Uncertainty of ammonium nitrogen determination in wastewater

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Abstract

The measurement uncertainty of result of ammonium nitrogen determination in wastewater was evaluated. Ammonium was determined using distillation and titration method (ISO 5664). The major sources of uncertainty of the result of measurement were identified: preparation of the sample, preparation of the reagents, titration and overall repeatability of the procedure. Identification and evaluation of uncertainty sources was followed by combined uncertainty calculations. The results show that the major sources of uncertainty arose from repeatability and volumetric steps, thus leading to the conclusion what is the target operation for reducing the measurement uncertainty of this determination.

1 Introduction

The determination of the ammonium nitrogen in wastewater is of highest importance for control of industrial and municipal wastewater treatment plants operation, wastewater effluent monitoring and taxation of wastewater pollution.

The result of a measurement is only an estimate of the true value of the measurand, and therefore needs to be accompanied by an estimate of the uncertainty – the range of the stated results. It is now widely recognised that the evaluation of the uncertainty associated with a result is an essential part of any quantitative analysis. The “Guide to the Expression of Uncertainty in Measurement” [1], published by the International Organization for Standardization established general rules for evaluating and expressing uncertainty for a wide range of measurements. The ISO guide has subsequently been interpreted for analytical chemistry by Eurachem [2]. The guide recommends uncertainty be estimated from its components and by using rules for
propagation of errors in order to combine them into total uncertainty. Additional
evidence of the use of this approach is needed in chemical analysis of water and
wastewater. Every laboratory needs to quantify the measurement uncertainty by
itself for the techniques applied, combinations matrix/analyte and in its own
environment. Measurement uncertainty evaluations of the result of measurement
is also one of the requirements of standard ISO/IEC 17025 [3] which must be
fulfilled by laboratories in order to obtain accreditation for certain test methods.

The purpose of this paper was to demonstrate a procedure for evaluation of the
uncertainty of the results of ammonium nitrogen obtained by a distillation and
titration method and to identify the steps in the analytical procedure that may be
improved with the goal of reducing the overall measurement uncertainty of the
result.

2 Materials and methods

The process of evaluation of the uncertainty of ammonium nitrogen determination
was divided into the following steps: description of the method, specification of
the measurand, identification of uncertainty sources, quantification of uncertainty
components and calculation of combined and expanded uncertainty.

2.1 Description of the method

The ammonium nitrogen concentration in the wastewater was determined
titrmetrically after distillation according to standardized method (ISO 5664) [4].
The ammonium nitrogen analyses embody two general procedural steps:
distillation and titrimetric determination. In brief, the steps of the method are as
follows. The certain volume of sample is pipetted to a test tube, which is placed
in the distillation apparatus (Kjeltec Auto 2300 System II, Foss Tecator). Sodium
hydroxide and steam are added, and ammonium is distilled off. The ammonium-
rich steam is condensed in the receiving flask (distillation). The content of
ammonium in the receiving flask is determined by end-point titration to pH 4.5
with 0.05 mol/l hydrochloric acid (titration). The blank signal is obtained by the
same procedure, using the same quantities of reagents as in the determination but
using deionised water instead of the sample. Samples and blank are measured in
triplicates.

The molarity of the acid is determined by titration of standard substance
(Na₂CO₃). A stock reference solution (C₅Na₂CO₃) with a concentration of 1.000 g/l
is prepared by drying sodium carbonate (Merck, Germany) to constant mass at
105 °C, weighing the salt and dissolving it in a volumetric flask with deionised
water (Millipore, France). The aliquot of sodium carbonate solution (C₅Na₂CO₃) is
titrated with hydrochloric acid solution using methyl orange as indicator solution.
Titration for standardization of hydrochloric acid is made in triplicates.

The limit of detection of the method (three times standard deviation of the
blank sample) was estimated to be 0.2 mg/l ammonium nitrogen. The method was
kept under continuous statistical control. A control chart was created from the
results obtained in the analysis of an RM (laboratory working reference standard).
In addition a CRM (QCP 042-1, Promochem, Germany) was analysed and no significant discrepancy between our results and the certified value was found. The laboratory also participates in proficiency tests (AQUACHECK, WRc plc, UK) and good performance in this determination has been obtained.

