Determination of Uncertainty for Volume Measurements Made Using the Titration Method

by Jürgen Peters

This application note provides the practical evaluation of uncertainty for volume measurements according to the *Guide to the Expression of Uncertainty in Measurement (GUM)*.[1–3] ISO 8655-7[4] covers nongravimetric methods of volume measurement. This methodology can serve as a rapid, automated test in lieu of traditional burette certification procedures recommended by manufacturers of automated titration systems.

Argentometric titration of sodium chloride

For the following example, a 20-mL cylinder built into a titrator was used. All data were generated using a Titroline alpha plus and TW alpha sample changer (**Schott Instruments,** Mainz, Germany). The requirements for systematic error of a 20-mL cylinder are 0.2% ± 0.07%.

Sample preparation

The sample, NaCl analytical degree (article no. 106404, **Merck KGaA,** Darmstadt, Germany), had a molecular weight of 58.443 g/mol. Because of the very small weight of about 11 mg for the 10% volume of the cylinder, a known solution of NaCl was made. Portions of this solution were used to get a higher weight instead of direct weight of solid NaCl. The test solution (sodium chloride) was as follows: NaCl weight—11.7043 g; water weight—1000.36 g. Because every gram of the solution contained 11.7009 mg NaCl, about 1 g for 10% of the volume of the cylinder had to be weighed instead of 11 mg.

Additional solutions used were polyvinylalcohol (**Merck** 114266)—2.000 g/L, nitric acid (**Merck** 100452)—diluted 1:4 with deionized (DI) water, and chloride-free DI water.

Each titration sample was prepared in the following manner. The test solution was weighed (see experimental results) and filled to 80 mL with DI water. Five milliliters of polyvinylalcohol solution and 2 mL of nitric acid were added.

Titration procedure

All titrations were done with the addition of dynamic titrant and precise drift control with a sample changer. Three blank samples were followed by 10 titrations (approx. 10% up to about 100% of the cylinder volume of 20 mL). After each titration, three rinsing positions were used to clean the electrode and titration tip.

For comparison purposes, another procedure was employed as well. This comprised 10 titrations for every volume of about 10%, 50%, and 100% of the cylinder volume, as typically outlined in traditional certification procedures: electrode—silver chloride with Ag/AgCl reference electrode ($NaNO_3$ electrolyte); reagent—$AgNO_3$ 0.1 mol/L (**Merck** 109081).

Cause and effect

Each step in sample preparation analysis has an associated uncertainty. Cause-and-effect diagrams very clearly show the influence of these uncertainties.

Weighing in NaCl

The weight of the NaCl depends on the real molecular weight of the actual NaCl used; the error of the balance; and the purity of the salt, as specified by the producer. The main factors are purity and weighing error. Assuming professional laboratory personnel are performing the analyses, it can be surmised that only the specified error of the balance is used. In the present case, a differential weight was not used but, rather, a well-dried salt. Although the air moisture is usually about 50%, the weighing process should be fast enough to avoid any moisture adsorption in this short period of time.

Filling with water

The weight of the water follows the same procedure. While the NaCl is weighed on an analytical balance with four decimal places, the water is weighed on a balance with two decimal places. Water has significant steam pressure, which must be taken into consideration.

Weighing the test solution

The test solution contains the uncertainty of the NaCl and the water. In addition, the single samples have some uncertainties. The weighing is done on a differential basis. Every weight has an uncertainty, the evaporation of the water important among them. Use of a syringe with small openings and nearly no evaporation is the preferred weighing method.

Total diagram

The total diagram includes all of the single uncertainties. The volume of the burette and the reproducibility of the titration must be taken into account.

