



High-throughput and precise measurement method for electrolytic conductivity in a higher conductivity range (10 S m^{-1} to 0.1 S m^{-1}) by chromatography system with conductivity detector



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ABSTRACT

Electrolytic conductivity is one of the most common parameters to evaluate solution characteristics, and has been widely used in various fields. Conductivity meters require standard solutions with accurate electrolytic conductivities to be calibrated their geometrical cell constants; therefore, supplying large amounts of reliable electrolytic conductivity standard solutions is highly demanded. Rapid, high-throughput and precise calibration methods for the standard solutions are needed to make a large production. This paper describes a high-throughput calibration method for the standards in a higher conductivity range using a commercial ion chromatography system equipped with a common autosampler and a conductivity detector. The accuracy of the results was examined based on certified reference materials of electrolytic conductivity standardized by primary and secondary Jones-type cells. Existing calibrations with the cells were time-consuming, a few data in a day, and costly procedures. The present method enables to obtain hundreds calibration results in a day, and the expanded uncertainty ca. 0.5%. The comprehensive evaluation of the uncertainties for the presented method was carried out, resulting in the reliable measurement results and a high-efficient production of a large amount of the standards.

1. Introduction

Electrolytic conductivity is one of the most common parameters to evaluate solution characteristics, and has been widely used in various fields. Several international or national documents have been issued to measure electrolytic conductivity and examine water quality: IUPAC [1], ISO [2], OIML [3,4], ASTM [5,6] and JIS [7–11]. The Pharmacopoeial Discussion Group (PDG) has been proceeding with the harmonization project among the European Pharmacopeia (EP), the United States Pharmacopeia (USP) and the Japanese Pharmacopeia (JP). The PDG document Stage 4 to harmonize three pharmacopeias included the following description for electrolytic conductivity [12]: “The cell constant is determined by immersing the conductivity sensor in a solution of known conductivity. Solutions of known conductivity can be obtained by preparation of specific recipes according to national authoritative sources, procurement of commercially available certified and traceable standard solutions, comparison to other reference conductivity measuring systems.” Demands for certified reference materials (CRMs) of electrolytic conductivity will be increasing to obtain reliable analytical results in the globalized world economy and

international trades. Against these situations, supplying large amounts of reliable electrolytic conductivity standard solutions is in highly demand; however, the large production using primary and secondary Jones-type cells was not easy. The present study describes the development of high-throughput, precise calibration and solution homogeneity testing methods in a higher conductivity range (10 S m^{-1} to 0.1 S m^{-1}) using a commercial ion chromatography system equipped with a common autosampler and a conductivity detector. The higher conductivity range is defined in JIS K 0130 [8]: aqueous potassium chloride solutions with different molalities as standard solutions (1 mol kg^{-1} , 0.1 mol kg^{-1} and 0.01 mol kg^{-1}). Existing calibrations with primary and secondary measurements were time-consuming and costly procedures. They produced a few measurements in a day, and needed special instruments such as a LCR meter, well-built cells and a thermostatic bath. A simple flow system mounted with a commercial electrolytic conductivity sensor would be inferior to the present method. The present method was expected to achieve higher reproducibility than that of a usual electrolytic conductivity meter that had ca. $\pm 0.5\%$ reproducibility. A common chromatography system has an autosampler by default and enables to obtain hundreds calibration

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results in a day without being assisted by a person. Most chemical manufacturers already have a chromatography system although that is not cheap. The target uncertainty was *well below* 5% because the Pharmacopeia defines that the measured cell constant of a conductivity sensor must be within that. The accuracy of the calibration results and the uncertainties were evaluated based on CRMs standardized by primary and secondary Jones-type cells. The reliable calibration results and a high-efficient production procedure were presented.

2. Principles of electrolytic conductivity, primary and secondary Jones-type cells

A solution resistance, R (Ω), is calculated from the resistivity, ρ (Ω m), the effective length between electrodes, l (m), and the effective cross-sectional area, A (m^2) [13]:

$$R = \rho \frac{l}{A} \quad (2-1)$$

A cell constant, K_{cell} (m^{-1}), is defined by the geometrical parameters; conductivity, κ (S m^{-1}), is defined as the reciprocal of resistivity:

$$K_{\text{cell}} = \frac{l}{A} \quad (2-2)$$

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \frac{l}{A} = \frac{K_{\text{cell}}}{R} \quad (2-3)$$

The cell constant is not easy to determine and is not always stable for an electrolytic conductivity meter in practical ways. Cell constants of commercial conductivity meters are sometimes varied by undesirable changes in the positions of the electrodes and/or chemical or mechanical modifications of the electrodes. Therefore, electrolytic conductivity meters require their calibrations with electrolytic conductivity standard solutions on regular basis. The calibration is determining the cell constant with the standard solutions by measuring the solution resistance.

