Nitrogen contents of ammonium chloride and amidosulfuric acid assayed by coulometric titration with electrogenerated hypobromite ions

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Introduction

There are few reports published on RMs of NH_4Cl in which NH_4^+ are accurately determined, though NH_4Cl is widely used as a standard of NH_4^+.
In this study, NH_4^+ were assayed by coulometric titration with electrogenerated hypobromite ions.

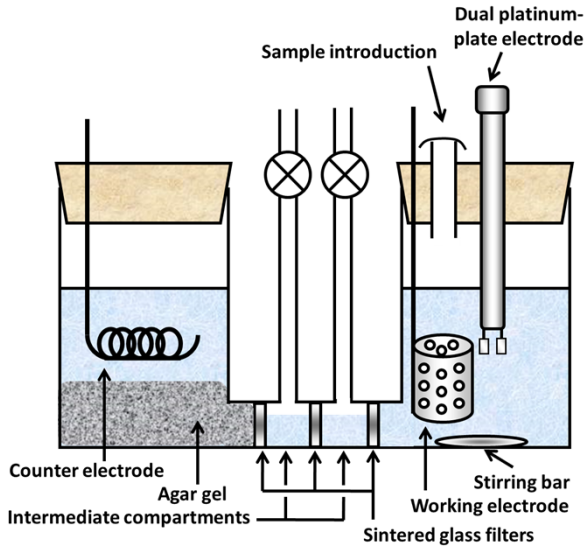
NH_2SO_3H is being used not only as a standard of acids to standardize bases such as NaOH but also as a standard of nitrogen in Kjeldahl method. The nitrogen content in high-purity NH_2SO_3H is also measurable as NH_4^+ by the coulometric titration after the acid decomposition of NH_2SO_3H.

The comprehensive evaluation of the uncertainties for NH_4Cl and NH_2SO_3H assays as nitrogen was carried out, resulting in the first establishment of CRMs for nitrogen contents with SI traceability.

NH_4Cl

NH_2SO_3H

Coulometric titration



Coulometric titration cell

Coulometric titration is one of the primary methods of measurement, and provides the link to the SI by measuring the electric charge (electrical current and time) in an electrochemical reaction based on Faraday's Laws of electrolysis.

Electrogenerated hypobromite ions are traceable to the SI, and oxidize ammonium ions to nitrogen gas. NH_4^+ in NH_4Cl are directly determined by the coulometric titration.
For NH_2SO_3H, NH_4^+ are obtained by hydrolyzing NH_2SO_3H in an acidic medium.

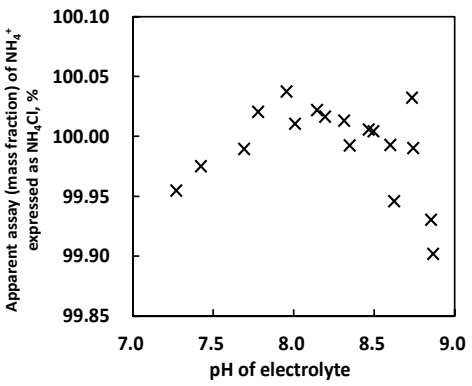
$$Br^- + 2OH^- \rightarrow BrO^- + H_2O + 2e^-$$

$$3BrO^- + 2NH_4^+ \rightarrow N_2 + 3Br^- + 2H^+ + 3H_2O$$

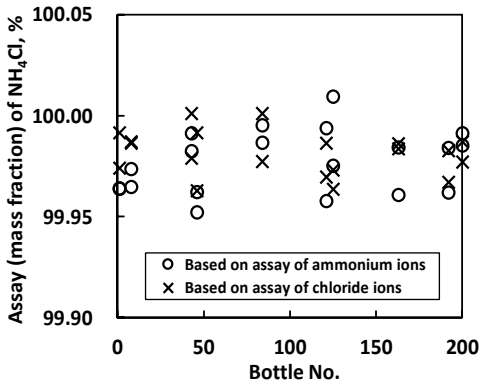
$$NH_2SO_3^- + H_2O \rightarrow NH_4^+ + SO_4^{2-}$$

$$\text{Nitrogen assay} = \frac{\text{Electric charge (C)}}{\frac{\text{Sample mass (kg)}}{\text{Molar mass (kg/mol)}} \times \text{Faraday const. (C/mol)} \times n}$$

