



Literature survey of the factors determining the uncertainty of coulometric Karl Fischer titration method

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Abstract

This survey gives an overview of the factors that determine the uncertainty of coulometric Karl Fischer (cKF) method for water determination. Distinction is made between uncertainty sources originating from the cKF method itself and uncertainty sources due to sample handling. The “compound” uncertainty sources – repeatability, reproducibility and bias that actually incorporate the contributions from these two classes of uncertainty sources – are also briefly discussed.

Based on the literature data the most influential uncertainty sources of coulometric KF titration method are possible chemical interferences, instrument stability and the accuracy of the end point determination. The uncertainty sources due to sample handling are more problematic with solid samples than with liquid samples. The most important sample preparation related uncertainty sources are change of water content in the sample before the measurement and incomplete transfer of water from the sample to the reaction vessel.

The general conclusion is that although the uncertainty sources of the cKF method are in general rather well known the discussion is almost always either qualitative or limited to the compound uncertainty sources and there is very limited quantitative information available on the contributions of the actual uncertainty sources.

Overview of the most important literature sources

Below the literature sources used for this survey are briefly characterized. Only such sources are incorporated that at least in some way address the measurement uncertainty (accuracy, precision, bias) of the cKF method. Sources describing routine applications of cKF and not giving useful insight from the measurement uncertainty point of view have been left out of consideration.

A series of articles has been published by S. A. Margolis and co-workers.^{1,2,3,4} The authors investigate cKF method from very different aspects (evaluation of precision and bias by interlaboratory comparisons, sources of bias, etc) and also address measurement uncertainty as well as uncertainty sources in their works. They do not however carry out component-by-component quantification of measurement uncertainty.

V. C. Dominguez et al have investigated a custom-built coulometric KF titrator and have briefly analyzed the accuracy of the results. They analyzed the pros and cons of the cell with diaphragm (as

¹ S. A. Margolis *Anal. Chem.* **1997**, *69*, 4864-4871.

² S. A. Margolis *Anal. Bioanal. Chem.* **2002**, *374*, 505-512.

³ S. A. Margolis, J. Paulsen, E. Park *Anal. Bioanal. Chem.* **2002**, *374*, 1274-1281.

⁴ S. A. Margolis, C. Hagwood *Anal. Bioanal. Chem.* **2003**, *376*, 260-269.

opposed to the cell without diaphragm) and concluded that the cell with diaphragm leads to lower uncertainty.⁵

A validation study of the combined cKF instrument has been carried out by Joseph and Le Goff from LGC⁶. The study also addresses measurement uncertainty. The authors identified the following uncertainty sources: stirrer speed, carrier gas flow, oven temperature, interferences, age of the reagents, vial and septum equilibration, blank reading, sample mass measurement. However, these uncertainty sources (except sample mass measurement) were not directly quantified and during validation several potentially important sources of bias (carrier gas flow, end-point determination parameters) were kept constant during validation, meaning that the possible bias (if it existed) was not revealed. The combined standard uncertainty was found by using uncertainty components due to bias, precision and mass measurement. The somewhat troublesome aspect of the uncertainty presentation in that study was that in the water content range of 0.01% to 1% the relative standard uncertainty was reported 0.04, but at levels below 0.01% it was reported as 0.61 (!). Such ultra-sharp uncertainty increase leaves it in fact completely undefined what the uncertainty was in the vicinity of water content 0.01%.

The group of A. Cedergren have investigated a series of papers^{7, 8, 9}, the cKF method with diaphragm-less cell and conclude that it is possible to achieve accurate results and low limits of quantification also using this cell.

V. Kestens et al have investigated the vaporization cKF method focusing specifically on the uncertainty due to transferring the water from the sample to the titration medium.¹⁰ They concluded that the agreement between the methods with and without vaporization is very good, although the uncertainty of vaporization was not quantitatively expressed.

Skutina and Terentjev have published the description of the primary coulometric titration setup of the Russian federation.¹¹ Their reported experimental setup is not limited to determination of water. A comprehensive uncertainty budget is presented, but only for acid-base titration, which is not very useful for the cKF method.

Overview of the most important uncertainty sources

The uncertainty sources are below divided into three categories. The first category contains the uncertainty sources that operate starting from the moment when the water from the sample is in the KF reaction cell. The second category contains the uncertainty sources that influence the transfer of water from the initial sample to the KF reaction cell, i.e. possible loss of water during transfer or contamination of the sample by atmospheric moisture. The third category contains the “compound” uncertainty sources – repeatability, reproducibility and bias that actually incorporate the contributions from these two classes of uncertainty sources.

⁵ V. C. Dominguez, C. R. McDonald, M. Johnson, D. Schunk, R. Kreuter, D. Sykes *J. Chem. Educ.* **2010**, *87*, 987-991.

⁶ B. Joseph, T. Le Goff *Validation of the Metrohm 774 Oven Sample Processor and 831 Karl Fischer Coulometer for Moisture Determination*. LGC/AT/2006/019, LGC, Teddington., **2006**.

