Reference materials for inductively coupled plasma methods (ICP standards) produced by VNIIFTRI

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Abstract. For the metrological assurance of the high-precision inductively coupled plasma methods, the Russian Metrological Institute of Technical Physics and Radio Engineering (VNIIFTRI) developed four types of certified reference materials (CRMs) of the mass fraction of metals in solutions (ICP CRM). The permissible certified values of the element mass fraction (mass concentration) in the developed ICP CRM range from 800 mg/kg to 1200 mg/kg (from 800 mg/dm$^3$ to 1200 mg/dm$^3$). The developed ICP CRMs can be used for ensuring the metrological traceability of measurements in inorganic analyses to the State Primary Standard for units of the mass fraction and mass (molar) concentration of inorganic components in aqueous solutions based on gravimetric and spectral methods GET 217-2018.

1. Introduction

Currently, one of the most important tasks of science and industry is the improvement of measurements. Therefore, the role of chemical metrology is constantly growing, especially in the field of analytical chemistry. Due to technical progress, quality control of different materials is an increasingly important element of the creating safe, reliable products of high quality.

Inductively coupled plasma spectrometers are widely used for elemental analysis of more than 70 elements. These methods are the most express, highly sensitive methods for qualitative and quantitative analysis. Like many other methods of chemical analysis ICP methods need calibration. The ICP calibration procedure requires the employment of standards whose values and their associated uncertainties are known and established following a metrological procedure. The most rational way to achieve comparable and reliable measurement results by ICP-MS and ICP-OES consists in establishing the metrological traceability of measurements using CRMs. The accuracy of measurements strongly depends on the quality of CRM and, therefore, their characterization and traceability is very important.

This paper presents the results of the development of four types of certified reference materials for inductively coupled plasma methods (ICP CRM) are developed in VNIIFTRI, their main features and differences. ICP CRMs produced by VNIIFTRI are a crucial link in the traceability chain of measurements to the State primary standard of mass fraction units and mass (molar) concentration of inorganic components in aqueous solutions based on gravimetric and spectral methods GET 217-2018.
2. Materials and methods

During the preliminary experiments the starting material was selected for each type of standard. In order to assess the purity of the starting material, the “100% minus the amount of impurities” method was chosen. The mass fraction of the main component \((W)\) was calculated by equation (1):

\[
W = 100\% - \sum_i w_i - \sum_j \frac{LOD_j}{2}
\]  

(1)

where

- \(w\) is the mass fraction of detected impurities, \%;
- LOD is the limit of detection of undetected impurities, %.

HNO\(_3\) were produced by double distillation of reagent grade acids through a quartz subboiling distillation unit. Deionized water was used for dilution of solutions. The impurity composition of the solvents (nitric acid and deionized water) was assessed on the GET 217-2018.

The main objective of the certification of a reference material is to determine its characteristics including their uncertainty.

The mass fraction of the certified component \((A_m)\) in the reference material was estimated by equation (2):

\[
A_m = \frac{\omega_1 m_1 + \omega_2 m_2}{m_1 + m_2}
\]  

(2)

where

- \(\omega_1\), \(\omega_2\) are the mass fractions of the certified component in the starting material and solvent, respectively;
- \(m_1\), \(m_2\) are the weights of the starting material and solvent, respectively.

The mass concentration of the certified component \((A_v)\) in the reference material was estimated by equation (3):

\[
A_v = A_m \cdot \rho
\]  

(3)

where

- \(A_m\) is the mass fractions of the certified component in the reference material,
- \(\rho\) is the density of the reference material.

The metrological characteristics of ICP standards was calculated in accordance with RMG 93-2015 Metrological characteristics evaluations of reference materials and GOST ISO Guide 35-2015 Reference materials. General and statistical principles for certification (In Russ.). The uncertainty components for the gravimetric preparation of CRM solutions are presented as a cause-and-effect diagram in figure 1.

*Figure 1. A cause-and-effect diagram uncertainty for uncertainty evaluation*
3. Results and discussion

The reliability of the certified value fraction was established by two independent methods, including the analytical experimental method of gravimetric preparation and the method of measuring the analyte mass fraction using the capacity of the GET 217-2018. The measurement results obtained using both above mentioned methods are in good agreement within the limits of their uncertainties. The certified value of the developed CRM is taken to be that obtained by the analytical experimental method of gravimetric preparation. Metrological characteristics of the ICP CRMs are given in the table 1.

| Product name                  | Element | Certified characteristics       | Interval of certified values | Expanded uncertainty, $U_x$ ($k = 2; P = 0.95$), % |
|-------------------------------|---------|--------------------------------|-------------------------------|-----------------------------------------------|
| Lithium standard for ICP (ICP CRM Li) | Li      | Mass fraction, mg/kg           | 800 - 1200                    | 0.5                                           |
| Cobalt standard for ICP (ICP CRM Co) | Co      | Mass concentration, mg/dm³     |                               |                                               |
| Cadmium standard for ICP (ICP CRM Cd) | Cd      |                                |                               |                                               |
| Lead standard for ICP (ICP CRM Pb) | Pb      |                                |                               |                                               |

As shown in table 1, the expanded uncertainty of the certified value is 0.5 %. Trace metallic impurities determined by ICP-OES and provided in the passport. Among other things, one of the main advantages of ICP CRM is the certified value of the mass fraction of the component in addition to the mass concentration. The characterization of the mass fraction of the component in the solution allows to use a more accurate method of preparation of calibration solutions. The introduction of the gravimetric preparation of solutions improves the quality of results from analytical measurements by reducing the uncertainty associated with the preparation of solutions. When using Class A volumetric flasks, the tolerances include up to 0.20 % limit of error. If transfer pipets are used, they can add up to an additional 0.60 % limit of error. This does not include the human error, or the influence of temperature changes. While the uncertainty of analytical balances is not more than 0.1 %, and most modern electronic analytical balances perform even better than this. The introduction of the gravimetric preparation of solutions presents a significant opportunity to improve the quality of results from analytical procedures by reducing the uncertainty associated with the preparation. In the case of an existing method, where the analyst should work with the mass concentration use, he also can use ICP CRM because of it have a second certified characteristic like a mass concentration of component.

ICP methods do not require a large volume of samples. Often 1 – 5 ml of solution is enough for analysis. The use of volumetric flask results in excessive use of expensive solvents and substances. Gravimetric sample preparation significantly reduces the amount of solvent and substance consumed and significantly reduces the amount of waste. The gravimetric sample preparation allow to use disposable laboratory plasticware, which will prevent the possibility of cross-contamination of samples from volumetric flasks.

4. Conclusions

Four types of CRM for ICP (figure 2) was successfully developed in VNIIFTRI. The homogeneity, stability, and uncertainty were sufficiently studied. ICP CRMs can be used for ensuring the metrological traceability of measurements in inorganic analyses by ICP methods. The certified value expressed in the mg/kg units allows a more accurate, gravimetric method of solution preparation to be
used, whereas the certified value expressed in the mg/dm$^3$ allows, if necessary, a more familiar and fast volumetric method to be used instead.

**Figure 2.** ICP CRMs developed in VNIIFTRI (ICP CRM Pb and ICP CRM Co)

**REFERENCES.**

[1] General Chapter <31> Volumetric Apparatus, USP 35-NF 30.
[2] RMG 93-2015 Metrological characteristics evaluations of reference materials
[3] GOST ISO Guide 35-2015 Reference materials. General and statistical principles for certification (In Russ.)