Determination of single uncertainties

Molecular weight of NaCl

The molecular weight of NaCl has an unexpected influence due to the high uncertainty of the chloride ion. The uncertainty of all elements is published annually by the International Union of Pure and Applied Chemistry (IUPAC) and on the Internet. IUPAC recommends a rectangular distribution. Therefore, every value (e.g., Cl) must be calculated as follows (see *Table 1* also):

$$u_{Cl} = \frac{0.002}{\sqrt{3}}$$

The standard uncertainty of NaCl is calculated by:

$$u_{NaCl} = \sqrt{(u_{Cl})^2 + (u_{Na})^2}$$

where u_{Cl} is the uncertainty of Cl and u_{NaCl} is the uncertainty of NaCl.

continued

Table 1 Determination of uncertainty for volume measurements

Element	Atomic mol wt	Uncertainty	Standard uncertainty
Na	22.989770	0.000002	0.0000012
Cl	35.453	0.002	0.0012
NaCl	58.443		0.0012

Weighing error—NaCl

The NaCl is weighed on an analytical balance. The linear error is defined by the manufacturer as 0.15 mg in the range used. In this case, a rectangular distribution is recommended as well.

$$u_{mKCl} = \frac{0.15}{\sqrt{3}}$$

where u_{mKCl} is the uncertainty of weighted mass KCl.

No back weight was used. The salt was weighed onto weighing paper, which had no influence on the weight. The uncertainty is therefore

$$u_{mNaCl} = 0.09 \text{ mg}$$

where u_{mNaCl} is the uncertainty of weighted mass NaCl.

Purity of NaCl

The purity of the NaCl is specified by the manufacturer as $P = 1.0000 \pm 0.0025$. Since a rectangular distribution is assumed, the uncertainty is:

$$u_{PNaCl} = \frac{0.0025}{\sqrt{3}}$$

$$u_{PNaCl} = 0.00144$$

where u_{PNaCl} is the uncertainty purity of NaCl.

NaCl weight

The combined uncertainty for the NaCl weight is therefore

$$u_{wNaCl} = \frac{(u_{mNaCl} + u_{PNaCl} + u_{NaCl})}{\sqrt{9}}$$

where u_{wNaCl} is the uncertainty weight of NaCl.

The value is calculated as

$$u_{NaCl} = \frac{\frac{0.0009}{11.7043} + \frac{0.0025}{1} + \frac{0.0012}{58.433}}{\sqrt{9}} = 0.000873 \text{ mg}$$

Evaporating water

Some tests gave a rate of evaporation of 0.4 mg/min. The procedure needed a maximum of 1 min. Of course, the rate depends on the type of vessel. In the present tests, a 1-L glass bottle with a GL 45 opening was used. Rectangular distribution was assumed to be:

$$u_{pwater} = \frac{0.0004}{\sqrt{3}}$$

$$u_{pwater} = 0.00023 \text{ g}$$

where u_{pwater} is the uncertainty evaporation of water.

Weighing error—water

For this procedure, a two-decimal balance was used with a linearity of 0.01 g and a random error of 0.02 g. Each error is based on a rectangular distribution. Therefore, two uncertainties give a triangular distribution:

$$u_{m1water} = \frac{0.01}{\sqrt{3}}$$

$$u_{m1water} = 0.00577 \text{ g}$$

$$u_{m2water} = \frac{0.02}{\sqrt{3}}$$

$$u_{m2water} = 0.0115 \text{ g}$$

where $u_{m1water}$ is the uncertainty of the water weight based on the linearity error of the balance, $u_{m2water}$ is the uncertainty of water based on the random error of the balance. u_{mwater} is the combined uncertainty of the water based on the errors of the balance.

The combined uncertainty is:

$$u_{mwater} = \frac{u_{m1water} + u_{m2water}}{\sqrt{6}}$$

$$u_{mwater} = \frac{\frac{0.00577}{10000} + \frac{0.0115}{1000}}{\sqrt{6}} = 0.0000071 \text{ g}$$

Purity of water

For acid–base titrations, the risk of contaminated water is much higher than for chloride determinations. In the present experiments, 21 blank samples were run. No chloride contamination was found in any of these titrations. One producer specifies 0.05 mg/L as possible contamination. Based on a rectangular distribution:

$$u_{puwater} = \frac{0.05}{\sqrt{3}}$$

$$u_{puwater} = 0.02887 \text{ mg/L}$$

where u_{pwater} is the uncertainty purity of water.

