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CALIBRATION AND TRACEABILITY IN SPECTROMETRY

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Abstract: *For ensuring the traceability and uniformity of measurement results, the main objectives of national metrology in chemistry are to calibrate and verify measuring instruments, to evaluate the uncertainty of measurement results, to intercompare the analytical results etc. The concept of traceability has developed recently in chemical measurements, thus, an attempt to implement the principles of metrological traceability especially by appropriateness calibration using the composition certified reference materials (CRMs), are underlined. The paper presents some aspects and practices in the field of spectrometric measurements regarding the metrological quality of the traceability by calibrating the instruments using suitable and reliable CRMs. The uncertainty of the results, as a measure of the reliability that can be placed on them, has been adequately described in different documents, and, as a consequence, some examples of evaluating the measurement uncertainty are described. The relationship between uncertainty and traceability, as two fundamental concepts of metrology which are intimately linked, is underlined.*
Keywords: Traceability, Estimation of Uncertainty, Reference Materials

1 INTRODUCTION

International comparability and traceability of measurements to stable references are required in measurements for environmental monitoring and protection, international trade, clinical practice health and safety and industrial production. In this respect, the paper presents some practical aspects of the traceability using certified reference materials (CRMs) and some exemples regarding the uncertainty evaluation in spectrochemical measurements.

It is possible to establish and confirm the traceability of measurement results by traceable calibration of the measuring instruments against national standards. The evaluation of the calibration uncertainty component is important; the uncertainty of results depends on the uncertainty of (CRMs) value used for the calibration and the relationship between uncertainty and traceability, as two fundamental concepts of metrology which are intimately linked, is evaluated. In this way the traceable instrument calibration is an important step in assuring the traceability of spectrochemical results.

2 SOME ASPECTS OF TRACEABILITY IN SPECTROMETRY

One of the most important tasks of the National Metrology Institutes is to assure the traceability of measurement results. It is defined as [1] “the property of the results of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through un unbroken chain of comparisons all having stated uncertainties”.
There are several possibilities to provide traceability of chemical measurements to SI units [2,3]:

- Traceability, which is generally applied in metrology, can be illustrated by a hierarchy of standards: on the top there is the national standard, traceable to the SI units, which realizes a specific unit, followed by the reference standard and the working standard. The results of measurements carried out using one of the standards of this hierarchy are comparable. In chemical measurements it is possible to transfer the metrological hierarchy of standards to CRMs which are the standards of chemical composition.
- An other way of providing a link between chemical laboratories and the SI units can use reference materials, reference methods and standard measuring devices which are made available by the National Metrology Institutes.

- A third possibility of making the traceability available to chemical laboratories is that reference laboratories act as the link to the SI. These laboratories must have demonstrated in high-level international comparisons that they are capable of producing SI-traceable measurement results in their specific field and they are, therefore, able to transmit the traceability to the field laboratories.
- An other possibility to establish the traceability of chemical measurements is to use the primary methods indicated by CCQM (isotope dilution with mass spectrometry, coulometry, gravimetry, titrimetry, determination of freezing-point depression), the methods which provide a direct traceability to the SI units.

In Romania the dissemination of the units (Figure 1) has been performed in accordance to the national regulations [4].

