ESTIMATES OF UNCERTAINTY IN OPTICAL EMISSION SPECTROMETRIC METHOD WITH ARC AND SPARKS EXCITEMENT (SEOASE).

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Abstract: The practice of technologically advanced countries and economic default and the current rules of the European Union (EU), all measurements have undergone a significant process of standards to ensure quality undisputed of the test results. In the spectrometric field there are standards of competence of laboratories, as well as of analytical method. SR EN ISO / IEC 17025, EN 13005 and European standards 04-16 EA, ILAC, etc. 2000. clearly specified scientific substantiation of the measurand to be modeled properly and to prepare the budget of uncertainty in knowledge. In this context, to estimate correctly the measurand spectrometric test is necessary to specify the current state of theoretical modeling of radiation emission by atoms. It is clear that attempts spectrochimice are affected by a relatively large number of influencing factors, which generates errors and thus contribute to the uncertainty budget method, in a way difficult to estimate. Accuracy and reliability spectrometric tests and / or calibrations performed by a laboratory are determined by many factors. These factors will be estimated and analyzed in this paper.

Keywords: Uncertainty budget,SEOASE, quality assurance, factors of influence, measurand

1. INTRODUCTION.

The practice of technologically advanced countries and economic default and the current rules of the European Union (EU), all measurements have undergone a significant process of standards to ensure quality undisputed of the test results. The promoter of this policy was the U.S. in this regard see the set of "Standard Practice for ..." published by ASTM [1,2]. This policy proved extremely profitable production practice, especially the "equipment" technologically advanced. Policy was taken, among many other states and the European Union (EU) and implemented by European standards become normative reference, default and Romania. In most cases the qualitative analysis of minerals or metals spectrometry is used the electric arc excitation, because the electric arc will transfer more substance in the discharge space than electric sparks, which favors the appearance of lines of analysis for dosed elements.

2.THEORETICAL ASPECTS OF QUALITY ASSURANCE OF TESTS RESULTS FROM ANALYSIS METHODS.

In the spectrometric field there are standards of competence of laboratories, as well as of analytical method. SR EN ISO / IEC 17025, EN 13005 and European standards 04-16 EA, ILAC, etc. 2000. clearly specified scientific substantiation of the measurand to be modeled properly and to prepare the budget of uncertainty in knowledge. In this context, to estimate correctly the measurand spectrometric test is necessary to specify the current state of theoretical modeling of radiation emission by atoms. It is clear that spectrometric tests are affected by a relatively large number of influencing factors, which generates errors and thus contribute to the **uncertainty budget** method, in a way difficult to estimate. Accuracy and reliability spectrometric tests and / or calibrations performed by a laboratory are determined by many factors.

These factors include contributions from
-human factors;
-working and environmental conditions;
-test and calibration methods and method validation;
-equipment;
-measurement traceability;
-sampling;
-handling test and calibration items.

The extent to which these factors contribute to the total uncertainty of measurement differs considerably on the type of tests and method, and the type of calibration. The laboratory shall take account of these factors in developing test methods and procedures

and calibration, in training and qualification, and selection and calibration of equipment they use.

2.1. THE ELECTIONS AND VALIDATION OF TEST METHODS AND ANALYSIS.

The laboratory shall use test methods and / or calibration, sampling methods, which meet customer needs and are appropriate testing and / or calibration that will do. Published methods in national standards, regional or international should be used preferably. The laboratory must ensure that utilizes the latest edition of the standard existing, unless it is not appropriate or possible to do so. When necessary, the standard must be supplemented with additional details to ensure proper application.

Validation is confirmation by examination and provision of objective evidence, that some specific requirements for the intended use are fulfilled. The laboratory must validate non-standard methods, methods designed / developed by the laboratory, standard methods used outside their scope, and extending and modifying standard methods to confirm that the methods are suitable for intended uses. Validation should be as comprehensive as necessary to meet the needs of the application or given scope. The laboratory shall record the results obtained, the procedure used for validation and a declaration that the method is suitable for use intended. Techniques used to determine the performance of a method should be one or a combination of the following:
-calibration using reference standards or reference materials;
-comparing the results obtained by other methods;
-interlaboratory comparisons;
-Systematic evaluation of factors influences the result;
-evaluation of the uncertainty of results based on scientific understanding of theoretical principles of the method and practical experience.When, in non-standardized validated methods, changes are made, their influence should be documented and if necessary, a new validation should be performed. Range and accuracy values that can be obtained by validated methods must be relevant to customer needs.Validation includes specification requirements, characterization methods, verification that the requirements can be met using the method, and a declaration on the validity.

