A New Robust Top-Down Method for Measurement Uncertainty Estimation of the ED(P)- XRFS Outcomes Carried on a Fluorescence Glass

ION PENCEA[1], MIHAI BRANZEI[1]*, MIHAI OVIDIU COJOCARU[1], RAMONA NICOLETA TURCU[1], CRISTIAN PREDESCU[2], ANDREI BERBECARU[2], ALINA POPESCU ARGES[1], BRINDUS COMANESCU[3]

[1] University Politehnica of Bucharest, Department of Metallic Materials Science, Physical Metallurgy, 313 Splaiul Independentei, 060042, Bucharest, Romania

[2] University Politehnica of Bucharest, Department of Metallic Material Processing and Ecometallurgy, 313 Splaiul Independentei, 060042, Bucharest, Romania

[3] SC OPTOELECTRONICA 2001 SA, 409 Atomistilor Str., Magurele, 77125, Bucharest, Romania

The rare earths doped glasses have been considered as the best solution to fulfil the increasing demand for cheaper fluorescent taggants. The ensuring a high quality of a spectral taggant batch imposes, among others, an exact chemical composition measurement. The most convenient method for elemental analysis of powdered specimens is Energy Dispersive (Polarised)- X-ray Fluorescence Spectroscopy (ED(P)-XRFS) because it has many advantages: non-destructive, large analytical range, robustness, easy sample preparation, cheaper consumables, less time consuming etc. ED(P)-XRFS has some inherent analytical drawbacks such as: interelements interferences, matrix dependence etc. The only way to overcome the drawbacks is a proper method for the measurement uncertainty (MU) estimation of the outcomes. Consequently, the paper argues that the bottom-up method for MU estimation is feeble as long as the sensitivity coefficients of the factors of uncertainty budget are not well known and documented, which is the habitual case of the ED and WD XRFS bottom-up published methods. The paper substantiates a new robust top-down method for MU estimation of the ED(P)-XRFS outcomes carried on a fluorescence glass. Also, the paper presents a representative case study of appliance of the developed top-down method. The other novelties addressed in the paper are: i. Introducing the robust statistics as further checks for the accuracy of mean and of standard deviation, according to ISO 13583:2015; ii. A new criterion for testing the normal distribution of the mean of a set of fewer outcomes based on Central Limit Theorem and on the central momentum of third orde; iii. The method was implemented for multiple simultaneous outcomes. The top-down method, given in the paper, can be applied to ED- and WD-XRFS routine measurements in industrial laboratories or in material science ones, but it can be adapted, without much effort, to other types of tests e.g. hardness, XRD etc.

Keywords: mesurement uncertainity, top-down method, bottom-up method, robust statistic, fluorescence glass

The increasing demand for the improving of the product security at a reasonable cost has driven an increased interest towards the development of cheaper fluorescent taggants [1-3]. Some rare earths (RE) doped glasses have been considered as potential candidate for such a task[4-6].

When a RE dopant is incorporated into a glass, new bonds are formed in the doped glass that alter the electron energy levels RE atoms. Accordingly, a specific glass composition gives rise to a specific fluorescent fingerprint. Such a security marker is very difficult to replicate by a counterfeiter. The demand for a high quality of a batch of spectral taggant requires a well defined and homogeneous chemical composition. Besides, the batch has to homogeneous phase contents and particle morphology (size, shape, surface-topography, etc). A well defined chemical composition critically depends on the measurement uncertainty (MU) of the analytical procedure. Notwithstanding that the entire philosophy of this paper subordinates to the following paradigm *If you don't know the uncertainty of the measurement, don't make the measurement at all! [7].*

The MU is the only one quantity that assesses quantitatively the quality of a numerical test results i.e. as the MU is smaller as the result quality is higher [8-11].

The achieving of the smallest MU is costly therefore a compromise between cost and MU level has always to be considered. In this regard, the most convenient method for elemental analysis of powdered specimens is X-ray fluorescence spectroscopy (XRFS) because it has many advantages: non-destructive, large analytical range, robust, easy sample preparation, cheaper additives, less time consuming etc [12,13].

On the other hand, XRFS has some inherent analytical drawbacks as: elements interference, particle size dependence of the analytical results, higher uncertainty for the trace elements etc. Therefore, the XRFS analytical exactness depends on matrix elemental composition and morphology [12-14].

Taking into account the advantages and the disadvantages of the XRFS it was decided that it is fitted to measure the composition of the envisaged RE doped glasses provided a carefully adjustment of the instrument settings in order to obtain the as lowest as possible MU. In this regard, the paper addresses a proper method for MU evaluation for a specific matrix using a Energy Dispersive (ED) spectrometer equipped with 3D irradiation geometry which enables a better excitation of the fluorescence of the lighter elements due to partially polarization of the sample irradiation X-rays, denoted as ED(P)-XRFS technique. In the instrumental chemical analytical field,

---

**email: mihai.branzei@upb.ro; Phone: +40745189310*

several approaches for the evaluation of measurement uncertainty (MU), based on the general principles of GUM, are known [15-19].

The three most popular approaches are: i. The modelling approach; ii. The single laboratory validation approach; iii. The inter-laboratory validation approach [15,20,21].

In the literature one can found a lot of modelling approaches for ED-XRFS and WD-XRFS [22-29].

To our present knowledge, all the papers dealing with MU evaluation in XRFS (ED, WD) make used of the formula:

$$u_c^2 = u_1^2 + u_2^2 + \cdots + u_n^2 \qquad (1)$$

where $\boldsymbol{u_c}$ is the combined uncertainty, $\boldsymbol{u_i}$ are the individual contribution of the $\boldsymbol{i_{th}}$ factor, ***(i = 1-n)***.