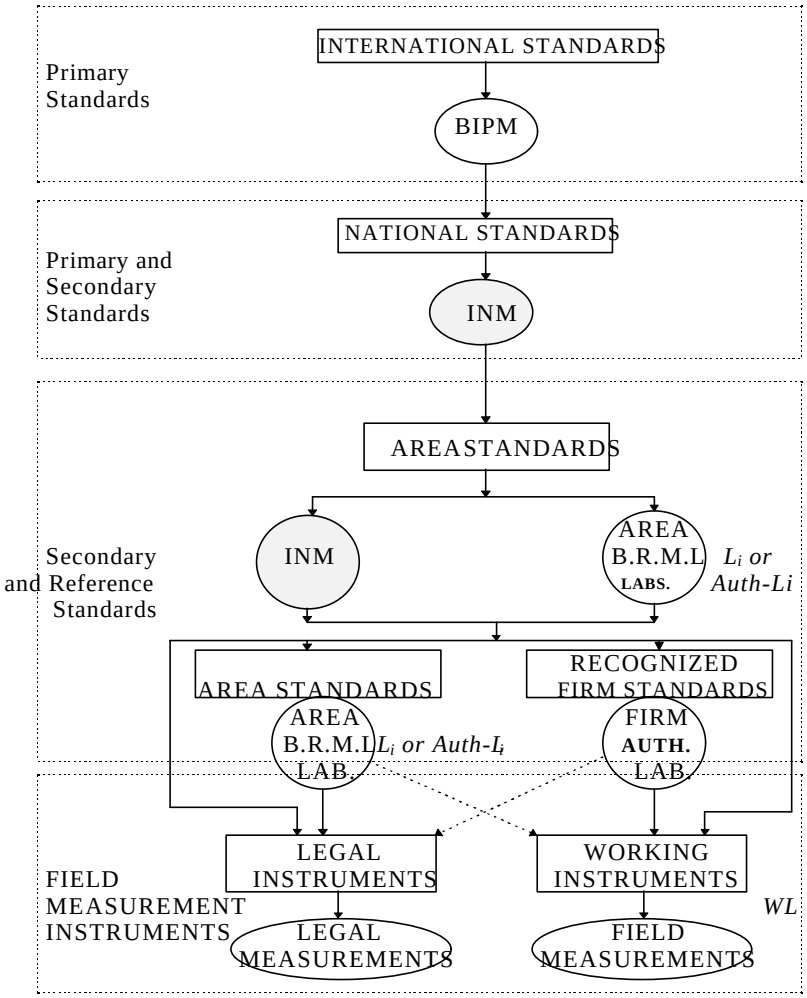

Fig. 1 The dissemination of the units in Romania

Any field measurement laboratory *WL* should try to link itself to the national standards by calibrating the instruments against national recognized standards from accredited laboratories *Li or Auth-Li*. In their turn, these laboratories link their own standards by calibrating them against the proper ones existing in INM, which are traceable to the international standards. The calibration to establish and confirm the traceability measurement results to national or international standards is essential because the traceability involves a chain of standards linked back to the appropriate superior standards through a series of calibrations. The above described vertical traceability should be completed through a sufficient condition to be achieved in interlaboratory comparisons.

In the case of chemical measurements, CRMs as standards of chemical composition, can be introduced into the calibration process. The traceability of certified value of reference materials, as an essential part of the certification process, is as important as that of chemical measurements. In this respect in the following there are presented the metrological approach of calibration process of spectro(photo)meters using spectrometric reference materials.

3 PRACTICAL EXEMPLES OF TRACEABILITY USING CRMs

In accordance with [5] there are many types of calibration procedures, and therefore, in the following there are presented some aspects regarding the method of calibration which compares the content of the sample to be analysed to a set of calibration samples of known content. This method implies the use of the standards generally consist of a determined quantity of analyte “diluted” in a large quantity of diluent (nonmatrix standards).

3.1 Instrument calibration in spectrometry

Usually, the calibration of the spectro(photo)metric instrument is a set of operations that establish, the relationship between the values indicated by the spectro(photo)meter (absorbance) and the corresponding concentration values assigned to the spectrometric reference materials.

In analytical spectrometry there are many types of calibration curves which are set up by measuring spectrometric reference solutions. The measurements yield a curve of absorbance versus concentration, and the points between the data of the reference solutions are interpolated by fitting a suitable curve, which normally, follows the Beer-Lambert law and which gives rise to a straight line through the origin of the coordinate system.

The calibration curves and the suitable equations by electrothermal atomic absorption spectrometry for chromium measurements (Figure 2) and for lead measurements (Figure 3) are obtained using VARIAN AA 250 PLUS atomic absorption spectrometer 1 (linear), 2 (quadratic) and 6 (cubic) and the graphs and the equations 3 (linear), 4 (quadratic) and 5 (cubic) are obtained using PERKIN-ELMER 3300 atomic absorption spectrometer.