2.2. ESTIMATION THE UNCERTAINTY OF MEASUREMENT.

Testing laboratories shall have and apply procedures for estimating uncertainty of measurement. In some cases the nature of the test method may not allow a rigorous calculation, and that is at the same time, metrologically and statistically valid for uncertainty of measurement. In such cases the laboratory shall at least attempt to identify all components of uncertainty and make a reasonable estimate and should ensure that the form of reporting will not fumiza a false impression of the uncertainty.Reasonable estimate should be based on knowledge of performance measurement method and the field and use, for example, previous experience and validation data.The degree of rigor required in estimating the uncertainty of measurement depends on factors such as:
-requirements test methods;
-customer requirements;
-the existence of tight limits that are based the decision to accordance with an specification. When estimating the uncertainty of measurement should be taken into account all uncertainty components which are important in the given situation, using appropriate analytical methods.

2.3. ASSESSMENT OF THE EFFECTS OF SOME FACTORS OF INFLUENCE ON UNCERTAINTY BUDGET FROM SPECTROMETRY TESTS (SEOASE).

In the case of testing optical emission spectrometry atomic or ionic excited by electric discharge in the spark or electric arc, significant influencing factors must be analyzed carefully because they can generate relatively large uncertainties.Thus:1.Errors due to sample: metal sample condition, tested respectively structural homogeneity, chemical homogeneity, the content of non-metallic inclusions , the content of compounds and precipitated, homogeneity surface processing by mechanical polishing, the state of contamination after processing, the content of O, N and H dissolved, the state of magnetization , thermal conductivity of the sample, type the discharge to thermal load, respectively the type of cooling determined by size and shape of the sample (sample, thick or thin washer etc).

2. Errors due to excitation of optical emission: vaporization and excitation are two factors coupled, which in turn depend on the nature and condition of the sample and the electrical parameters of discharge, respectively the size and shape space discharge (discharge gap), the power dissipation during a discharge (sparks), the frequency of spark or arc discharge, alternatively, the amount of material

vaporized during a discharge, the distribution of individual discharges, respectively discharge craters on the surface of the sample (a patch discharge), the number of atoms suffering ionisation into discharge space and emitting ionic lines, the number of excited atoms emitting characteristic atomic lines, respectively line of analysis.

Thus, during on sparking, comprising all the sparks produced when making the measurement "the intensity" spectral lines, vaporize about 10^{-4} g of sample (eg Fe), this mass is composed of about 10^{16} atoms of Fe. [3] If the detection limit of Al in Fe is 10 ppm then the number of Al atoms on which must contain "the plasma" of discharge is:

$N_{Al}=10·10^{-6}·N_{Fe}·M_{Fe} / M_{Al} \approx 10^{-5}·10^{16}·56/27 \approx 2·10^{11}$ atomi, unde:

atoms, where:

    N_{Al} - number of aluminum atoms
    N_{Fe} - number of iron atoms
    M_{Al}= 27 g/mol molar mass of aluminum
    M_{Fe} = 56 g / mol molar mass of iron
    Although N_{Al} is evaluated approximately large enough, it is clear that in order to be detected aluminum as an alloying element of Fe is necessary that "the plasma" of discharge to have a representative number of about 10^{11} atoms, atoms respectively issue.

Note: was noted "plasma" because the spark discharge is not a plasma, but plasma is called in many works, because discharge emits light like a plasma arc excited.

From the above it follows that the number of atoms of the analyte in the "plasma" is relatively high and can vary widely because of local factors which intervened in each initiation sparks. According to statistical theory, the error of "counting" of atoms is of the order $\sqrt{N_{Al}} = 5 . 10^5$ which shows the relative error is:

$E_r \approx 5 . 10^5/10^{11} = 5 . 10^{-6} =5$ ppm

3. Errors due to optical spectrometer:
- Errors generated by the optical measurement are due to:
- •different processing of radiation flow line data analysis and the reference line;
- • optical fibers in different opacity depending on the wavelength (different spectral opacity);
- • diffraction aging network and the emergence of "ghosts" that overlap analyte line;
- • profile modification on source of radiation because of mechanical factors (size

spectrum download, profile stand, magnetized samples, etc.).

Errors introduced by the optical measurement are insignificant when the device is operating under optimum conditions and the operator complies with the test procedure. Evaluation of uncertainty due to optical spectrometers can be done only by specialists using special equipment.

4. Errors due to fluctuation electronics, measuring the intensity of spectral lines, and electrical signal processing (CCDs and+ PC)

Electronics errors of measurement are negligible under normal conditions of operation of the device. [3,4] These can be evaluated by testing of repeatability with chemically and structurally homogeneous samples, respectively certified standards.

5. Errors due to contamination state of argon in which the electric discharge:

Contamination of argon with oxygen, nitrogen, water vapor and hydrogen, etc.., But particularly with oxygen and water vapor, introduces errors as large because it favors the oxidation of the discharge area of surface sample and reduces vaporization efficiency. This factor of influence is reduced to insignificant level by using a spectral pure argon (purity $\geq$ 99, 998) or by using argon purification filter cartridges, filter installations of "BOC rare gas purifier", "KAS purifier for Argon", etc. [3].