On the other hand, the $\boldsymbol{u_c}$ has to be calculated according to uncertainty (error) propagation law [30].

It implies the knowing of the measurement function:

$$C = f(co;\ x_1,\ x_2,\ .....xj,...\ xn) \qquad (2)$$

where **C** is the measured concentration of an element, $\boldsymbol{c_o}$ is the true value of ***C*** and ***xj (j=1-n)***, are the values of the other input quantities that influence the outcome.

Once knowing the measurement function then the $\boldsymbol{u_c}$ can be calculated as:

$$u_c^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 * u_1^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 * \\ * u_2^2 + \cdots + \left(\frac{\partial f}{\partial x_n}\right)^2 * u_n^2 \qquad (3)$$

where u_j^2 is the uncertainty assigned to the *Xj* variable (***j = 1-n)***, and the $(\frac{\partial f}{\partial x_j})^2$ is the sensitive coefficient of the ***Xj*** contributor.

The usage of (1) assumes that $\frac{\partial f}{\partial x_j} = \pm 1$, for ***j = 1-n***, for ***j = 1-n***, but no author has bring evidence supporting this assumption.

The rel.(1) can be applied for MU evaluation only if:

$$C = C_0 + a_1 * X_1 + ...a_i * X^i ... + a_n * X_n \qquad (4)$$

and $\boldsymbol{a_i = \pm 1}$, for ***i = 1-n***

The above assumption is absurd as long as it implies the same magnitude of the contributions of the influence factors to the outcome as the measurand itself. Accordingly, any bottom-up or modelling MU evaluation method that make use of (1) without a well documented measurement function is fundamentally wrong.

As the bottom-up method for MU evaluation is irrelevant for ED-XRF measurements, the top-down approach remains the alternative [31].

Experimental part

Materials and methods

The fluorescence glass under investigation was obtained by classical route i.e. smelting and pouring. The composition of the smelted batch is given in table 1.

The powdered precursors are well mixed before putt in a platinum crucible to be heated up to 1,150 °C, using the Vulcan 2MA Fusing Machine, Fluxana GmbH, Germany. After heating, the melting material is poured into a pre-heated platinum mould and fast chilled. To enhance the fluorescence yield an annealing treatment at 570÷630 °C is applied. Subsequently, the glass is crashed and milled until a micron powder is obtained.

The ED(P)–XRFS measurements were performing with a XEPOS bench-top spectrometer (SPECTRO, AMETEK Materials Analysis Division) equipped with a Rh X-ray tube and 3 secondary targets i.e. HOPG, corundum (Al_2O_3) and Mo. The Rh tube was operated at 40kV and 1mA and the achieved spectrometric data were processed using Turboquant software.

The samples were prepared as pressed pellets of 40 mm diameter and 3 mm height. The powder under investigation was mixed thoroughly with microcrystalline cellulose powder in a ratio of 4/1 (w/w) in a Retch MM1 mill. Pellets were prepared using an special manual Specac press that provide a maximum force of 1.5* 10^5N.

The SRM NIST 611 and SRM NIST 620 were used to assess the traceability of the XEPOS spectrometer. The certifications of SRM 611 and SRM 620 are valid indefinitely, within the measurement uncertainties specified, provided the SRMs are handled and stored in accordance with the instructions given in their certificates. The certified values of the oxide concentrations of the SRM 620 and their standard uncertainties, taken from its certificate, are given in table 2 [37].

The glass matrix of SRM 611 has a nominal composition of 72 % SiO_2, 14 % Na_2O, 12 % CaO, and 2 % Al_2O_3 (wt.%) [38].

To the matrix of SRM were added 61 elements whose concentrations are in the range of 100 mg/kg to 500 mg/kg, among ones Er and Yb that are of interest for our purpose. The MUs for major elements into SRM 611 and the concentration values of Er and Yb are not specified by its certificate. Hence, the data from literature were used. (table 3) [39,40].

Table 1
THE OXIDE CONCENTRATION OF THE GLASS PRECURSORS

Compound	SiO_2	Al_2O_3	B_2O_3	CaO	K_2O	Na_2O	Er_2O_3	Yb_2O_3
Concentration, [%wt]	69.5	3.0	6.0	3.0	5.0	12.5	0.5	0.5

Table 2
THE OXIDE CONCENTRATIONS OF THE SRM 620 AND THEIR STANDARD UNCERTAINTIES

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	As_2O_3	SO_3
Concentration [wt. %]	72.08	1.80	0.043	7.11	3.69	0.410	14.39	0.018	0.056	0.28
St. uncertainty [wt. %]	0.08	0.03	0.004	0.05	0.05	0.030	0.06	0.002	0.003	0.02

Table 3
THE OXIDE CONCENTRATIONS OF SRM 611 AND THEIR STANDARD UNCERTAINTIES [38,39]

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	Er_2O_3	Yb_2O_3
Concentration [wt. %]	69.63	2.22	0.07	11.71	0.07	0.06	12.87	0.08	0.12	0.05	0.05
Standard uncertainty [wt. %]	0.27	0.01	0.02	0.03	0.01	0.01	0.08	0.01	0.02	0.01	0.01

Taking into account that the SRM 611 and SRM 620 are slabs while the developed fluorescence glass should be used as micronized powder, there were planed two type of XRFS measurements on each SRM i.e. as received and as micronized powder. For the second kind of measurement, the slabs were primary crashed and subsequently milled in an agate ball mill until the particle size is less than 20 µm. The SRM powders were prepared as pellets using the same procedure as for the fluorescence glass specimens.