A primary Jones-type cell is capable to determine the electrolytic conductivity of solutions on an absolute basis [10,11,13–15]. It has a removable central tube placed between two electrodes. The difference of solution resistances for two configurations of the Jones-type cell, long and short configurations with/without the central tube, is corresponding to the solution resistance filled in the central tube. The electrolytic conductivity can be calculated on an absolute basis from the geometry (length and cross-sectional area) of the central tube measured by a coordinate measuring machine, and the solution resistance measured by a LCR meter. A LCR meter is usually used to measure solution resistances to decrease double-layer capacitance on electrode surfaces with alternate current (AC) [16]. An analysis of impedance spectra is necessary because solution resistances significantly depend on the measurement frequency.

Electrolytic conductivity depends on temperature and changes by ca. 2% per 1 °C [17]. Electrolytic conductivity is also affected by ambient circumstances. An air-thermostatic bath is superior than those with oil or water [17–19].

A secondary Jones-type cell is constructed with a rigid geometry: the cell volume and the positions of the electrodes are rigidly fixed [20]. This type of cell is calibrated its geometry by using standard solutions. The geometry is more stable than that of commercial electrolytic conductivity meters. Similar attentions for primary measurements are necessary in secondary measurements to obtain accurate results.

As well known, these existing calibration methods with primary and secondary cells were time-consuming and costly procedures. This was a motivation of the present study.

3. Materials and methods

3.1. Preparation of solutions

JIS K 0130 [8] defines aqueous solutions of potassium chloride with different molalities as standard solutions (1 mol kg^{-1} , 0.1 mol kg^{-1} and 0.01 mol kg^{-1}) which have electrolytic conductivities ca. 10 S m^{-1} to 0.1 S m^{-1} . Solutions were gravimetrically prepared by dissolving potassium chloride in pure water. IUPAC defines “molality” as amount of substance divided by the mass of solvent not solution [21]. The amount of substance in the solution is not proportional to the mass of the solution in a molality base.

Analytical reagent grade potassium chloride obtained from Wako Pure Chemical Industries, Ltd., Osaka, Japan, was used for the preparation of solutions [22]. Potassium chloride was dried at 500 °C for 4 h without crushing and then held at room temperature for one hour in a desiccator with silica gel. The purity was determined by gravimetric titration with a silver nitrate solution standardized based on standard sodium chloride (NMIJ CRM 3008-a) through precipitation reaction [23–25]. The certified value (mass fraction) of the CRM, “purity expressed as sodium chloride for argentometry”, was $100.001\% \pm 0.045\%$ ($k = 2$). Coverage factor, $k = 2$, gives a level of confidence of approximately 95%. A type HM-30R potentiometer (pH meter) with a silver working electrode and a mercury-sulfate reference electrode of DKK-TOA Corporation, Tokyo, was used for the end point determination. The inflection point calculated by third order polynomial approximation was decided as the end point. Detailed titration procedures were previously reported [11].

The density and the molar mass of potassium chloride were 1.988 g cm^{-3} and $74.5498 \text{ g mol}^{-1}$, respectively [26,27]. Buoyancy corrections for solids and solutions were always applied.

3.2. Apparatus

Solution densities were measured by a type DMA 5000 M density meter obtained from Anton Paar Japan K.K., Tokyo.

The balances calibrated under Japan Calibration Service System (JCSS) in the Japanese Measurement Act were used for preparation of potassium chloride aqueous solutions: a type XP26 (resolution of 0.001 mg), XP205 (resolution of 0.01 mg), and PR1203 (resolution of 1 mg) of Mettler Toledo, Tokyo, Japan.

A thermometer used was a type 1502A of Fluke Corporation, Everett, WA, USA, with a Pt 100 platinum resistance temperature probe (readability 0.001 °C, the expanded uncertainty 0.008 °C ($k = 2$) calibrated under JCSS).

An air-thermostat used was a custom-built air-thermostat box with a type RP845C thermostat of LAUDA DR. R. WOBSE GmbH & Co. KG, Lauda-Königshofen, Germany, and was a different system from the reported one [11].

A LCR meter used was a type E4980A of Agilent Technologies, Santa Clara, CA, USA. The expanded uncertainty of AC resistance of the LCR meter was 0.05% in the ranges of 10 Ω to 1 M Ω at the frequency 400 Hz and at 1 kHz after calibrated under JCSS.

An ion chromatography system employed was a type ICS-5000 obtained from Dionex Corporation, CA, USA. It was equipped with an autosampler AS, a default dual pump DP, and a conductivity detector DC. Other components such as a suppressor and a column were dismounted. The eluent was water; the flow rate of the eluent was kept constant at 1 mL min^{-1} ; the oven temperature was 30 °C; the volume of the sample loop was 5 μL .

The primary and secondary Jones-type cells were previously described [11]. The primary Jones-type cell had two bare-platinum electrodes of diameter ca. 30 mm placed 170 mm apart. The geometry of the removable cylindrical tube was ca. 60 mm in length and ca. 19 mm in inner diameter. It was accurately measured by a coordinate measuring machine and traceable to the SI. The secondary Jones-type

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