



Voltammetric determination of caffeic, syringic and vanillic acids taking into account uncertainties in both axes



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ABSTRACT

This work presents a metrological insight into correctness of the results obtained in standard addition voltammetric determination of the selected antioxidants on a carbon-fiber microelectrode. The key issue is taking into account the uncertainty in both axes during the process of estimation of the calibration curve coefficients and results of analysis. It has been shown that in many cases, taking into account more sources of uncertainty leads to more accurate results than when using typical linear regression. Additionally, the level of the uncertainty is also lower. The problem was demonstrated on the examples of determination of micromolar concentrations of caffeic, syringic and vanillic acids in laboratory samples and artificial wine, which was regarded as a model matrix. It was observed that sensitivity for caffeic acid was ca. 8–9 times higher than for syringic acid and vanillic acid. In all experiments correlation coefficient was greater than 0.996, while recovery was between 91.5 and 117.5%. The obtained result of determination of 2 μM caffeic acid was $2.33 \pm 0.10 \mu\text{M}$, while considering uncertainties in both axes was $2.31 \pm 0.04 \mu\text{M}$. Similarly, for 5 μM syringic acid we obtained $5.91 \pm 0.47 \mu\text{M}$ and $5.52 \pm 0.37 \mu\text{M}$, while for 10 μM vanillic acid it was $9.21 \pm 1.05 \mu\text{M}$ and $9.29 \pm 0.80 \mu\text{M}$.

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1. Introduction

Operation in accordance with the rules of chemical metrology is fundamental for obtaining correct results in analytics. In physical measurements, correctness of results mainly depends on the calibration of the instrument. However, a calibration of the measurement method is additionally considered during chemical experiments [1]. The evaluation of measurement uncertainty is one of the most useful tools for assessing the reliability of an analytical work [2,3]. Detailed examination of the uncertainty sources is a principal rule of modern analytics and is absolutely necessary in presentation of the final results of measurements. Determination of the uncertainty of the calibration line parameters plays also important role.

Understanding the uncertainty of the chemical measurements could not be possible without understanding of the whole process leading to the result. First, it should be noted that the conditions of chemical analysis have never been completely defined and cannot be controlled. It is associated with the fact that usually the experimenter looks for concentrations of selected analytes instead of total composition of the sample. This means that often some components of the sample are not tested and therefore their influence on the final results are not taken into account. Moreover, in analytics, there are many sources of uncertainty. Several groups of factors as equipment, reagents, measuring procedure or the skills and commitment of people should be considered. Indirect

measurements based on the calibration procedure translate their uncertainty directly into uncertainty of the final result.

The classical concept of measurement uncertainty and the principles for its correct application were described in a Guide to the Expression of Uncertainty in Measurement (GUM) [4] edited by ISO. It internationally harmonizes the estimation and reporting of measurement uncertainties. It was subsequently adapted for the analytical chemistry by the Eurachem organization. The guide Quantifying Uncertainty in Analytical Measurement by EURACHEM/CITAC [5] can be recommended for (analytical) chemists. Good explanations and examples from the calibration field can be also found in Guidelines to the Expression of the Uncertainty of Measurements in Calibrations [6]. This modeling approach encompasses the identification and estimation of numerous possible components of uncertainty of the measurement. The individual standard uncertainties are included in the uncertainty budget in order to calculate the combined standard uncertainty of the final result. The basic principles may be formulated as a 3-step procedure:

- calculating/estimating uncertainties for each source separately,
- combining of the contributions from each uncertainty source,
- stating the uncertainty of a result.

Voltammetry is an indirect analytical method, and thus the final result of determination is always preceded by calculation of the calibration line. Estimation of uncertainty of the tested sample concentration is often calculated using classical approach based on assumption that the uncertainty on x-axis is significantly lower than the uncertainty of measured value and also the precision of the measurement is constant in considered range. However, in that approach only the observed

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variability of the dependent variable (y -axis) is taken into account. Due to the strategy of measurement in voltammetry it is reasonable to consider the uncertainty of the concentration and volume of the standard. This is due to the fact that successive portions of the standard are added to the measurement cell, spiking the real samples. Therefore, successive points for calibration are determined with the increasing uncertainty of the independent variable. In voltammetry the transfer of the electrodes to the next cell after measuring of each standard sample is not applied due to undesired contact with atmospheric air. This concerns first of all solid electrodes. The aim of this work, inspired by the works [7–9] is to check whether taking into account uncertainties in both axes has an impact on the quality of the result in standard addition voltammetry, i.e. its accordance with the true value and the level of uncertainty. The study involves comparison with the classical method which takes into account the uncertainty only on the y -axis, with a method that takes into account the uncertainties in both axes. We have also studied the compatibility of calibration coefficients, calculated using both methods, and their level of uncertainty. The calculations were realized for the data obtained during the determination of micromolar concentrations of caffeic, syringic and vanillic acids in laboratory samples and artificial wine, which was regarded as a model matrix.