Procedure

Theoretical bases

A pragmatic approach for estimating uncertainty in the analysis of a fluorescence glass by ED(P)-XRFS should consider the *black-box* model of the measurand given in ISO5725-2 and widely used when the modelling approach is feeble [32].

$$c = c_o + b + \varepsilon \qquad (5)$$

where ***c*** is the measured value of ***C*** measurand, $\boldsymbol{c_o}$ is the true value of ***C***; b is the bias or the systematic error of the method and $\boldsymbol{\varepsilon}$ is the random uncertainty/error.

Terms ***b*** and $\boldsymbol{\varepsilon}$ in (5) incorporate the hole MU budget of the measurement process i.e. equipment, robustness, sample preparation, environment, quantification etc. The bias of the method can by estimated using certified reference materials (CRM) with similar matrix to the measured specimens.

It is customary that the contributions of individual random errors to the mean of a set of n repeated measurements decrease as much as n increases. Obviously, in laboratory practice n is rarely greater than 10 due to experimental costs. Hence, for n ≤ 10 it is doubtful where or not the ε_j ***(j = 1-n),*** cancel each other. Supposing that the random error contribution to the mean is negligible then the bias is:

$$b = \overline{c_{CRM}} - c_o \qquad (6)$$

where $\overline{c_{CRM}}$ is the observed mean value of the CRM and $\boldsymbol{c_o}$ is the CRM certified value.

The corrected value for the bias of an observed mean value $\bar{c}$ for an unknown specimen is:

$$c_{cor} = \bar{c} - b = \bar{c} - \overline{c_{CRM}} + c_o \qquad (7)$$

According to uncertainty propagation law, the uncertainty assigned to c_{cor}, $\boldsymbol{u_{ccor}}$ is

$$u_{ccor}^2 = u_{\bar{c}}^2 + u_{\overline{cCRM}}^2 + u_{Co}^2 \qquad (8)$$

Even if ***b = 0***, because its estimation was done with an uncertainty, denoted $\boldsymbol{u_{tras}}$, the analyst has to take into account $\boldsymbol{u_{tras}}$ contribution to the overall combined uncertainty assigned to the result of the test carried on an unknown specimen.

It worth emphasizing that all of considered uncertainties in (8) are listed in the same units of measurement and they are similar, therefore the sensitivity coefficients can be considered 1 for all of them.

Procedure flow chart

The flowchart of the procedure for uncertainty estimation consists in 4 steps as follows:

Step 1: Verification of traceability

For verifying traceability (i.e. no significant bias exists) it is compared the observed mean value $\overline{c_{CRM}}$ with the CRM certified value $\boldsymbol{c_o}$ using the Student *t*-test [33]:

$$t_{cal} = \frac{|c_{CRM} - \bar{c}|}{\sqrt{u_{CRM}^2 + \frac{s_{CRM}^2}{n}}} \qquad (7)$$

where: $\boldsymbol{u_{CRM}}$ is the standard uncertainty of the CRM calculated as $\boldsymbol{U_{CRM}}$/ ***k*** into which $\boldsymbol{U_{CRM}}$ is the extended uncertainty given in its certificate while ***k*** is the expanded factor; $\boldsymbol{s_{CRM}}$ is the standard deviation of test results carried on the CRM and ***n*** is the test number.

The Student *t*-test value depends on the test significance (***α***) and of the number of free degrees (***ν= n-2***), denoted ***t(α,ν)***. The values of ***t(α,ν)*** are tabulated, but can be calculated using its formula given in statistical books [31,33]. In case of $\boldsymbol{t_{cal} < t(\alpha,\nu)}$ then no significant bias is found and the procedure can continue with step (2).

Step 2: Uncertainty of verification of traceability

Even though the bias is negligible, the $\boldsymbol{b \cong 0}$ was estimated with an uncertainty $\boldsymbol{u_{trac}}$ that incorporates the $\boldsymbol{u_{CRM}}$ and the standard uncertainty of the mean. Hence, the equation of $\boldsymbol{u_{trac}}$ is:

$$u_{trac} = \sqrt{u_{CRM}^2 + \frac{s_{CRM}^2}{n}} \qquad (8)$$

Step 3: Uncertainty of the analytical procedure

This component is estimated from the standard deviation of the outcomes provided by ED(P)-XRFS measurement carried on the unknown specimens provided that they will be similar in concentration to the CRMs. The standard uncertainty is calculated as follows:

$$u_{proc} = s_m^2 \qquad (9)$$

where the S_m^2 is the standard deviation of mean

Step 4: Calculating the combined standard uncertainty

The combined standard uncertainty $\boldsymbol{u_c}$ is calculated as follows:

$$u_c = \sqrt{u_{trac}^2 + u_{proc}^2} = \sqrt{u_{CRM}^2 + \frac{s_{CRM}^2}{n} + s_m^2} \qquad (10)$$

Step 5: Calculating the extended uncertainty

The Central Limit Theorem (CLT) stipulates that in case of sufficient large n replicated tests the mean of the outcomes follows the normal density distribution $\boldsymbol{N(\mu,\sigma/n^{1/2})}$, into which $\boldsymbol{\mu}$ is the true value of the measurand and $\boldsymbol{\sigma^2}$ is its variance. Some books indicate $\boldsymbol{n \geq 30}$ [31,34,35].

