NIST - NCL Joint Assay Protocol, PCC-12

Measuring the Electrolytic Conductivity of Nanoparticle Suspensions

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This protocol assumes an intermediate level of scientific competency with regard to techniques, instrumentation, and safety procedures. Rudimentary assay details have been omitted for the sake of brevity.

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1. Introduction

This document provides a protocol for measuring the electrolytic conductivity (κ) of nanoparticle suspensions of composition similar to NIST Reference Materials (RMs) 8011, 8012, and 8013, which contain gold nanoparticles in a dilute electrolyte solution. The κ value is measured by dip cell calibrated with two κ standards. Traceability is to the κ values of the respective standards. The measurement as described may be applied to small volumes (4 mL to 5 mL) and is therefore applicable to the contents of a single ampoule of each of the above RMs.

To minimize consumption of the nanoparticle suspension, the protocol for pH measurement (see procedure PCC-13) may be performed following this measurement of κ of the same sample, provided that κ is measured according to the below protocol. However, seepage of KCl from the reference junction of the pH electrode during the measurement of pH contaminates the sample with K^+ and Cl^- ions, thereby increasing any κ value obtained subsequently. For this reason, in a serial measurement of pH and κ on a single sample, the κ measurement must be performed first.

Nanoparticle suspensions of significantly different composition from NIST RMs 8011, 8012, and 8013 may require substitution of different κ standards to account for κ values outside the range 100 µS/cm to 500 µS/cm. If such a substitution is performed, the two conductivity standards selected should bracket the value of the sample being measured.

2. Reagents and Equipment

CAUTION: PERSONAL PROTECTION EQUIPMENT SUCH AS SAFETY GOGGLES, LAB COAT, AND RUBBER GLOVES (LATEX OR NITRILE) MUST BE USED WHEN OPERATING UNDER THIS PROTOCOL.

2.1 Reagents

- 2.1.1 Conductivity standard, nominal κ = 100 µS/cm at 25°C, NIST Standard Reference Material® (SRM) 3191 or equivalent
- 2.1.2 Conductivity standard, nominal κ = 500 µS/cm at 25°C, NIST SRM 3192 or equivalent
- 2.1.3 Light mineral oil, Chemical Abstracts Service (CAS) reg. no. 8042-47-5
- 2.1.4 Deionized water, resistivity at delivery >17 MΩ·cm

2.1.5 Ethanol, American Chemical Society (ACS) reagent grade, 95 %, CAS reg. no. 64-17-5

2.1.6 Compressed dry air or nitrogen (ca. 1 L/min flow rate)

2.2 Equipment

2.2.1 Conductivity dip cell, nominal cell constant (K_{cell}) 1.0 cm^{-1}, Yellow Springs Instruments[1] 3403 or equivalent ("dip cell").

2.2.2 Conductivity bridge, Altex RC-20 or equivalent, measurement frequency (f), 1 kHz.

2.2.3 Test tubes, 13.5 mm inside diameter, Corning 9800-16 or equivalent. Size may vary from that specified, provided that the electrode portion of the dip cell is entirely immersed in the solution being measured, with the surface of the solution at least 2 cm above the top of the upper electrode of the dip cell. The test tubes used for the measurements of the κ standards and the samples should have similar dimensions (reproducibility of commercial test tubes is sufficient)

2.2.4 Water or oil bath, minimum volume of bath fluid 5 L, temperature controlled at (25.0 ± 0.1)°C.

2.2.5 Vessel (ca. 500 mL) to immerse in bath (only required if water bath is used).

2.2.6 Frame to hold test tubes (Section 2.2.3) vertically in the bath (Section 2.2.4) or oil vessel (Section 2.2.5).

3. Experimental Procedure

3.1 Clean and dry sufficient test tubes to equal the number of samples to be measured plus three: two for the κ standards and one "temperature equilibration test tube". Use ethanol and a compressed air or nitrogen stream to dry the insides of the test tubes after rinsing.

[1] Certain commercial equipment, instruments, or materials are identified in this procedure to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

3.2 Transfer 4 mL to 5 mL of the sample to be measured into separate clean, dry test tube(s).

3.3 Transfer a similar volume of each κ standard into a separate clean, dry test tube.

3.4 If a water bath is being used, fill the 500 mL vessel with light mineral oil and place it in the water bath. The oil surface should be below the bath level.

3.5 Place the calibrant, sample, and temperature equilibration test tubes into the oil bath (or vessel). The surface of the liquid in each test tube should be below the oil fluid level. Allow all the test tubes to equilibrate in the bath, set to 25.0°C, for at least 15 min before commencing measurements.