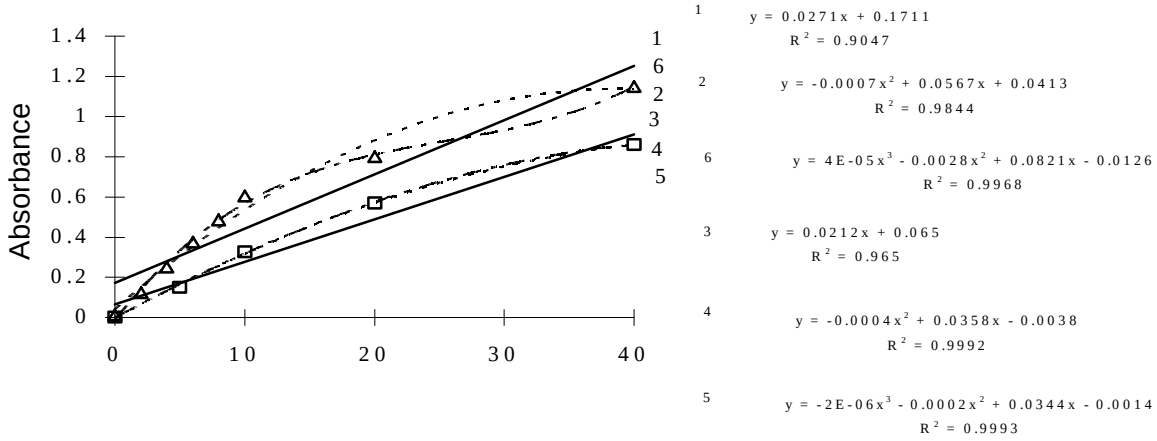

Fig. 2. The calibration curves for chromium measurement by atomic absorption spectrometry

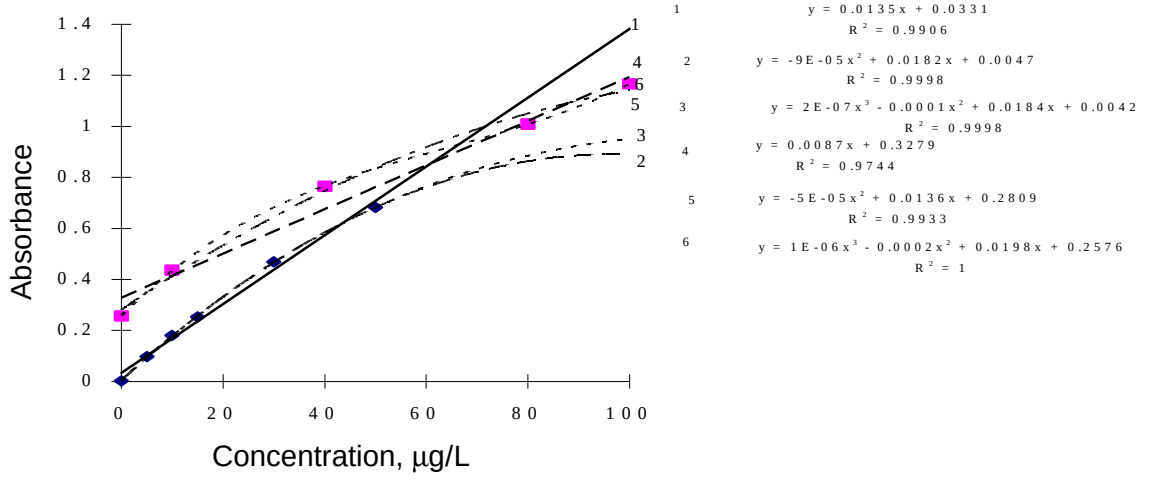

Fig. 3. The calibration curves for lead measurement by atomic absorption spectrometry

Even though, in many analytical applications, the correlation coefficient r has the acceptable values (above 0.995) for the quadratic and cubic calibration curves, a spectrometric instrument, which is calibrated in concentration units, usually uses a linear curve which is established using several spectrometric reference materials which are introduced into the calibration process.

The manganese determination by molecular absorption spectro(photo)metry can be made using different types of instruments which have various technical performances. Some results are shown (figure 4) for manganese concentration measurements with DR 2000-wide bandwidth 8 nm (series 1), Hewlett Packard 8452 A bandwidth 2 nm (series 2) and Specord M 40-wide bandwidth 1 nm (series 3).