Based on own calculation, if the characteristic function of an X measurand is $\boldsymbol{C_X(t)}$ then the characteristic function of the mean of n test results, denoted $\boldsymbol{C_M(t)}$, can be expressed as:

$$C_M(t) = C_X^n\left(\frac{t}{n}\right) \qquad (11)$$

where ***t*** is a real number

Taylor series development of $\boldsymbol{ln(C_M(t))}$ function is:

$$\ln\left(C_M(t)\right) = i\mu * \frac{t}{1!} - \frac{\sigma_X^2}{n} * \frac{t^2}{2!} - \frac{i\mu}{n^2} * * M_3 * \frac{t^3}{3!} + 0_4(t) \qquad (12)$$

Where ***i*** is the imaginary complex number, $\boldsymbol{i^2 = -1}$, $\boldsymbol{M_3}$ is the central momentum of the third order of the ***X*** variable and $O_4(t)$ is a zero of the forth order of the Taylor series.

The natural logarithm of the characteristic function $\boldsymbol{C_N(t)}$ assigned to $\boldsymbol{N(\mu,\sigma)}$ is [36]:

$$\ln\left(C_N(t)\right) = i\mu t * \frac{t}{1!} - \frac{\sigma^2}{2} * t^2 \quad (13)$$

If the coefficient C_3 of the t^3 and the $O_4(t)$are sufficient small as to be considered negligible then the forms of the $\ln(C_M(t))$ and $\ln(C_N(t))$ are the same and one can consider that the density distribution of the mean is normal i.e. $N(\mu,\sigma/n^{1/2})$.

Setting as $C_3=\frac{\mu}{n^2} * M_3$ is negligible, it is a very important since the coverage factor can be calculated based on the normal distribution theory.

Taking into account the above derivatives, it was stipulated that if the $C_3 \le 10^{-3}$ then it is negligible and also $0_4(t)$. In this regard, the analyst has to establish a specific n, then has to calculate the $\frac{\mu}{n^2} * M_3$ value and if it is less or equal to 10^{-3}, then the expanded uncertainty with 95% confidence level can be calculated as:

$$U(95\%) = 2*u_c \quad (13)$$

Results and discussions

The outcomes of the 10 repeated measurements carried on the SRM 620 slab using XEPOS and its Turboquant fusion method are shown in table 4.

The outcomes in table 4 were statistically processed by two routes i.e. classical one (arithmetic mean, standard deviation) and the robust one (median, ***MADe(x)***). The robust route is given in ISO 5725-5 and recommended by ISO 13528[41,42]. The robust statistical methods are resistant to outliers and provides a supplementary check of the quality of the ED(P)-XRFS results. The data in table 4 clearly show an adequate concordance between the statistics obtained on both routes as the differences between ***SD*** and ***MADe(x)*** are manifested at the 3-rd significant digit.

To achieve data for traceability assessing there were performed 10 reproductive measurement on powdered SRM 620 specimen. For the sake of typewriting saving space, the ED(P)-XRFS results obtained on the powdered SRM 620 specimen are synthetically given in table 5. It means that tables 5 includes the outcomes statistics as mean, ***SD***, median, ***MADe(x)***, M_3, C_3 and the calculated t parameter (t_{calc}) of the t-Student test.

The t_{calc} has a 20 degree of freedom (***df***) as the SRM 620 certificate specifies that the assigned values is the average of 12 outcomes while the observed value is the average of 10 runs. The t-test critical value for $\alpha = 0.05$ and $df = 20$ is $t(0.05;20) = 2.086$. Accordingly, the traceability test was passed for all the measurands in table 5.

The differences among the values calculated using classical statistics and the robust ones are in the limits of assigned uncertainties, hence the influences of the possible outliers are negligible.

The results of the measurements carried on powdered SRM 611 are synthetically presented in table 6.

Table 4
THE OUTCOMES OF THE XRFS MEASUREMENTS CARRIED ON SRM NIST 620 SLAB USING TURBOQUANT FUSION ANALYTICAL PROGRAM

Oxide/runs	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	As_2O_3	SO_3
1	72.21	1.83	0.04	7.11	3.90	0.54	14.51	0.03	0.04	0.21
2	72.29	1.82	0.05	7.08	3.92	0.37	14.36	0.03	0.07	0.22
3	72.01	1.70	0.05	7.04	3.50	0.49	14.32	0.02	0.07	0.39
4	72.21	1.71	0.05	7.26	3.62	0.46	14.24	0.01	0.05	0.14
5	71.96	1.85	0.04	7.11	3.78	0.35	14.39	0.01	0.04	0.17
6	72.31	1.70	0.04	7.19	3.63	0.50	14.57	0.01	0.05	0.31
7	71.96	1.73	0.03	7.22	3.84	0.50	14.38	0.01	0.04	0.29
8	72.06	1.72	0.03	7.15	3.88	0.34	14.46	0.03	0.07	0.14
9	72.14	1.75	0.05	7.09	3.82	0.36	14.31	0.02	0.04	0.17
10	71.82	1.89	0.03	7.03	3.76	0.39	14.21	0.03	0.07	0.29
Mean	72.10	1.77	0.042	7.13	3.76	0.43	14.38	0.020	0.054	0.23
SD	0.16	0.07	0.008	0.07	0.14	0.08	0.11	0.008	0.015	0.08
SDm	0.051	0.023	0.002	0.024	0.044	0.024	0.036	0.002	0.005	0.026
Median	72.10	1.74	0.04	7.11	3.80	0.42	14.37	0.02	0.05	0.22
MADe(x)	0.4	0.06	0.01	0.08	0.13	0.10	0.11	0.00	0.02	0.10
SD- MADe(x)	0.02	0.01	0.00	-0.01	0.01	-0.03	0.00	0.00	-0.01	-0.02