3.6 Perform a κ measurement on a single solution (see below for order of solutions) as follows:

3.6.1 Rinse the dip cell with deionized water to clean it. Rinse the clean dip cell with ethanol and dry it in a stream of dry compressed air or nitrogen.

3.6.2 Place the clean, dry dip cell in the temperature equilibration test tube for at least 5 min.

3.6.3 Transfer the dip cell directly from the temperature equilibration test tube to the solution to be measured. Immerse the dip cell in the test tube containing the sample. If the volume of solution is such that the displaced solution will overflow the test tube, soak up this excess displaced solution at the rim of the test tube with a clean paper towel. After immersing the dip cell to the maximum depth, verify that no bubbles are in the chamber of the dip cell. If bubbles are present, move the dip cell up and down until all bubbles are expelled.

3.6.4 Connect the dip cell to the conductivity bridge.

3.6.5 Null the bridge at f = 1 kHz. Record the resistance (R) or conductance (G).

3.6.6 Disconnect at least one lead of the dip cell from the conductivity bridge.

3.7 Perform Step 3.6 for the 500 µS/cm κ standard.

3.8 Perform Step 3.6 for the 100 µS/cm κ standard.

3.9 Perform Step 3.6 for each sample (X) to be measured. Sub-steps 3.6.1 and 3.6.2 may be deleted between solutions of nominally identical κ value.

3.10 Perform Step 3.6 for the 100 µS/cm κ standard.

3.11 Perform Step 3.6 for the 500 µS/cm κ standard.

4. Calculations

4.1 Calculate K_{cell} from the initial measurements performed in Steps 3.7 and 3.8. Use Equation (a) or (b) as applicable, where κ and R or G are the certified (κ) or measured (R or G) values for the given standard:

$$\text{(a)}\ K_{cell} = \kappa R \qquad \text{(b)}\ K_{cell} = \frac{\kappa}{G}$$

Repeat this calculation separately for the 100 µS/cm and 500 µS/cm κ standards.

4.2 Repeat Step 4.1 for the final measurements obtained in Steps 3.10 and 3.11.

4.3 Calculate $\overline{K}_{cell}$, the grand mean of all four K_{cell} determinations; $\overline{K}_{cell}(100)$, the average of the two K_{cell} values based on the 100 µS/cm standard; and $\overline{K}_{cell}(500)$, the average of the two K_{cell} values based on the 500 µS/cm standard. Calculate the relative deviation, RD:

$$RD = \left| \frac{\overline{K}_{cell}(100) - \overline{K}_{cell}(500)}{\overline{K}_{cell}} \right|$$

The quantity RD is used to characterize the effect of uncompensated fringe effects in the test tubes used in the dip cell measurements.

4.4 Using Equation (c) or (d) as applicable, calculate κ for each sample measured in Step 3.9 using $\overline{K}_{cell}$ from Step 4.3:

$$\text{(c)}\ \kappa = \frac{\overline{K}_{cell}}{R} \qquad \text{(d)}\ \kappa = G\overline{K}_{cell}$$

5. Acceptance Criteria

5.1 $RD < 0.03$ (3 %) in Step 4.3.

5.2 The relative standard deviation of the initial (Step 4.1) and of the final (Step 4.2) K_{cell} measurements for either κ standard (calculated separately) should not exceed 0.01 (1 %).

5.3 Measured κ values for replicated measurements of a given sample should not exceed the expanded uncertainty for κ stated in the certificate for NIST RMs 8011, 8012, and 8013.

6. References

1. R.H. Schreiner and K.W. Pratt, "Primary Standards and Standard Reference Materials for Electrolytic Conductivity", *NIST Special Publication 260-142, 2004 Ed.*, Technology Administration, U.S. Department of Commerce, May 2004.
2. P. Spitzer, in H. Czichos, T. Saito, and L. Smith (Eds.), *Springer Handbook of Materials Measurement Methods*, Springer-Verlag, Heidelberg, Germany, 2004, Section 9.3., p 444-452.

7. Abbreviations

ACS	American Chemical Society
C	Celsius
ca.	circa
CAS	Chemical Abstracts Service
cm	centimeter
f	frequency
G	conductance
κ	electrolytic conductivity
K_{cell}	cell constant
KCl	potassium chloride
kHz	kilohertz
L	liter
mL	milliliter
min	minute
mm	millimeter
MΩ	megohm
μS	microsiemens
NIST	National Institute of Standards and Technology
R	resistance
RD	relative deviation
RM	Reference Material
SRM®	Standard Reference Material®