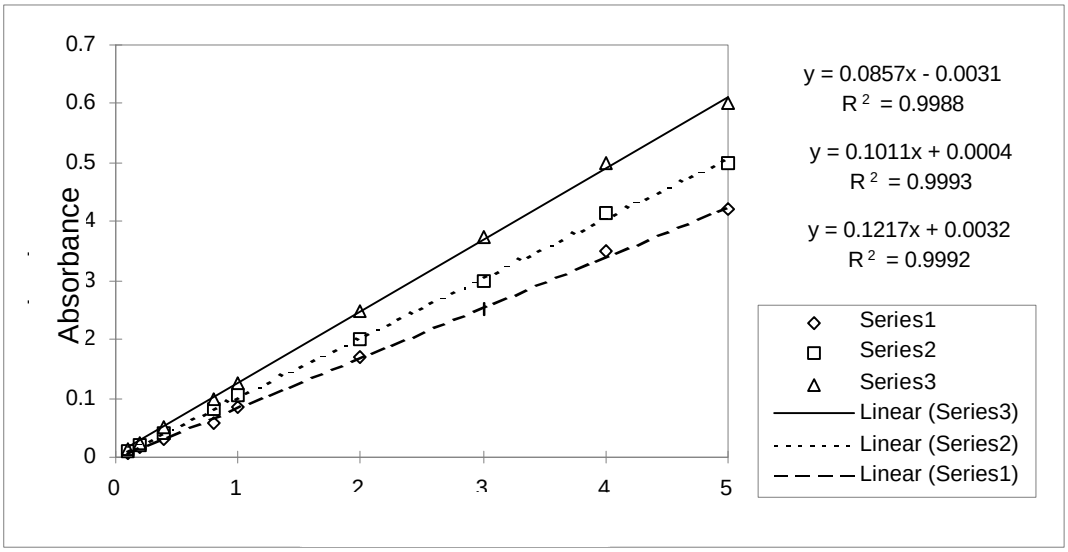

Fig. 4. The calibration curve for concentration solution of manganese

Even though linearity tests are satisfactory (correlation coefficient r is above 0.995) for characterizing the spectro(photo)meter performance, in most of the cases, the curves show that the increase of the spectral bandwidth causes an apparent decrease in absorbance from the true absorbance. The accuracy of the spectro(photo)metric results is related both to the performance of the instrument and to the uncertainty due to the linear calibration curve (of the instrument), and, therefore, this uncertainty component must be evaluated.

3.2 Evaluation of the calibration uncertainty

A linear calibration curve of spectro(photo)meters is given by the relationship c = (A-a)/b where: A is the absorbance, c is the concentration, a and b are the parameters of the linear curve. The uncertainty in a predicted value A_m-absorbance using liniar regression to a given value c-concentration, can be estimated in several ways [6].

In the following, there are presented some aspects regarding the way to evaluate the uncertainty due the linear calibration curve by evaluating the calibration data. The linear calibration uncertainty is estimated by the interval that can be expected to encompass a large fraction of the distribution of values that could resonable be attributed to the linear curve. This interval, indicated in Figure 5, is due to the linear adjustement of the concentration values used to determine the regression line and obtained values of the absorbance.

The evaluation of the linear calibration uncertainty can be performed against the standard deviation of the linear calibration curve, s_0 ; the slope of the curve, b; the number N of CRMs used for calibration curve; the number *n* of replicates; and the average absorbance signals A_m of the sample and of the CRMs (A) using the calibration curve. Some results of the calibration uncertainty evaluation

due to the linear calibration curve of copper determination by molecular absorption spectro(photo)metry using Cecil 2020 instrument is ilustrated in Table 1.

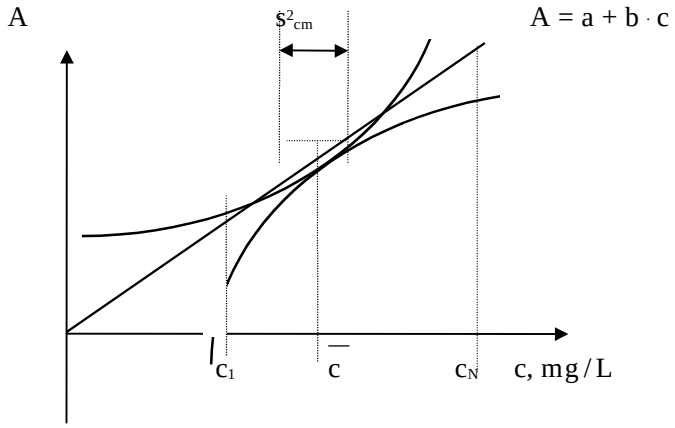

Fig. 5. The confidence interval of linear calibration curve

Note that at the end of linear range (0...10) mg/L the calibration uncertainty is bigger than in the middle of the linear range: for a concentration of 0.987 mg/L copper the uncertainty component due to the calibration is 3.0% and for a concentration of at 6.010 mg/L copper the uncertainty component due to the calibration is 0.56%.

