Talanta 78 (2009) 113–119

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Uncertainty due to volumetric operations is often underestimated

Bruno Wampfler*, Matthias Rösslein

Empa, Swiss Federal Laboratories for Materials Testing and Research, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland

ARTICLE INFO

Article history:
Received 29 July 2008
Accepted 29 October 2008
Available online 7 November 2008

Keywords:
Measurement uncertainty
Combined standard uncertainty
Titration
Volumetric measurement
Weighing
Collaborative study
Reproducibility standard deviation

ABSTRACT

Fifteen international titration standards were evaluated to determine minimum and maximum combined standard uncertainties. Assuming most thorough performance of the analyses revealed minimum values, whereas maximum values of uncertainty were obtained assuming that the analyses had been done under high time pressure. Minimum and maximum uncertainties were compared with the corresponding reproducibility standard deviations. Since the combined standard uncertainty is expected to lie between the reproducibility standard deviation and the maximum combined standard uncertainty, realistic standard uncertainties of individual influence quantities of volumetric and weighing procedures could be calculated. This top-down approach revealed up to 4 times higher uncertainties for volumetric operations compared to the bottom-up approach according to the current literature. Hence, uncertainty due to volumetric operations is obviously strongly underestimated. The present study additionally contains a ranking of the contributions to the uncertainty of titrimetric results.

1. Introduction

There are several guidelines which specify how to evaluate the uncertainty of a measurement result (e.g. [1–3]). Although these guidelines are very helpful to chemical analysts, a certain expertise is needed to obtain meaningful uncertainty estimates. When quantifying influence quantities, the analysts often are forced to choose a value within a wide range. When analysts tend to choose either rather low or rather high values, the resulting uncertainty will be under- or overestimated, respectively. This can be examined by comparing the calculated combined standard uncertainties (u_c) with the corresponding reproducibility standard deviations (s_R) from collaborative studies. s_R is a useful quantity for a rough estimation of the combined standard uncertainty [4,5]. As s_R does not include all contributions to uncertainty [4,5], u_c is expected to be higher than s_R. Nevertheless, most uncertainty evaluations lead to $u_c < s_R$ [6–8]. The authors [7] suggest that calibration procedures cause underestimation, whereas weighing and volumetric operations give rise to combined standard uncertainties close to or higher than the corresponding s_R values. If this is true uncertainty calculation in titrimetry would provide meaningful value of u_c with respect to the corresponding value of s_R. Titrimetry is based on volumetric determination of the amount of an analyte which stoichiometrically reacts with the reference substance. Since the concentration of the reference substance is known, the amount of the analyte can be calculated from the volume of the reference solution which is required to reach the end point. Thus, titrimetry is based solely on gravimetric and volumetric operations. Accurately considered estimates of contributions to the uncertainty nevertheless are often unrealistically small according to our experience in titrimetric procedures, when following the EURACHEM/CITAC guide [2]. Metrologists suggest applying even smaller uncertainties for volumetric operations [9]. This might be applicable in metrological laboratories, where relative combined standard uncertainties of less than 0.04% are reached in titrimetry (e.g. [10]). Collaborative studies of field and application laboratories however seldom yield relative reproducibility standard deviation of less than 1%. The present paper aims at listing realistic standard uncertainties that can be used for the evaluation of the standard uncertainty of weighing and volumetric operations at the level of research and application laboratories. For this purpose, 15 titration procedures approved as international standards (AOAC, ASTM, DIN/EN, ISO, IUPAC) were investigated and their reported s_R values were compared with u_c values evaluated in the present study. u_c was calculated twice for each procedure: in the first calculation we assumed that the analyses were performed most accurately (minimum combined standard uncertainty, $u_{c,min}$), whereas in the second one it was assumed that the analyses were done under high time pressure (maximum combined standard uncertainty, $u_{c,max}$). Since $u_c > s_R$, and $u_{c,min}$ is considered under the most optimistic conditions, one can expect that $u_{c,min} < s_R < u_c < u_{c,max}$. In the present study, appropriate values for the quantification of individual influence quantities were evaluated from a set of international standards fulfilling this

---

* Corresponding author. Tel.: +41 274 77 86; fax: +41 274 77 88.
E-mail address: bruno.wampfler@empa.ch (B. Wampfler).

0039-9140/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2008.10.047

condition. These values can be used in future uncertainty evaluations.