⁷ M. Rosvall, L. Lundmark, A. Cedergren *Anal. Chem.* **1998**, *70*, 5332-5338.

⁸ W. Larsson, A. Cedergren *Talanta* **2005**, *65*, 1349-1354.

⁹ A. Cedergren, S. Jonsson *Anal. Chem.* **2001**, *73*, 5611-5615.

¹⁰ V. Kestens, P. Conneely, A. Bernreuther *Food Chemistry* **2008**, *106*, 1454-1459.

¹¹ A. V. Skutina, G. I. Terentjev *Measurement Techniques* **2011**, *54*, 964-970.

1. Uncertainty sources originating from the cKF method

Interfering substances

It is universally recognized that possible existence of interfering substances, which either react with iodine or iodide ion or produce additional water, in the solution is an important uncertainty source in cKF method. However, there have been no attempts published to rigorously quantify this uncertainty source. This is not surprising, as it is hardly possible to do that unless the material under study is rigorously analysed with respect to all the possible chemical interferents. The influence of this uncertainty source decreases significantly if instead of dissolving (or suspending) the whole sample in the measurement cell the water from the sample is evaporated and then collected in the measurement cell.

Instrument instability

Instrument instability is manifested by somewhat differing results obtained under identical experimental conditions. Most often this uncertainty source is quantified via the repeatability of the results. In the case of the oven cKF method (i.e. the repeatability of the vaporization process is also included) relative repeatability standard deviations in the range of 0.01 and 0.02 in the water concentration range 1% to 10%.⁶ At concentration 0.1% the relative repeatability standard deviation was 0.03 and at 0.01% concentration level 0.14.⁶

The instability can be viewed also from another point of view – it is generally recognized that water constantly enters the cKF system and this constant influx has to be taken into account. In all contemporary cKF instruments the influx of water is constantly monitored. It is advisable to begin titration only when the influx has remained constant. This influx then is recorded by the instrument and used for correcting the result. However, if the influx of water changes during titration then this introduces additional uncertainty and can be viewed as a manifestation of instability of the cKF instrument.

Inaccurate end point determination

The titration end point in the cKF method is generally determined by the bivalentammetric approach. A constant small alternating current is maintained between two platinum electrodes immersed in the titrated solution. Constancy of the current is achieved by automatic adjustment of the potential difference between the electrodes. As long as the free iodine content in the solution is negligible, the required potential difference is high. As soon as the equivalence point is reached the potential difference drops sharply and this is used for determining the end point. It is recognized that the coulometric KF titrator actually most of the time slightly overtitrates. This can in principle be compensated by titrating reference materials), but this is rarely done. Careful choice of the electrochemical parameters for the end point is very important. If too rigorous end point detection criterion is used then overtitration is the consequence. If too relaxed criterion is used then undertitration can result.

Partial cathodic reduction of iodine

This uncertainty source refers to the possible diffusion of the iodine generated on the anode to the cathode compartment and its reduction. This causes parasitic current – not corresponding to water in the sample – in the system. It is generally recognized that this uncertainty source is influential in the case of a diaphragm-free system but is negligible in a diaphragm system.

2. Uncertainty sources originating from handling of the samples

Mass of sample

The contribution of sample mass uncertainty to the overall uncertainty of cKF is well understood and often quantified using the common approaches of calculating of uncertainty of mass measurement. Quantifying this uncertainty source is not challenging.

Contamination

Contamination of samples is a well-recognized effect in cKF measurement. It originates in the diffusion of water through joints between bottle necks and bottle cap septa, through plastic films, during opening of the containers, etc. As with many other uncertainty sources, quantitative information on its magnitude is almost non-existent, although experiments for measuring their contributions are actually possible.

Transfer of water from the sample to the cKF cell

This uncertainty source is recognized as a potentially important one, if sample is not directly introduced into the cKF cell. However, no quantitative investigation of its influence has been carried out, except via overall repeatability of the results, see above.

3. Compound uncertainty sources: Repeatability, reproducibility and bias

Repeatability of titration refers to the agreement between results of repeated measurements carried out under identical experimental conditions. Reproducibility of titration refers to agreement between results of repeated measurements carried out under changed experimental conditions. Of the possible changes the most important is time while keeping the other parameters of the method the same. This type of reproducibility is termed within-laboratory (long-term) reproducibility or intermediate precision.

Many of the above and below mentioned uncertainty sources also contribute to the repeatability (see above for such cases) and almost all of them contribute to reproducibility and bias. Thus, repeatability¹², reproducibility and bias are not separate uncertainty sources but rather ways of uncertainty evaluation whereby several uncertainty sources are taken into account in “one batch”.

Conclusion

The uncertainty sources of the cKF method are in general rather well known. Nevertheless, in the literature the discussion on uncertainty sources – except the uncertainty sources for which the quantification is well established, such as mass measurement – is almost always either qualitative or limited to the compound uncertainty sources and there is very limited quantitative information available on the contributions of the actual uncertainty sources.

¹² Strictly saying, in the case of repeatability this applies only to the overall repeatability of the procedure. Repeatabilities of individual steps are actual uncertainty sources.