0.00%
	Electrolyte impurities				$4.70 \times 10^{-6}$	0.10	$4.70 \times 10^{-7}$	0.49%
	Gas impurities				$6.50 \times 10^{-5}$	0.10	$6.50 \times 10^{-6}$	94.4%
	Rinse				$6.00 \times 10^{-7}$	0.10	$6.00 \times 10^{-8}$	0.01%
	Diffusion losses				$2.00 \times 10^{-7}$	0.10	$2.00 \times 10^{-8}$	0.00%
						$u_B$	$6.69 \times 10^{-6}$	

## Conclusion

The Czech Metrology Institute has developed the primary measurement standards for the physical chemistry quantities important for the industry in Czech Republic. The National Standard of Electrolytic Conductivity works in the range  $(0.005 - 10) \text{ S}\cdot\text{m}^{-1}$  with the expanded uncertainty from 1.7% to 0.1%, confirmed in international comparisons. The primary pH standard bases on the Harned cell measuring the potential

difference between a hydrogen electrode and a silver/silver chloride electrode provide the traceability in the range from 1.679 to 10.012 of pH with the stated uncertainties 0.020. The coulometry standard built in 2014 has also successfully participated in the international key comparison. The pH and electrolytic conductivity reference materials production are accredited according to ISO/EN 17034 by Czech Accreditation Institute.

## Простежуваність до державних первинних еталонів у галузі фізичної хімії у СМІ

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### Анотація

Описано фактичні досягнення у галузі фізичної хімії та надано методи простежуваності, що використовуються у підрозділі первинної метрології фізичної хімії у галузі електролітичної провідності, рН та кулонометрії. Підрозділ первинної метрології фізичної хімії знаходиться у Брно, другому за величиною місті Чехії.

Описано основну теорію та побудову первинного еталона електролітичної провідності. Створення еталона було розпочато в 1999 р. Первинна кондуктометрична комірка складається з трьох частин. Параметри довжини найважливішої середньої частини вимірюються прецизійно. Початкову кондуктометричну комірку було модифіковано для зменшення об'єму вимірюваної рідини. Еталон брав участь у ключових звіреннях із подальшим опублікуванням результатів у KCDDB, а в 2018 р. його було затверджено як державний еталон електролітичної провідності в діапазоні  $(0,005-10) \text{ S}\cdot\text{m}^{-1}$ .

У 1999 р. було розпочато побудову первинного еталона рН. Первинний еталон складався з п'яти комірок Харнеда без передавання. Проблемою була конструкція комірок Харнеда. У 2005 р. було використано нову, простішу їх конструкцію. Після визначення стандартного потенціалу п'яти референтних електродів визначається функція кислотності буферного розчину. Еталон брав участь у ключових звіреннях із подальшим опублікуванням результатів у KCDB, а в 2014 р. його було затверджено як державний еталон рН. Чеський інститут метрології також є виробником сертифікованих референтних матеріалів для рН та електролітичної провідності. У 2015 р. його було акредитовано Чеським інститутом акредитації відповідно до стандарту EN/ISO 17034. У 2015 р. було введено в дію новий первинний еталон кількості речовини. Кулонометрія як основний метод використовується для реалізації та передавання одиниці речовини за допомогою первинних референтних матеріалів. У 2019 р. еталон успішно взяв участь у ключовому звіренні CCQM-K73.2018. Найближчим часом планується затвердити первинний еталон кількості речовини як державний еталон.

**Ключові слова:** простежуваність до первинних еталонів; фізична хімія; електролітична провідність; рН; кулонометрія.

## Прослеживаемость к государственным первичным эталонам в области физической химии в СМІ

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### Аннотация

Описаны фактические достижения в области физической химии и представлены методы прослеживаемости, используемые в подразделении первичной метрологии физической химии в области электролитической проводимости, рН и кулонометрии. Описана основная теория и создание первичного эталона измерения электролитической проводимости. Эталон участвовал в ключевых сличениях с последующим опубликованием результатов в KCDB, а в 2018 г. был утвержден как государственный эталон электролитической проводимости в диапазоне (0,005–10) S·m<sup>-1</sup>.

В 1999 г. началось создание первичного эталона рН. Первичный эталон состоял из пяти ячеек Харнеда без передачи. В 2005 г. была использована новая, более простая конструкция ячеек Харнеда. После определения стандартного потенциала пяти референтных электродов определяется функция кислотности буферного раствора. Эталон участвовал в ключевых сличениях с последующим опубликованием результатов в KCDB, а в 2014 г. был утвержден как государственный эталон рН. Чешский институт метрологии является производителем сертифицированных референтных материалов для рН и электролитической проводимости. В 2015 г. был введен в эксплуатацию новый первичный эталон количества вещества. Кулонометрия как основной метод используется для реализации и передачи единицы вещества с помощью первичных референтных материалов. В 2019 г. эталон успешно принял участие в ключевом сличении CCQM-K73.2018. В ближайшее время планируется утвердить первичный эталон количества вещества как государственный эталон.

**Ключевые слова:** прослеживаемость к первичным эталонам; физическая химия; электролитическая проводимость; рН; кулонометрия.

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