Table 5
THE OUTCOMES OF THE XRFS MEASUREMENTS CARRIED ON SRM NIST 620 AS POWDER USING TURBOQUANT PELLET ANALYTICAL PROGRAM

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	As_2O_3	SO_3
Mean	72.04	1.80	0.042	7.07	3.65	0.42	1.44	0.02	0.051	0.29
Median	72.00	1.78	0.040	7.04	3.63	0.425	14.32	0.02	0.05	0.31
SD	0.20	0.07	0.01	0.09	0.14	0.043	0.18	0.005	0.008	0.05
MEDe(x)	0.23	0.05	0.01	0.06	0.15	0.030	0.17	0.010	0.009	0.03
SDm	0.12	0.04	0.007	0.06	0.09	0.03	0.12	0.003	0.005	0.03
M_3	2.2 E-4	-8.0 E-3	8.0 E-6	-1.0 E-3	-1.0 E-3	1.0 E-3	4.0 E-4	-9.0 E-7	2.0 E-5	-2.0 E-3
C_3	1.5 E-4	-1.4 E-4	3.3 E-9	-7.0 E-5	-3.5 E-5	4.2 E-6	5.7 E-5	-1.8 E-10	1.0 E-08	-5.8 E-6
t_{calc}	0.6	0.0	0.3	0.9	0.8	0.5	0.1	0.8	1.7	0.5

Table 6
THE SYNTHETIC OUTCOMES OF THE XRFS MEASUREMENTS CARRIED ON POWDERED SRM NIST 611

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	Er_2O_3	Yb_2O_3
Mean	69.69	2.22	0.08	11.65	0.070	0.065	12.92	0.086	0.110	0.046	0.047
Median	69.89	2.18	0.08	11.57	0.07	0.05	12.97	0.090	0.114	0.046	0.049
SD	0.47	0.09	0.01	0.19	0.002	0.064	0.14	0.020	0.016	0.009	0.016
MEDe(x)	0.365	0.096	0.015	0.159	0.002	0.006	0.107	0.018	0.013	0.013	0.023
SDm	0.15	0.03	0.00	0.06	0.001	0.02	0.05	0.01	0.005	0.004	0.01
U(95%)	0.30	0.06	0.01	0.12	0.00	0.04	0.09	0.01	0.01	0.01	0.01
M_3	-3.5E-03	1.5E-04	-2.1E-07	3.3E-03	-3.6E-09	9.8E-05	-1.9E-03	-2.4E-06	-1.9E-06	9.3E-08	-3.4E-07
C_3	-2.5E-04	3.3E-06	-1.6E-10	3.9E-04	-2.5E-12	6.4E-08	-2.5E-04	-2.1E-09	-2.1E-09	4.3E-11	-1.6E-10
t_{calc}	0.3	0.0	0.6	1.0	0.0	0.2	0.8	0.8	0.9	0.7	0.5

Both ways of calculation of the assigned values (mean, median) give the same values for all the measurands in the limits of their MUs. (***SD, MEDe(x)***) (table 6). All the t_{calc} values are much less than critical value $t_{(0.05;20)} = 2.086$, therefore the traceability of the measurement process under test is demonstrated.

As in the case of SRM 620, the quality of the outcomes of the measurements carried on the SRM 611 as slab is better than of those presented in Table 6, but these results are not presented herein as they have no influence on traceability checking.

According to the top-down procedure, the traceability test succeeded for all measurands and the next step can be performed i.e. the calculation of u_{trac} using (8). Hence, two types of SRM were used to check the traceability the u_{trac} were calculated for each set of measurements as it is shown in table 7. Being aware of uncertainty underestimation, the maximum u_{trac} value was chosen as representative for the developed top-down procedure as is shown in table 7.

Once the u_{trac} was estimated for each measurand the third step can be performed e.g. estimation of the u_{proc}. Taking into account the literature recommendations 10 measurements were carried on the fluorescence glass specimens in reproductive conditions i.e. 10 specimens prepared in the same conditions in two different days [32]. The results obtained on these specimens are shown in table 8 together their statistics.

The outcomes in table 8 show that the luminescent glass contains the desired oxides given in table 3, but unexpected MgO, Fe_2O_3, TiO_2, P_2O_5, As_2O_3 and SO_3. The means and medians of the oxide concentrations in table 8

Table 7
THE VALUES ASSIGNED TO THE MEASURANS FOR EACH TYPE OF REFERENCE SPECIMENS

Uncertainty	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	As_2O_3	SO_3	SiO_2	Al_2O_3	Fe_2O_3
u_{trac} SRM 611	0.20	0.03	0.02	0.06	0.01	0.02	0.06	0.01	0.01	0.01	0.01	-	-
u_{trac} SRM 620	0.14	0.05	0.01	0.08	0.10	0.04	0.13	0.01	0.01	-	-	0.04	0.14
u_{trac}	0.20	0.05	0.02	0.08	0.10	0.04	0.013	0.01	0.01	0.01	0.01	0.04	0.14