Note: The condition of argon used ,affect (in most cases) the accuracy of measurements that need special attention would acquiring the special type of Ar spectral.

Evaluation of uncertainty due to Ar can be performed using the Ar standard spectrometry certified for use. The uncertainty due to the Ar should be reduced at minimum level by using a suitable type of Ar.

Influence factors specified above, place a standard deviation of the form:

$$s^2 = s_1^2 + s_2^2 + s_3^2 + s_4^2 + s_5^2 \qquad (1)$$

For evaluation (calculation) of s^2 should be evaluated standard dispersions s_1^2 ….s_5^2 which, in turn, consist of dispersions factors that influence them. For example, , s_1^2 is evaluated using the relation:

$$s_1^2 = s_{os}^2 + s_{oc}^2 + s_i^2 + s_{ep}^2 + s_{pm}^2 + s_{cont}^2 + s_m^2 + s_t^2 \qquad (2)$$

where:

s^2os - standard dispersion associated with structural homogeneity,

s^2oc - standard dispersion associated chemical homogeneity,

s^2i - standard dispersion associated content inclusions,

s^2cp - standard dispersion associated content compounds and precipitates,

s^2pm - standard dispersion associated metal processing,

s^2cont - standard dispersion associated contamination

s^2m - standard dispersion associated with the sample magnetization,

s^2t - discharge dispersion associated technical discharge of sample.

3. DISCUSSION.

For those in the previous section, it is clear that attempts spectrometric are affected by a relatively large number of influencing factors, which generates errors and thus contribute to the uncertainty existing in a difficult to estimate.

For ensure a reduction of the effects factors listed above influence is frequently used in spectroscopy, in addition to certified reference materials (CRMs) and other calibration standards, ie Setting Up Sample (UP).

Spectral standards (MRC) for ferrous materials must meet a number of conditions to be used in the analytical chemical characterization of

a) the condition representativity is expressed primarily by the fact that these standards must contain the same chemical elements, and range of concentrations similar to the types of materials to be analyzed.

b) chemical and structural homogeneity of the spectral standards are based on their condition in the direction to obtain accurate results.

Standards (MRC) for ferrous materials are used to calibrate spectral instruments and standards SUS are used for periodic recalibration of instruments.

Certified reference materials can be obtained from various manufacturers. They provide materials certified by official analysis, or released by an institute. Rules governing this procedure is ISO Guide 35. Reference materials (SUS) does not satisfy fully the requirements of this standard, but most manufacturers of spectrometers using MRC-SUS successful combination for drawing the calibration curves.

Due to the special needs that require such materials (MRC and SUS) their costs are high.

4.CONCLUSIONS.
ESTIMATES OF UNCERTAINTY IN OPTICAL EMISSION SPECTROMETRIC METHOD

According to Deming concept the most important route to optimize the process is to improve knowledge about the process. From studies on electrical discharge spark, used as a spectral source, revealed that it can be given a budget of uncertainty, composed of the following factors significant influence:

1. instability of the electronic parameters of discharge stand,

2. reactivity of the environment discharge ,the debt by Ar contaminated ,

3. the distance electrode-sample variation due to poor of sample preparation,

4. "Attack" selective scintillation due of the effects to combined source--environment discharge-sample,

5. Understand enough, i.e. inconsistent theoretical modeling of the process of discharge[1.5, 6.7]

Factor 1, the instability of electronic parameters, belonging to spark stand, can not be approached by the operator but only the manufacturing company. At present, current and voltage stability in a SEOSE spectrometer is <0.1%, which makes this factor to be considered to have contributed negligibly to the uncertainty budget of SEOSE tests.

Factor 2, medium reactivity discharge of the debt by Ar contaminated, would be controlled by ensuring the Ar spectral, certified purity> 99, 999. Otherwise, the fault of the operator would not provide adequate quality. Also, the presence of oxygen in the discharge space, one can see by the look of the sparked area macrostructure. An operator with the necessary experience can estimate, sufficiently good the Ar quality and its impact on quality discharge as macroscopic aspect of the area sparkle.

Factor 3, electrode-sample the distance variation due to improper of sample preparation, can be controlled by the operator, by correct preparation of sample, and by analyzing samples with proper geometry, ie plates or cylinders with flat surfaces, where can enroll an imaginary circle with diameter> 2 cm. Exceptions to this chapter, leading to large uncertainty analysis. The operator should periodically check the electrode-sample distance, with specific resources, delivered by the supplier, along with equipment.

Factor 4, "attack" selective sparkle, due to combined effects of source--enviroment discharge-sample, is for the specialist physician in this case, the party, which may bring theoretical and experimental contributions, and also to respond to Deming concept, transformed in influence factor and a contributor to the budget of uncertainty [7].

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