Water weight

The combined uncertainty for the water weight is:

$$u_{water} = \frac{u_{pwater} + u_{puwater} + u_{mwater}}{\sqrt{9}}$$

where u_{water} is the uncertainty of water weight, u_{pwater} is the uncertainty of water based on evaporation, $u_{puwater}$ is the uncertainty purity of water, and u_{mwater} is the uncertainty weight of water.

The combined value for the water is:

$$u_{NaCl} = \frac{\frac{0.00023}{1000} + \frac{0.00002887}{1000} + \frac{0.0000071}{1000}}{\sqrt{9}} = 0.00000009 \text{ g}$$

Weight—test sample

The solid NaCl was weighed directly. The single portions are weighed in a syringe. In the first step the syringe was weighed with NaCl solution in water; in the second step the syringe was weighed back empty. The difference is the NaCl solution weight. Thus, the uncertainty of the linearity of the balance has to be calculated twice.

$$uts = \sqrt{2^{*}(0.09)^2} = 0.1273 \text{ mg}$$

where uts is the uncertainty weight of the test.

Evaporation of water

See above comments.

continued

Table 2 Calculated NaCl

	Weight test solution	NaCl calculated	EQ* in mL	NaCl found by titration	Delta mL**
1	1.1162	13.061	2.204	13.051	–0.002
2	2.1288	24.909	4.205	24.899	–0.002
3	3.1928	37.359	6.306	37.340	–0.003
4	3.9452	46.162	7.801	46.192	0.005
5	**4.9509**	**57.930**	**9.785**	**57.940**	**0.002**
6	6.2026	72.576	12.252	72.548	–0.005
7	7.0846	82.896	14.003	82.916	0.003
8	8.1115	94.912	16.027	94.901	–0.002
9	9.0806	106.251	17.932	106.181	–0.012
10	**9.7940**	**114.599**	**19.383**	**114.773**	**0.030**

*EQ = equivalence point.

**Delta mL = difference of the filtration result in EQ in mL and the calculated result based on the weight of the standard.

Table 3 RSD for titration method

NaCl mg	Recovery Standard of NaCl in %
13.051	**100.076**
24.899	100.039
37.340	100.050
46.192	99.935
57.940	**99.982**
72.548	100.038
82.916	99.976
94.901	100.011
106.181	100.066
114.773	**99.848**
Mean	100.002
SD	0.066
RSD	**0.066**

$$u_{pwater} = \frac{0.0004}{\sqrt{3}}$$

$$u_{pwater} = 0.00023 \text{ g}$$

Test solution of NaCl

The combined uncertainty for the test solution in the case of a 1-g sample is:

$$u_{Test} = \frac{u_{pwater} + u_{ts} + u_{NaCl} + u_{water}}{\sqrt{9}}$$

$$u_{Test} = \frac{\frac{0.00023}{1} + \frac{0.0001273}{1} + \frac{0.00000009}{1} + \frac{0.000000873}{1}}{\sqrt{9}} = 0.00011 \text{ g}$$

where u_{Test} is the uncertainty of test solution NaCl in water used for titration, u_{pwater} is the uncertainty evaporation of water test sample, u_{ts} is the uncertainty weight of test sample, u_{NaCl} is the uncertainty of NaCl weight, and u_{water} is the uncertainty weight.

Volume burette

The volume of the burette of the titrator is defined by three factors:

- Uncertainty of systematic error. The manufacturer's specifications are 0.1% of the cylinder volume, i.e., with a triangular distribution of

$$uVs = \frac{0.02}{\sqrt{6}} = 0.0082 \text{ mL}$$

where uVs is the uncertainty of the cylinder volume burette.