### 2.2 Uncertainty budget of the ammonium nitrogen determination

The sample concentration of ammonium nitrogen, \( C_N \), can be expressed as:

\[
C_N = \frac{M_N \cdot (V_2 - V_1) \cdot C_{HCl}}{V_0}
\]  

where \( M_N \) is the molar mass of the nitrogen, \( V_2 \) is volume of hydrochloric acid used for titration of the sample, \( V_1 \) is volume of hydrochloric acid used for titration of the blank, \( C_{HCl} \) is molarity of hydrochloric acid and \( V_0 \) is volume of the sample analysed. Assuming the absence of any correlation between the input quantities, the uncertainty of \( C_N \) \( (u(C_N)) \) is expressed following the law of propagation of errors [1, 5]:

\[
u(C_N)^2 = \sum_{i=1}^{5} \left( \frac{\partial C_N}{\partial X_i} \right)^2 u(X_i)^2 \]  

where \( u(X_i) \) designates the standard uncertainty of one of the five input quantities expressed in equation 1, and where \( \partial C_N / \partial X_i \) is the partial derivative of the function, \( C_N \), with respect to the uncertainty component number \( X_i \). The partial derivative is called the sensitivity coefficient because it describes how the measurement result varies with changes in the value of input estimates [1, 2].

The standard uncertainties \( u(V_1) \), \( u(V_2) \), \( u(C_{HCl}) \) and \( u(V_0) \) are themselves composed from various uncertainty contributions, which were likewise obtained from uncertainty budgets. Molar mass of nitrogen was assumed to be constant with no uncertainty [6].

Relative uncertainty variance contributions are used to illustrate the relative impact of different uncertainty components. The relative uncertainty variance contribution \( (r_i) \) of an uncertainty component \( X_i \) to the combined standard uncertainty is defined here as:

\[
r_i = \frac{\left( \frac{\partial C_N}{\partial X_i} \right)^2 \cdot u(X_i)^2}{u(C_N)^2} \cdot 100
\]
2.3 Quantification of the uncertainty components

In this step uncertainties arising from each of the identified sources were quantified. Uncertainty components of a measurement result were deduced from two basically different types of evaluation: in type A, evaluations were estimated from a series of repeated observations by calculating the standard deviation of the mean, and type B evaluations were estimated as standard deviations from data from other sources, for example from information in the calibration certificates, or estimated by the analyst based on experience or general knowledge. Before calculating combined uncertainty, type B uncertainties were expressed as one standard deviation. If there were no data on the distribution, it was estimated as normal, rectangular, or triangular and then converted to a normal distribution [2].

2.3.1 Uncertainty of \( V_2 \) and \( V_1 \)

The uncertainty of volume of hydrochloric acid used for titration of the sample (\( u(V_2) \)) was split into four components: a) the uncertainty of volume of piston burette (\( u(V_{p,b}) \)), b) the uncertainty associated with the use of burette at a temperature different from that of calibration (\( u(V_T) \)), c) uncertainty of end-point of titration, and d) the repeatability of the titration of the sample (\( u(V_{rep}) \)), which assumes repeatability of volume delivery and repeatability of end-point detection. The uncertainty sources of volume of hydrochloric acid used for titration of the blank (\( u(V_1) \)) were identical.

The limits of accuracy of the piston burette were indicated to be of type B uncertainty, declared by the manufacturer with no data on distribution. A triangular distribution was assumed because values are expected to be more likely in the centre than near the bounds. Therefore to obtain the standard deviation, values were divided by \( \sqrt{6} \). The second component corrects for errors associated with the use of calibrated volumetric equipment at temperatures different from those at which it was calibrated according to the manufacturer’s instructions (20 °C). The uncertainty of this effect, \( u(V_T) \), was calculated from an estimate of the temperature range and the volume expansion coefficient. A temperature variation of \( \pm 5 \) °C was taken as a reasonable estimate. The volume expansion of water is considerably larger than that of glass, so only the former was considered. Our solutions can be treated as pure water because of their low concentrations. The temperature variation of \( \Delta T \), and the volumetric expansion coefficient of water of \( 2.1 \times 10^{-4} \text{ °C}^{-1} \) lead to a variation of volume \( V \) (\( u(V_T) \)) and was calculated as \( V \times \Delta T \times 2.1 \times 10^{-4} / \sqrt{3} \), assuming rectangular distribution.

Bias of the end-point detection was assumed to be negligible.

The standard uncertainties of repeatability of the titrations were determined experimentally and were expressed as a standard deviation of the mean [1].

All uncertainty contributions were then combined to obtain the uncertainty of the volume of hydrochloric acid used for titration of the sample (\( u(V_2) \)) and the blank (\( u(V_1) \)).
\[ u(V_2) = \sqrt{u(V_{cal})^2 + u(V_T)^2 + u(V_{rep})^2} \]  
\[ u(V_1) = \sqrt{u(V_{cal})^2 + u(V_T)^2 + u(V_{rep})^2} \] (4) (5)

2.3.2 Uncertainty of \( V_0 \)
Uncertainty of the sample volume \( (V_0) \) was split into three components: a) the uncertainty of volume of bulb pipette, b) the uncertainty of associated with the use of pipette at a temperature different from that of calibration, and c) repeatability. The uncertainties were evaluated and the combined uncertainty was obtained similar as described in equation 4.