Table 8
THE OUTCOMES OF THE XRFS MEASUREMENTS CARRIED ON FG05E05YB SPECIMENS USING TURBOQUANT PELLET ANALYTICAL PROGRAM

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	As_2O_3	SO_3	SiO_2	Al_2O_3	Fe_2O_3
1	72.35	3.24	3.37	5.55	13.61	0.542	0.571	0.179	0.184	0.104	0.492	0.068	0.255
2	72.30	3.18	3.37	5.35	13.73	0.499	0.543	0.122	0.235	0.111	0.405	0.068	0.221
3	72.66	3.21	3.28	5.40	13.76	0.513	0.563	0.165	0.215	0.127	0.364	0.089	0.199
4	71.64	3.19	3.27	5.45	13.74	0.547	0.562	0.170	0.185	0.113	0.474	0.096	0.214
5	71.42	3.21	3.37	5.43	13.53	0.540	0.498	0.138	0.212	0.100	0.362	0.081	0.233
6	72.15	3.23	3.36	5.39	13.66	0.502	0.503	0.141	0.174	0.119	0.477	0.092	0.255
7	72.11	3.22	3.34	5.39	13.64	0.478	0.493	0.164	0.242	0.122	0.386	0.083	0.217
8	72.82	3.21	3.34	5.47	13.55	0.576	0.510	0.154	0.211	0.123	0.523	0.086	0.207
9	71.42	3.18	3.28	5.40	13.65	0.564	0.569	0.162	0.235	0.108	0.426	0.068	0.246
10	72.37	3.15	3.34	5.35	13.66	0.537	0.521	0.142	0.206	0.144	0.537	0.077	0.263
Average	72.12	3.20	3.33	5.42	13.65	0.468	0.533	0.154	0.210	0.117	0.445	0.081	0.231
Median	72.22	3.21	3.34	5.40	13.66	0.538	0.532	0.158	0.212	0.116	0.450	0.082	0.227
STDEV	0.489	0.026	0.040	0.060	0.076	0.031	0.032	0.017	0.023	0.013	0.065	0.010	0.023
MEDe(x)	0.354	0.049	0.051	0.043	0.052	0.072	0.090	0.104	0.045	0.018	0.037	0.011	0.079
SDm	0.155	0.008	0.013	0.019	0.024	0.010	0.010	0.006	0.007	0.004	0.020	0.003	0.007
M_3	-2.9E-04	-6E-06	-3.8E-05	0.000176	-8.1E-05	-0.04003	-1.3E-07	-1.6E-06	-1.4E-06	1.2E-06	8.73E-06	-8.1E-08	8.48E-07
C_3	-2.1E-04	-1.9E-07	-1.3E-06	9.55E-06	-1.1E-05	-0.00019	-6.8E-10	-2.4E-09	-2.9E-09	1.4E-09	3.88E-08	-6.5E-11	1.96E-09
u_{trac}	0.2	0.05	0.02	0.08	0.10	0.04	0.013	0.01	0.01	0.01	0.01	0.04	0.14

Table 9

THE u_c VALUES ASSIGNED TO THE MEASURAND OF THE UNKNOWN LG-E05Y05 SPECIMENS

oxide	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Er_2O_3	Yb_2O_3	MgO	Fe_2O_3	TiO_2	P_2O_5	As_2O_3	SO_3
u_c	0.25	0.05	0.02	0.08	0.10	0.04	0.02	0.01	0.01	0.01	0.02	0.04	0.05
U(95%)	0.51	0.10	0.05	0.16	0.21	0.08	0.03	0.02	0.02	0.02	0.05	0.08	0.10

Table 10

THE OUTCOMES OF THE XEPOS MEASUREMENT CARRIED ON LG-E05Y05 AND THEIR UNCERTAINTIES

Oxide	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Er_2O_3	Yb_2O_3	MgO	Fe_2O_3	TiO_2	P_2O_5	As_2O_3	SO_3
C[%]	72.1	3.20	3.33	5.40	13.60	0.47	0.53	0.15	0.21	0.12	0.45	0.081	0.23
U(95%)	0.50	0.10	0.05	0.20	0.20	0.08	0.03	0.02	0.02	0.02	0.05	0.08	0.10
RU[%]	0.70	3.10	1.50	3.00	1.50	17.1	5.60	13.0	9.50	17.1	11.2	98.8	43.3

are close to each other in the limit of their ***SDs***, therefore the mean can be considered as representative for the concentration value of an oxide.

According to the 4-th step of the current procedure the standard combined MUs were calculated as it is shown in table 9.

Table 9 shows the values of the standard combined uncertainties calculated according to the 4-th step of the above mentioned procedure.

The values of the M_3 and C_3, calculated for each measurand (table 5 to table 8), are less than 10^{-3} therefore one can consider that the mean values of the measurands are normally distributed. Accordingly, the covered factor for a 95% confidence level can be taken as $k=2$. Hence, the final step of the procedure can be accomplished with the calculation of the expanded uncertainty as is given by the 3-rd line of table 9.

According to the EN ISO17025:2017 and SR EN Guide 98-3 the results of the XRFS analysis can be reported as follows (table 10).

The relative MUs, denoted RU in table 10, give are relevant for the quality of the results i.e. as RU is smaller than 10% it can be tolerable while as it exceeds 10% as the quality of the result decreases. Hence, in the cases of MgO, Fe_2O_3, TiO_2, P_2O_5, As_2O_3 and SO_3 the quality of the resuts is feable, but contens of 2 times greater than they were measured do not much influence the fluorescence yield.

The exactness of the concentrations of the main oxides into LG-E05Y05 are good enough except for Er_2O_3. In this direction futher investigations have to be done to decrease the RU below 6% as for the Yb_2O_3.

On the other hand, the paper firstly addresses the MU evaluation procedure and secondly the exactness of the ED(P)-XRFS measurement process designed for assessing the oxide composition of the LG-E05Y05 glasses.

Notwithstanding that it was measured 10 LG-E05Y05 pellets and the sample preparation MU was included in the MU budget. Hence, the sample preparation can be responsible for the higher MU and it will be carefully investigated.