- Uncertainty of random error, which is 0.07% following the same assumption:

$$uVs = \frac{0.014}{\sqrt{6}} = 0.0057 \text{ mL}$$

- Uncertainty of influence of temperature; for a 19-mL volume and a water expansion coefficient of 0.00021 °C, a temperature change of 3 °C and a 95% confidence level is achieved:

$$uVt = \frac{19*0.00021*3}{1.96} = 0.006 \text{ mL}$$

The uncertainty of the volume can be calculated by:

$$u_{vol} = \sqrt{(0.0082)^2 + (0.0057)^2 + (0.006)^2} = 0.0117 \text{ mL}$$

where u_{vol} is the uncertainty of the volume.

Reproducibility

The reproducibility of the titration, remaining after these points, depends mainly on such parameters as electrode behavior, correct titration parameters, equivalence point evaluation, and signal-to-noise ratios. Since it is preferable to avoid these problems than to correct them, the researchers employed precise parameters and were able to calculate error-free equivalence points.

The signal-to-noise ratio for a chloride titration in the case of low concentrations is 1/300; it can reach 1/1000 in other cases. In some instances, the uncertainty of the titration has been neglible.

From a practical point of view, an uncertainty would be defined as:

$$u_{titration} = 0.001 \text{ mL}$$

Titration result

The uncertainty of the burette is the sought-after parameter. The titration result is calculated without the volume uncertainty of the volume by:

$$u_{Tit} \sqrt{(0.00011)^2 + (0.001)^2} = 0.001 \text{ mL}$$

where u_{Tit} is the uncertainty of titration.

Experimental results

The titer of the $AgNO_3$ solution was determined independently via many titrations and was found to be 1.013354. The calculation of the NaCl by weight is:

NaCl [mg] = weight [g] * 11.7009 [mg/g]

The NaCl found by the titration is calculated as follows (see *Table 2* also):

NaCl [mg] = EQ [mL] * 5.8433[mg/mL] * 1.103354

The RSD is sufficient for this method (see *Table 3*). The linearity of the method is shown in *Figure 1*.

The volumes for 10%, 50%, and 100% (see Table 2) were marked and compared using a procedure of 10 titrations for every volume. The results were comparable (see *Tables 4–6*).

It is precise enough to make 10 titrations covering the entire range from 10% to 100% burette volume. The results are the same for each of the 10 titrations (see *Table 7*).