2. Procedure

2.1. International standards

Only international standards have been considered whose precision values are known as repeatability standard deviation (s_r) and reproducibility standard deviation (s_R) or as repeatability limit (r) and reproducibility limit (R). Given limits were divided by the expansion factor 2.8 [11] to get the corresponding standard deviations. Different international standards from different fields of activity were consciously chosen, thus covering all important titration methods and involving a broad range of analytes and matrices (see Table 1). When evaluating the combined standard uncertainty, repeatability standard deviation is usually taken from validation data. In the present study, the repeatability standard deviation s_r from the corresponding collaborative study was used instead. In international standards, the quoted equation of the measurand does usually not completely reflect all steps performed during the application of the method. For instance, several constant parameters are often combined into one single constant, and this constant is then presented in the equation of the measurand as a single number without any units. This might facilitate the use of standard methods, but many of the parameters hidden behind such a number have an uncertainty. Therefore, all equations of the measurand were expanded to permit the complete and correct evaluation of influence quantities.

2.2. Evaluation of the measurement uncertainty

The measurement uncertainty was evaluated following the methodology of the Eurachem/CITAC Guide “Quantifying Uncertainty in Analytical Measurement” [2]. This guide describes a pragmatic and practice oriented approach to evaluate the uncertainty of volumes by involving capacity tolerance of volumetric instruments and volume change caused by temperature variation. In the present study, a third influence quantity was included when volumetric flasks and pipettes were used, namely the volume bias due to inexact filling up to the meniscus. Such bias can be caused by non-horizontal focusing on the graduation line. In addition, capacity tolerances are only valid for pure water with its typical concave meniscus. They are probably larger for organic solvents or for aqueous solutions containing surface active agents. Uncertainty due to temperature variation can accurately be calculated via density of the involved solutions [12]. The Eurachem/CITAC guide describes a more manageable way by neglecting the dependence of the volumetric expansion coefficient on the temperature. We followed Eurachem’s guide as this approach is easier to perform. The calculations were performed using the software UncertaintyManager® [13,14]. The software required the following parameters as input: equation of the measurand, manufacturers and types of instruments used for the measurement, steps of sample preparation, and validation data including conditions under which precision had been determined. The model of the uncertainty influences (cause-and-effect diagram) is built automatically. The software additionally suggested values for the quantification of the individual contributions. These values were taken from the database of the software whose data content is based on specifications of manufacturers of equipment as well as on ISO standards. The suggestions were adapted according to whether the minimum or the maximum uncertainty was calculated. Finally, the calculation was made using the Monte Carlo method [15,16] with 100,000 runs. The approach is described in detail by the following example.

2.3. Calculation of the minimum and maximum combined standard uncertainty explained by using ASTM D 4377-00 (Water in crude oils)

ASTM Standard D 4377-00 (method 15) describes a common Karl Fischer titration. Karl Fischer reagent is standardized by titration of a weighed portion of water:

$$\gamma_{KFR} = \frac{m_R}{V_{TR}} \tag{1}$$

where γ_{KFR} (mg/ml) is the water equivalence of the Karl Fischer reagent, m_R (mg) is the mass of water added, and V_{TR} (ml) is the volume of the reagent required to titrate the added water.

In order to determine the water content of crude oil, methanol with some additives is dried in a titration vessel by adding Karl Fischer reagent until the electrometric end point is reached. An aliquot of the previously homogenized crude oil is added and, after having stirred to homogenize the mixture, titrated to the electrometric endpoint again using Karl Fischer reagent. Water content is calculated according to the following equation:

$$w = \frac{V_{TS} \cdot \gamma_{KFR}}{m_S} \cdot \frac{1}{10} \tag{2}$$

where w (%) is the mass fraction of the analyte, V_{TS} (ml) is the Karl Fischer reagent required to titrate the sample, m_S (g) is the mass of the sample aliquot, and 1/10 is the factor for converting to percent.

Table 1
International standards used in the present study.

No	Analyte/matrix	Standard method	Titration method
1	Iodine value of edible oils	IUPAC 2.205	Redox
2	Peroxide value of edible oils	IUPAC 2.501	Redox
3	Methyltrioctylammoniumchloride in raw materials and products	DIN/EN 14668	Tenside, two phases
4	Anionic tensides in detergents and cleansers	DIN/EN 14669	Tenside, two phases
5	Saponification value of oils and fats	DIN EN ISO 3657	Acid-base
6	Acid value of refined palm oil	IUPAC 2.201	Acid-base, non-aqueous
7	Nitrogen in milk	ISO/FDIS 8968-3	Acid-base
8	Lead in PbS-concentrates	ISO 11441	Complexometry
9	Total hardness in water	ASTM D 1126-02	Complexometry
10	Calcium hardness in water	ASTM D 1126-02	Complexometry
11	Chloride in cheese	ISO 5943	Precipitation
12	Chloride in aggregates	DIN EN 1744-1	Precipitation
13	Water in pet foods	AOAC 991.02	Karl Fischer
14	Water in spray-dried coffee extract	DIN 10772-2	Karl Fischer
15	Water in crude oils	ASTM D 4377-00	Karl Fischer