2. Theory

In the strict mathematical analytical method which is well compliant with the GUM [4] (chapter 3) all components are estimated separately and the single uncertainties are combined applying the law of propagation of uncertainty. In calculation we have taken into account combination of type A and type B of standard uncertainty estimation.

2.1. Uncertainty of the standard concentration

The estimation of the combined standard uncertainty of the standard concentration is of great importance for the construction of the uncertainty budget of the analytical procedure (Fig. 1). This action enables the proper estimation of the uncertainty of the analyte concentration, what is a key issue for the quality assurance in the instrumental analysis.

In classical approach, when this factor is omitted, an essential component of the uncertainty budget is not taken into account.

Standard concentration is a parameter, the value of which cannot be obtained in a direct measurement. It is a relation between mass of sample m_s , volume of solution V_s , purity P and molar mass M . It is necessary to measure each component directly. However, it can be considered that each result is burdened with uncertainty. The combined uncertainty $u(c)$ of the stock standard concentration c is the sum of the uncertainties of each parameter and is described by formula:

$$u(c) = c \sqrt{\left(\frac{u(m_s)}{m_s}\right)^2 + \left(\frac{u(V_s)}{V_s}\right)^2 + \left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(M)}{M}\right)^2}. \quad (1)$$

An uncertainty of the mass $u(m_s)$ of sample used for the preparation of solution includes uncertainties, connected with calibration of balance and its resolution. Both these parameters are received from manufacturer. For the calculation of type B uncertainties rectangular distribution is used. An important factor of $u(m_s)$ is a repeatability of balance indications (standard deviation of the arithmetic mean). As the sample is weighed in a container, gross weight and net weight must be considered in the calculation of the uncertainty in the mass.

In calculation of the uncertainty in volume $u(V_s)$ tolerance of the volume of volumetric flask, which is specified by the manufacturer (type B method of evaluation, triangle distribution) was taken into account. Temperature during measurements was also an important factor, because calibration of volumetric flasks is realized at specified temperature. Laboratory conditions most often vary from these during calibration process and the thermal expansion coefficient of water was included in calculation of uncertainty of the volume due to temperature difference from 20 °C (type B method of evaluation, rectangular distribution). However, the most important uncertainty source that affected the value of $u(V_s)$ was a result of the manual abilities of the experimenter filling the volumetric flask. Uncertainty in the purity of standard $u(P)$ has a rectangular distribution. The value was received from the manufacturer. Uncertainty in the molar mass $u(M)$ can be calculated according to the atomic weights of the elements building considered chemical

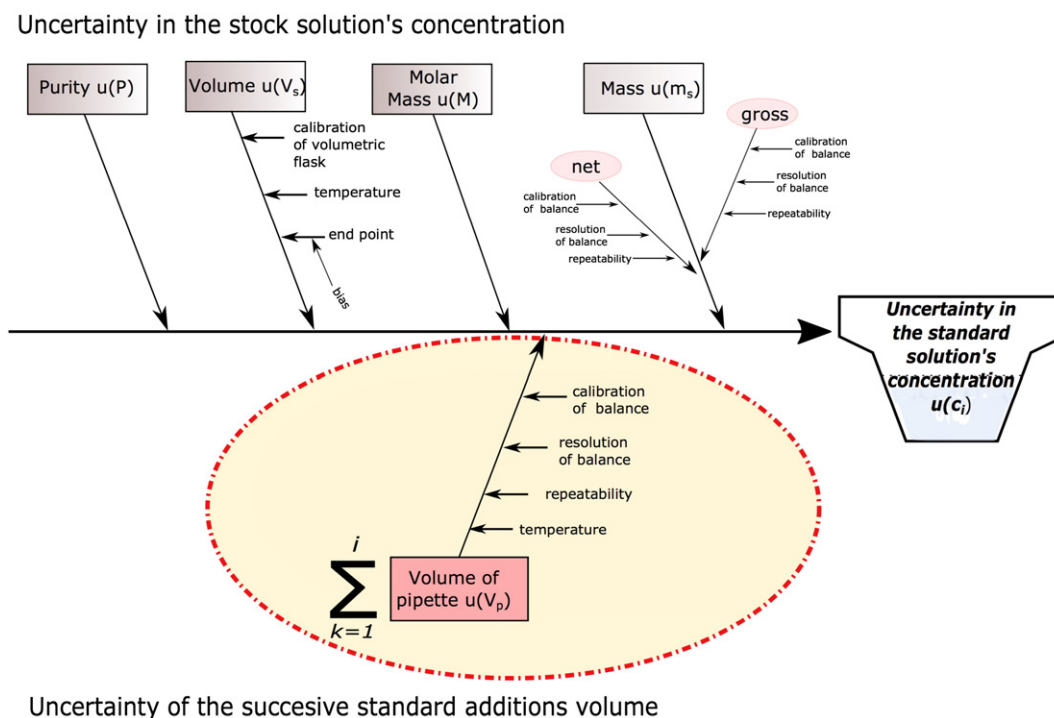


Fig. 1. Combined uncertainty in concentrations of standard solution additions.

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