continued

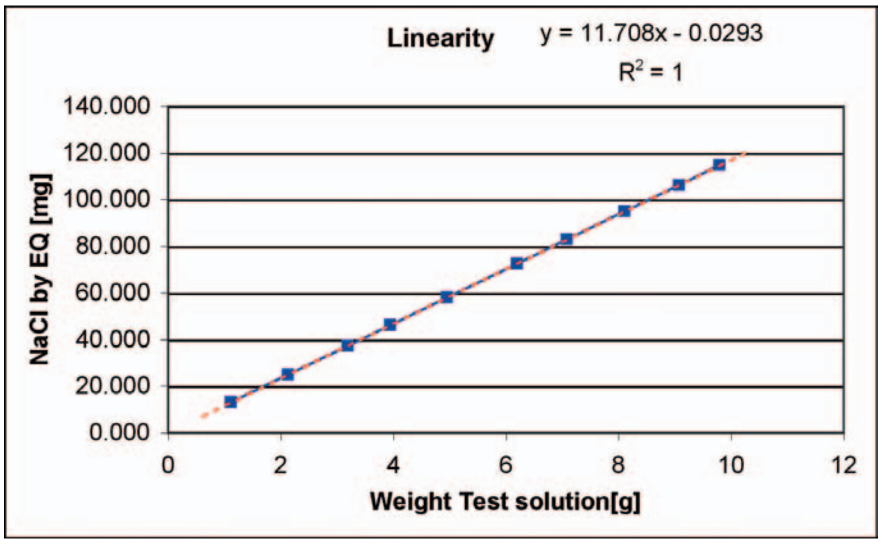

Figure 1 *Linearity of titration method.*

Table 4 Titration procedure using 10%

	Weight test solution	NaCl calculated	EQ in mL	NaCl found by titration	Delta mL
1	1.0361	12.123	2.045	12.109	–0.002
2	1.0367	12.130	2.046	12.115	–0.003
3	1.1795	13.801	2.328	13.785	–0.003
4	1.0915	12.772	2.154	12.755	–0.003
5	1.1145	13.041	2.200	13.027	–0.002
6	1.2036	14.083	2.378	14.081	0.000
7	1.1357	13.289	2.245	13.293	0.001
8	1.1925	13.953	2.354	13.939	–0.002
9	1.1998	14.039	2.368	14.022	–0.003
10	1.2047	14.096	2.378	14.081	–0.003
				Mean	**–0.002**
				SD (20)	**–0.009**

Table 5 Titration procedure using 50%

	Weight test solution	NaCl calculated	EQ in mL	NaCl found by titration	Delta mL
1	4.5294	52.998	8.952	53.008	0.002
2	4.8393	56.624	9.565	56.638	0.002
3	4.9503	57.923	9.797	58.011	0.015
4	4.9614	58.053	9.815	58.118	0.011
5	5.0027	58.536	9.886	58.538	0.000
6	5.0624	59.235	9.997	59.196	–0.007
7	5.0803	59.444	10.042	59.462	0.003
8	5.2025	60.874	10.278	60.859	–0.002
9	5.2517	61.450	10.378	61.452	0.000
10	5.6478	66.084	11.162	66.094	0.002
				Mean	**0.003**
				SD (20)	**0.015**

Table 6 Titration procedure using 100%

	Weight test solution	NaCl calculated	EQ in mL	NaCl found by titration	Delta mL
1	8.9282	104.468	17.673	104.648	0.031
2	9.2744	108.519	18.351	108.662	0.025
3	9.5155	111.340	18.825	111.469	0.022
4	9.6103	112.449	19.026	112.659	0.036
5	9.6849	113.322	19.151	113.399	0.013
6	9.7934	114.592	19.381	114.761	0.029
7	9.7940	114.599	19.383	114.773	0.030
8	9.8331	115.056	19.457	115.211	0.027
				Mean	**0.027**
				SD (20)	**0.133**

Table 7 Results for 10 titrations covering the range from 10 to 100%

% Volume	Linear method	RSD	10 Single titrations	RSD
10	–0.002	0.066	–0.002	0.052
50	0.002	0.066	0.003	0.060
100	0.030	0.066	0.027	0.034

Conclusion

The titration methodology described here is suitable for the determination of the systematic and random error of volumetric burettes. It can be used in place of burette certification procedures and/or as a rapid confirmation of burette certification procedures. The technique is recommended for digital burettes and automatic titrators with motor-driven piston burettes.

References

1. *Guide to the expression of uncertainty in measurement, 1st ed., 1993, corrected and reprinted, 1995. International Organization for Standardization (ISO), Geneva, Switzerland.*
2. *ANSI/NCSL, Z540-2-1997. U.S. guide to the expression of uncertainty in measurement, 1st ed., Oct 1997.*
3. *Eurachem/CITAC. Quantifying uncertainty in analytical measurement, 2nd ed., 2000.*
4. *ISO 8655. Piston operated volumetric instruments, parts 1–7.*

Dr. Peters is an Applications Specialist, ***Schott Instruments GmbH,*** *Hattenbergstr. 10, 55 122, Mainz, Germany; tel.: +49 6131 66 5062; fax: +49 6131 66 5001; e-mail: juergen.peters@schottinstruments.com.* ***Schott Instruments*** *is a* ***NOVA Analytics Co.*** *(Woburn, MA).*