Table 1

The evaluation of the liniar calibration uncertainty

Sources of uncertainty	Method of evaluation	Experimental results
Linear regression	$s^2_{c_m} = \frac{s_0^2}{b^2}\left[\frac{1}{N}+\frac{1}{n}+\frac{(\bar{A}_m-\bar{A})^2}{b^2\sum_i (c_i-\bar{c})^2}\right]$	c_m s_{cm}, mg/L 0.987 0.030 1.980 0.026 3.995 0.023 6.010 0.034 A = 0.002 + 0.1217· c a = - 0.002; s_a = 0.0042; t · s_a= 0.0098 b = 0.1217; s_b = 0.0011; t · s_b= 0.0025 r = 0.9999 s_0 = 0.0042
Spectro(photo)metric method	Against optical filters	0.010 in acordance with Lambert-Beer law $\Delta A/A=\Delta c/c$
CRMs used for calibration	From the CRMs Certificate	$U_{certified}$ /$3^{1/2}$ = 0.006
Combined uncertainty	Square sums of components	u_{cal} = 0.036 for 6.010 mg/L Cu
Overall uncertainty	k = 2	$U_{cal} = 2 \cdot u_{cal}$ =0.072

In addition to the uncertainty due to the linear regression which was 0.034 for 6.010 mg/L copper the overall uncertainty of the instrument calibration includes the uncertainty due to the photometric measurement and the uncertainty due to the CRMs and was 0.036 for 6.010 mg/L copper. Even thought between the linear regression uncertainty and the overall uncertainty does not exist a significant difference, this approach takes into account all sources of uncertainty and underlines the link between the field measurement results and the values of the standards used for the instrument's calibration. The ratio uncertainty between the CRMs and the photometer involved, gives the strength of the traceability link.

Moreover, the evaluation of the overall uncertainty in spectrochemical measurements must take into account the steps of spectrometric measurement process: sampling, measurement, calibration, data treatment. For each point of the process, the associated standard uncertainties below need to be estimated: u_s-for sampling, which includes uncertainty due to the chemical preparation u_P; u_M-for reproducibility of the analytic spectro(photo)metric system, which includes the dilution factor, the

weight of the sample etc; u_{CRM} - for the value of the calibration standards; u_R-for reproducibility of the calibration, and u_{DA} -for suitability of the method of calibration, which includes the data treatment.

In this respect the uncertainty evaluation of the spectrometric measurement is ilustrated in Table 2 for copper determination in water by atomic absorbtion spectrometry and by molecular absorption spectro(photo)metry.

Table 2

The evaluation of the overall measurement uncertainty by linear calibration of the instrument

Method measurement: AA Spectrometry and UV-VIZ spectrophotometry				
Mathematical model: Linear curve c = (A-a).f / b				
Low of uncertainty propagation: $u_c^2 = u_s^2 + u_M^2 + u_R^2 + u_{MRC}^2 + u_{DA}^2$				
	Instrument			
Estimation	Varian AA 250 PLUS	Unicam Solaar 939	Specord M40 C.Z.Jena	DR2000
a	0.0165	0.0322	-0.002	0.0015
b	0.0632	0.0821	0.1218	0.1217
r	0.9991	0.9989	0.9999	0.9998
s_0	0.0093	0.0162	0.0021	0.003
u_s	0.03	0.03	0.03	0.03
u_M	0.03	0.03	0.03	0.03
u_R	0.06	0.10	0.08	0.07
u_{MRC}	0.006	0.006	0.006	0.006
u_{DA}	0.00	0.00	0.00	0.00
A_m	0.142	0.193	0.230	0.242
c_m	1.985	1.961	1.910	2.006
$u_{c,}$	0.073	0.109	0.091	0.082
I_c	0.25	0.39	0.98	0.02

The overall measurement uncertainty for copper in water was 3.6% using atomic absorption spectrometer type Varian AA 250 PLUS and 4.8% using molecular absorption spectro(photo)meter type Specord M40 C. Z. Jena. The compatibility of results was evaluated as the compatibility index I_c which was acceptable (less than 1) in all of the cases presented in Table 2.

This approach of considering the potential sources of error eads to the identification of the components having a significant contribution, and, therefore, to the decrease of their effects.

4 CONCLUSIONS

The paper presents some aspects regarding the uncertainty evaluation and the traceability assurance of spectrochemical results using CRMs. In this approch, the calibration uncertainty is a important component of traceability chain and uncertainty of results depends on the uncertainty of the certified value of reference materials used for the calibration. Thus, the results are traceable to the standards used for the instrument calibration. The traceability of certified values of reference materials is as important as that of spectrometric measurements. Therefore, it is necessary to use the CRMs that are characterized in a metrological mannier. In this framework, the uncertainty and traceability as two fundamental metrological concepts are intimately linked.

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