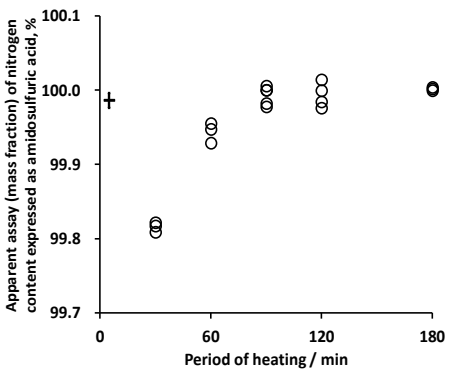
Results



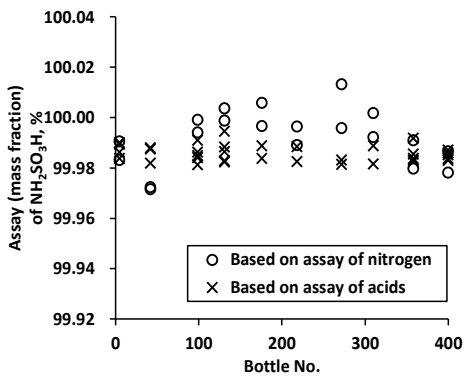
Dependency of NH_4Cl assays on pH.
The assays had a maximum around pH 8.0 to pH 8.5. The lower assays were understood as a result of the evaporation of NH_3 at higher pH values and the insufficient BrO^- electrogeneration (*e.g.*, Br_2 generation) at lower pH values.



Homogeneity test for NH_4Cl.
Ten bottles were chosen from 200 bottles for the homogeneity test. Cl^- were determined by gravimetric titration with $AgNO_3$ standardized based on NMIJ CRM NaCl through precipitation reaction.



Decomposition of NH_2SO_3H with H_2SO_4 by heating. NH_2SO_3H seemed to be completely decomposed more than 90 min by heating; the assays were close to 100 %. The bar on the left indicates the certified value (k = 2) of NH_2SO_3H as an acid determined by coulometric titration with electrogenerated OH^-.



Homogeneity test for NH_2SO_3H.
Ten bottles were chosen from 400 bottles for the homogeneity test. Both NH_4^+ and H^+ were determined by coulometric titration.

Uncertainty budget for NH_4^+ in NH_4Cl.

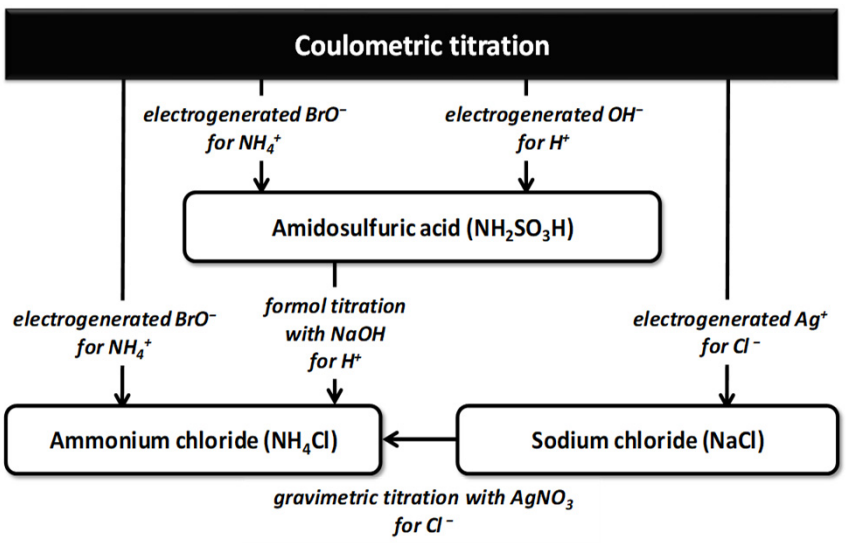
Uncertainty source	Relative standard uncertainty, %
Repeatability and homogeneity	0.017
Faraday constant	0.000 002 2
Standard resistor	0.000 65
Reference frequency	0.000 050
Voltmeter	0.000 29
Weighing and preparation	0.003 5
Molar mass	0.002 2
Current efficiency	0.004 9
Combined standard uncertainty, %	0.0182

NMIJ CRM 3011-a Ammonium chloride

Ammonium ions expressed as NH_4Cl	99.977 % ± 0.065 % (k = 2)
Chloride ions expressed as NH_4Cl	99.981 % ± 0.077 % (k = 2)

NMIJ CRM 3004-a Amidosulfuric acid

Acids expressed as NH_2SO_3H	99.986 % ± 0.010 % (k = 2)
Nitrogen expressed as NH_2SO_3H	99.992 % ± 0.031 % (k = 2)



The relationship among NH_2SO_3H, NH_4Cl and NaCl was clarified through different reactions, neutralization, redox, and precipitation reactions. The assays of these materials were all consistent within their uncertainties; consequently, the accuracy of measurement methods presented was ascertained. Providing with the CRM with the SI traceable nitrogen content enables to obtain reliable analytical data in several applications such as Kjeldahl method.

References
[1] T. Asakai *et al*., "Certified reference material for ammonium ions in high-purity ammonium chloride: Influence of pH on coulometric titration of ammonium ions with electrogenerated hypobromite", *Microchem. J*., 114 (2014) 203-209.
[2] T. Asakai, "Nitrogen content of amidosulfuric acid assayed by coulometric titration with electrogenerated hypobromite ions: establishment of SI traceability of nitrogen involving amidosulfuric acid, ammonium chloride and sodium chloride", *submitted*.