Conclusions

The paper argues that the bottom-up method for MU estimation is feeble as long as the sensitivity coefficients of the uncertainty budget factor are not well known and documented, which is the habitual case of the ED and WD XRFS bottom-up published methods [22-29].

The authors purposed the top-down method for MU evaluation to overpass the drawbacks of the bottom-up method. The purposed top-down method is compliant with those given in Eurolab technical report 2007 [32]. Even though a similar method was applied for SDAR-OES spectrometry [32], the adaptation of this method and its implementation for ED(P)-XRFS spectrometry is a novelty. Besides, this method was implemented for the case of multiple simultaneous outcomes.

But, the main novelty consist in introducing a criterium for testing the normal distribution of the mean of a set of fewer outcomes based on CLT. The derivation of the criterium make use of characteristic function of the mean and is easily applicable using an Excel spreadsheet for the calculation of the central momentum of the third order M_3 and the C_3 coefficient.

Another novelty consists in introducing the robust statistics median and MEDe(x) as further checks for the accuracy of the mean and of SD, according to ISO 13583:2015.

The top-down method given in the paper can be applied for ED and WD XRFS routine measurements in industrial laboratories or material science ones.

The case study presented in the paper is representative for the case when no commercial CRM is similar to the sample composition that laboratory has to measure and the sample composition has to be guarded with 2 or more CRMs.

The top-down method addressed in the paper can be adapted, without much effort, to the other types of tests e.g. hardness, XRD etc.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-BG-2016-0338, within PNCDI III.

References

1. NECSOIU, T., BOSTAN, G., STERIAN, P., BERTEANU, M., Materials for Security Elements Used in Protected Documents, Optical Examination Methods. A Review. Annals of the Academy of Romanian Scientists Series on Science and Technology of Information, **10/1**, 2017, p. 25

2. KRISHNA, M.G. K., CHANDRASHEKHAR, R. M., APPA, R. B., Intense Upconversion Fluorescence in Tm^{3+}/Yb^{3+} Codoped Alumina Lead Borate Glasses, IOP Conf. Series: Materials Science and Engineering 149, 2016, p. 1

3. DEJNEKA, M., SNITZER, E., RIMAN, R.E., Blue, Green and Red Fluorescence and Energy Transfer of Eu^{3+} in Fluoride Glasses, Journal of Luminescence, 65/5, 1995, p. 227

4.**** US8927892, Rare Earth Downconverting Phosphor Compositions for Optically Encoding Objects and Methods and Apparatus Relating to Same, Parallel Synthesis Technologies, 2015.

5.*** EP2990390A1, Luminescent Glass Composition, D. Swarovski KG, 2016.

6. BRICE, I., ROGULIS, U., ELSTS, E., GRUBE, J. Photoluminescence of Eu and Ce Activated Oxyfluoride Glass and Glass Ceramics, Latvian Journal of Physics and Technical Sciences,6/(I), 2012, p. 44

7. *** BEAMEX Calibration White Paper, Calibration Uncertainty Fornon-Mathematicians, www.beamex.com, 2018.

8. *** ISO/IEC Guide 98-3, Uncertainty of Measurement-Part 3: Guide to the Expression of Uncertainty in Measurement, 2008.

9. NEGOITA, M., ADASCALULUI, A., IORGA, E., CATANA, L., CATANA, M., BELC, N., Internal Validation of the Method for Determination of Acrylamide in Bread by Gas Chromatography Tandem Mass Spectrometry Rev. Chim. (Bucharest),**66**, no. 4, 2015, p. 464

10. LICSANDRU, A., NACEA, V., BOSCENCU, R., Investigation of Uncertainty Contributions for Elemental Analysis of Sesized Street Heroin by ICPMS, Rev. Chim. (Bucharest),**64**, no. 11, 2013, p. 1237

11. CAPRA, L., MANOLACHE, M., ION, I., RADU, E., ION, A. C., The Optimization and Validation of a Method for Sb Determination from PET by ICP-OES, Rev. Chim. (Bucharest), **68**, no. 9, 2017, p. 1969

12. PENCEA, I., Methods and Instrumental Techniques for Elemental Analysis of Materials, Chapter 8.2. in the Materials Science and Engineering Treaty, vol. 5 - Finished Processing Technologies of Metal Materials, Agir Publishing House, 2011, p. 1149

13. ***, Industrial Minerals -EDXRF for Direct Analysis without Digestion, Bruker_ AXS_ Industrial_ Minerals_ EDXRF_ Webinar, https://www.bruker.com/fileadmin/user_upload/8-PDF-Docs/X-rayDiffraction_ElementalAnalysis/XRF/Webinars/Bruker_AXS_Industrial_Minerals_EDXRF_Webinar.pdf

14. NEMES, O.F., BRATU, I., MARUTOIU, C., KACSO, I., MICLAUS, M., MIHALI, D., NICA BADEA, D., Spectroscopy Investigation of Triptych Icon from the Borsa Church, Maramures County, Rev.Chim. (Bucharest), **69**, no. 1, 2018, p. 76

15. ***, Guide to the Expression of Uncertainty in Measurement 1st corr. Edition, ISO, Geneva 1995.

16. PAPADATU, C.P., BORDEI, M., ROMANESCU, G., SANDU, I., Researches on Heavy Metals Determination from Water and Soil in Galati County, Romania, Rev.Chim. (Bucharest), **67**, no. 9 , 2016, p. 1728

17. AHMED, O.M.H., HABBANI, F.I., MUSTAFA, A.M., MOHAMED, E.M.A., SALIH, A.M., SEEDIG, F., Quality Assessment Statistic Evaluation of X-Ray Fluorescence via NIST and IAEA Standard Reference Materials. World Journal of Nuclear Science and Technology,**7**, no.2, 2017, p.121.