2.3.3 Uncertainty of \( \text{C}_{\text{HCl}} \)
The concentration of hydrochloric acid, \( \text{C}_{\text{HCl}} \), can be expressed as:

\[ \text{C}_{\text{HCl}} = \frac{V_{100} \cdot 2 \cdot m_{\text{Na}_2\text{CO}_3} \cdot P}{V_{\text{HCl}} \cdot M_{\text{Na}_2\text{CO}_3} \cdot V_{1000}} \] (6)

where \( V_{100} \) is volume of sodium carbonate solution \( (C_{\text{Na}_2\text{CO}_3}) \), used for titration, \( V_{\text{HCl}} \) is volume of hydrochloric acid used for titration of sodium carbonate reference solution, \( M_{\text{Na}_2\text{CO}_3} \) is molar mass of sodium carbonate, \( m_{\text{Na}_2\text{CO}_3} \) is mass of sodium carbonate, used for preparation of reference solution, \( P \) is purity of sodium carbonate, and \( V_{1000} \) is volume of the volumetric flask for preparation of sodium carbonate reference solution. It is assumed that stoichiometry of the reaction is well defined so stoichiometric factor of 2 is taken as a constant value with no uncertainty.

The uncertainty of hydrochloric acid concentration depends on uncertainty of volume of 100 ml pipette, uncertainty of mass of \( \text{Na}_2\text{CO}_3 \), purity of the reagent, volume of \( \text{HCl} \) used for titration, and volume of 1000 ml volumetric flask.

Uncertainty components of volumetric equipment \( (V_{100}, V_{1000}, V_{\text{HCl}}) \) were evaluated in the same way as uncertainty of \( V_1 \).

Molar mass of \( \text{Na}_2\text{CO}_3 \) has uncertainty which depends on uncertainty of atomic weights of different elements [6]; in fact, these uncertainties are very low compared to other and were neglected.

The manufacturer’s literature identifies three uncertainty sources for the tared weighing \( (m_{\text{Na}_2\text{CO}_3}) \): a) the repeatability, b) the readability, and c) the calibration function of the scale. The calibration function has two potential uncertainty sources, identified as the sensitivity of the balance and its linearity. The sensitivity can be neglected because the mass was weighed by the same balance over a very narrow range.

Uncertainty of purity of the reagent was evaluated according to manufacturer’s certificate.
Assuming the absence of any correlation between the input quantities, the uncertainty of \( C_{\text{HCl}} \), \( u(C_{\text{HCl}}) \), is expressed following the law of propagation of errors [1, 5]:

\[
u(C_{\text{HCl}})^2 = \sum_{i=1}^{6} \left( \frac{\partial C_{\text{HCl}}}{\partial X_i} \right)^2 u(X_i)^2
\]

where \( u(X_i) \) designates the standard uncertainty of one of the six input quantities expressed in equation 6, and where \( \partial C_{\text{HCl}} / \partial X_i \) is the partial derivative of the function \( C_{\text{HCl}} \) with respect to the uncertainty component number \( X_i \).

### 3 Results and discussion

The values of \( M_N, V_1, V_2, C_{\text{HCl}} \) and \( V_0 \) as well as their respective standard uncertainties \( u(M_N), u(V_1), u(V_2), u(C_{\text{HCl}}) \) and \( u(V_0) \) and the corresponding sensitivity coefficients are given in Table 1.

The combined standard uncertainty \( u(C_N) \) was estimated to 0.31 mg/l. Using an coverage factor of 2, the result of the measurement should be reported as 100.41 mg/l ± 0.62 mg/l. Corresponding relative standard uncertainty is 0.62 %. It is expected that the uncertainty budget will equal the observed variation. The agreement between observed variation (0.9%) and the predicted uncertainty indicates that all major uncertainty components have been considered. Since there are no unknown sources of variability the method is in statistical control.

The relative contributions \( r_i \) from \( u(M_N), u(V_1), u(V_2), u(C_{\text{HCl}}) \) and \( u(V_0) \) to the combined standard uncertainty are shown in Figure 1.