18. ARUS, V.A., JINESCU, G., NISTOR I.D., MIRON, N.D., URSU, A.V., ISOPENCU, G., MARES, A.M., Preparation and Characterization of Anionic Clays Used as Kinetic Modifiers in Lactic Fermentation, Rev. Chim. (Bucharest), **61**, no. 11, 2010, p. 1100

19. RAZAK, R.A., MOHD MUSTAFA AL BAKRI ABDULLAH , KAMARUDIN, H., KHAIRUL NIZAR ISMAIL2 , SANDU, I. HARDJITO, D., YAHYA Z., Study on Radioactivity Components, Water Quality and Microstructure Characteristic of Volcano Ash as Geopolymer Artificial Aggregate, Rev. Chim. (Bucharest), **64**, no. 6, 2013, p. 593

20. DRAGAN, C.I., MATEI, E., PREDESCU, A.M., PREDESCU, C., COMAN, G., Identifying of Uncertainty Sources: A Useful Tool for Validation Process of Heavy Metals in Waters, U.P.B. Sci. Bull., Series B, **79**/2, 2017, p. 218

21. ***, ELLISON S. L. R. and WILLIAMS A., Quantifying Uncertainty in Analytical Measurements, Eurachem/CITAC Guide CG 4, **3rd** ed, QUAM, 2012.

22. *** IAEA TECDOC **1401**, Quantifying Uncertainty in Nuclear Analytical Measurements, IAEA, Vienna, 2004

23. ROUSSEAU R. M., Detection Limit and Estimate of Uncertainty of Analytical XRF Results, Rigaku J., **18**(2), 2001, p. 33

24. REMYA DEVI, P.S., TRUPTI, A. C., NICY, A., DALVI, A. A., SWAIN, K. K., WAGH, D. N., VERMA, R., Evaluation of Uncertainty in the Energy Dispersive X-ray Fluorescence Determination of Platinum in Alumina, Anal. Methods, **7**, 2015, p. 5345

25. SCAPIN, M.A., SALVADOR, V.L.R., COTRIM, M.E.B., PIRES, M.A.F., SATO, I.M., Uncertainty Measurement Evaluation of WDXRFS and EDXRF Techniques for the Si and U_{tot} Determination in U_3Si_2 Used as Nuclear Fuel Material, Int. Nuclear Atlantic Conference, Rio de Janeiro, 2009, p. 213

26. MARKOWICZ, A., An Overview of Quantification Methods in Energy-Dispersive X-ray Fluorescence Analysis, Pramana, **76**(2), 2011, p. 321

27. PERRING, L., NICOLAS, M., ANDREI, D., FRAGNIERE RIME, C., RICHOZ-PAYOT, J., DUBOSCOUX, S., POITEVIN E., Development and Validation of an ED-XRF Method For the Fast Quantification of Mineral Elements in Dry Pet Food Samples, Food Analytical Merthods, **10/5**, 2017, p. 1469

28. YUAN, Q., Shishua Liu, Qiannan Li, Wei Han, Evaluation of Measurement Uncertainty for the Determination of MgO in Magnesia Refratories by XRF, Key Engineering Materials, **768**, 2018, p. 36

29. CHERKASHINA, T.Y., BOLORTUYA, D., REVENKO, A.G., ZUZAAN, P., Development of X-ray Fluorescence Technique for the Uranium Determination in Mongolian Coal, Coal Ash and Phosphate Ore, Analitika and Control, 18/4, 2014, p. 404

30. Dr. GRIGORESCU, L.E., Elements of Mathematical Statistic for the Experimentalists, Bucuresti-Magurele, 2013, p. 55

31. ***, EUROLAB Technical Report 1/2007, Measurement uncertainty revisited

32.***Alternative approaches to uncertainty evaluation, www.eurolan.org, 2018.

33.***, ISO 5725-2:1998 Accuracy (trueness and precision) of Measurement methods and results

34. PENCEA I., Multiconvolutional Approach to Treat the Main Probability Distribution Functions Used to Estimate the Measurements Uncertainties of Metallurgical Tests, Chapter 6, INTECH, 2012, p. 117

35. CEAUSESCU, D., Statistical Treatment of the Chemical Analytical Data, Ed Technical, Bucharest, 1973, p. 73

36. VENTSEL, H., Probability theory, Ed. Mir-Moscou, 1973, p. 291

37. MIHOC, G., MICU N., Elements of Probability and Statistic Theory, Didactic and Pedagogic Ed., Bucharest, 1966, p. 220

38. ***, NIST, Standard Reference Material 620, Washington DC, 20234

39. ***, NIST, Standard Reference Material 611, Washington DC, Gaithersburg, MD 20899

40. ***, NIST, Certificate of analysis, standard reference material 611, trace elements in a glass matrix, nominal element concentration 500 mg/kg, 1992

41. HOLLOCHER, K., RUIZ J., Major and Trace Element Determinations on Nist Glass Standard Reference Materials 611, 612, 614 AND 1834 by Inductively Coupled Plasma-Mass Spectrometry, Geostandards and Geoanalytical Research, 2007

42. ***, ISO 5725-5, Accuracy (trueness and precision) of Measurement Methods and Results, 1998

43. ***, ISO 13528, Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparison, 2015

Manuscript received: 22.02.2018