<p>| Table 1. Values of uncertainty components of ( C_N ), their standard uncertainty and sensitivity coefficient |</p>
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Standard uncertainty</th>
<th>Sensitivity coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_N )</td>
<td>14.01 mg/mmol</td>
<td>0.004 mg/mmol</td>
<td>-28</td>
</tr>
<tr>
<td>( V_1 )</td>
<td>0.11 ml</td>
<td>0.007 ml</td>
<td>28</td>
</tr>
<tr>
<td>( V_2 )</td>
<td>3.68 ml</td>
<td>0.007 ml</td>
<td>28</td>
</tr>
<tr>
<td>( C_{\text{HCl}} )</td>
<td>50.19 mmol/l</td>
<td>0.098 mmol/l</td>
<td>2.0</td>
</tr>
<tr>
<td>( V_0 )</td>
<td>25.00 ml</td>
<td>0.017 ml</td>
<td>-4.0</td>
</tr>
<tr>
<td>( C_N )</td>
<td>100.41 mg/l</td>
<td>0.62 (k=2)</td>
<td></td>
</tr>
</tbody>
</table>
The largest contributions are from $u(V_2)$ and $u(C_{HCl})$ while the other contributions as $u(V_0)$ and $u(V_1)$ are of lower magnitude. The most relevant contributions, $u(C_{HCl})$ and $u(V_2)$, need to be analysed further. $u(V_2)$ contributes 42% to the combined standard uncertainty variance. The volume of HCl used for titration, $V_2$, is itself affected by three influencing quantities, which are repeatability of the titration, the calibration of the burette and the difference in
temperature between the temperature of the solution and temperature of the calibration of the burette. Checking the size of each contribution (Figure 2), the repeatability is by far the largest one. Therefore, measurement uncertainty can most effectively be reduced by increasing number of replicates.

Uncertainty of \( C_{\text{HCl}} \) contributes 39 \% to the combined standard uncertainty variance (Fig. 1). The concentration of HCl (\( C_{\text{HCl}} \)) is affected by six influencing quantities, which are mass of \( \text{Na}_2\text{CO}_3 \), purity of \( \text{Na}_2\text{CO}_3 \), volume of 1000 ml volumetric flask, volume of 100 ml pipette, volume of the burette and repeatability of titration for standardization of HCl. The largest contributions come from volume of HCl (\( V_{\text{HCl}} \)) and repeatability (Figure 3). Uncertainty can be reduced by replacing a burette for titration with another device with lower uncertainty and by increasing number of replicates.

In the present study all uncertainty sources were included in the calculation of combined measurement uncertainty. In routine calculation of measurement uncertainty all components smaller than one third of the largest one have no significant influence on the final result and can be neglected. For the purpose of this paper, all sources were taken into account and discussed in order to assess the implications of each of the uncertainty components and their influence on the final result.

For the selected case presented here, measurement uncertainty was calculated for one single determination of ammonium in a wastewater sample. The magnitudes of uncertainty components vary with the concentration level of the measurand and in further studies it is important to take into account the changes in the combined standard uncertainty with the level of the measurand by restricting the specified procedure to a small range of measurand concentrations.

![Figure 3: Relative uncertainty variance contributions from influencing quantities to the overall uncertainty of a single parameter \((C_{\text{HCl}})^2\)](image)
4 Conclusions

The splitting of the uncertainty budget of ammonium nitrogen determination using distillation and titration method shows that the uncertainty of the volume of hydrochloric acid \( (u(V_2)) \) used for titration of the sample and the uncertainty of the concentration of hydrochloric acid \( (u(CHC1)) \) are the greatest contributions to the total uncertainty. Further analysis of the uncertainty budget of the volume of the hydrochloric acid \( (u(V_2)) \) shows, that the main contribution of uncertainty is the repeatability of the procedure, while temperature and the burette calibration are of lower importance. Therefore, measurement uncertainty can most effectively be reduced by increasing number of replicates. Another significant source of uncertainty in the uncertainty budget of ammonium nitrogen determination is the uncertainty of hydrochloric acid concentration, used for titration \( (u(CHC1)) \). The main sources of uncertainty of \( CHC1 \) are the uncertainty of the volume of hydrochloric acid used for standardization of the hydrochloric acid \( (u(VHCl)) \) and the repeatability of the procedure. Measurement uncertainty of the concentration of hydrochloric acid can be decreased by increasing the number of replicates and by using piston burette with lower measurement uncertainty.

Systematic uncertainty budgets, such as the design presented here, facilitate the uncertainty evaluation process and makes it easier to compare contributions of uncertainty components to the total uncertainty budget. Component by component approach provides information about the relative size of the components. Detection of the major uncertainty components offers a tool for improving the performance of the determination.

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