The Scientific Bulletin of VALAHIA University
MATERIALS and MECHANICS –Vol. 19, No. 21

DOI 10.2478/bsmm-2023-0017



ASPECTS REGARDING THE EFFECTS OF SOME INFLUENCE FACTORS ON THE UNCERTAINTY BUDGET OF OPTICAL EMISSION SPECTROCHEMICAL TESTS WITH EXCITATION BY SPARK OR ELECTRIC ARC

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Abstract. *In this work, a number of significant factors are highlighted that affect the optical emission spectrochemical tests with spark or electric arc excitation on stainless steels with multiple synergistic purposes such as: acquiring new knowledge, increasing the amount of information obtained about the material, increasing the efficiency and quality of the tests , the characterization of special purpose alloys and the assessment of their compliance with the specified requirements. In this direction, it requires both knowledge of testing methods (theoretical basis, test method, procedure related to the method, quality assurance testing) and the characteristics of the investigated materials. These aspects are necessary for the analysis of the test system and the most correct preliminary interpretation of the experimental results.*

.**Keywords***: The AISI 316 alloys, optical emission spectrochemical tests with spark or electric arc excitation, the uncertainty budget.*

1. INTRODUCTION

The main factors that influence the reliability and correctness of tests and/or calibrations that are carried out in a laboratory can be:
- the human factor;
- the environmental and work factor;
- the test and calibration method, as well as the validation method used;
- apparatus and equipment;
-traceability of measurements;
-sampling stages;
- handling of testing and calibration instruments.
These factors, in general, contribute to the assessment of total measurement uncertainty considerably, but differently depending on the type of test and the type of calibration.

2. METHODS AND MATERIALS

The significant influencing factors on the uncertainty budget of spark or electric arc excited optical emission spectrochemical tests (SEOES) are:

1. The errors due to the samples studied

- depending on the state in which the metal sample is, we can list errors given by the structural homogeneity of the sample, the chemical homogeneity, the degree of non-metallic inclusions, the number of compounds and precipitates, the homogeneity of the surface treatment carried out by mechanical grinding, the contamination state of the sample . metals after processing, the percentage of O, N and H dissolved, the degree of magnetization, the thermal conductivity of the sample, the process of discharging thermal loads, the cooling process determined by the size and shape of the sample (if the samples are thick or thin, etc.).

2. Errors due to optical emission excitation

Vaporization and excitation are two coupled factors which in turn depend both on the nature and state of the sample and on the electrical parameters of the discharge, respectively on the size and shape of the electrical discharge space (discharge gap), on the power dissipated during a discharge (spark), by the frequency of discharges by spark or alternating electric arc, by the volume of vaporized material during a discharge, by the distribution of individual discharges or discharge craters on the surface of the sample (of the discharge spot), by the number of atoms that undergo ionization in the space of discharge and emit ion lines, by the number of excited atoms that emit characteristic atomic lines, respectively the analysis line[1].

3.Errors due to the optical geometry of the spectrometer

These errors are due to:

• different interpretation of the radiation fluxes given by the analysis line and the reference line;

• differentiated spectral opacification of optical fibers depending on the wavelength;

• distortion of the diffraction grating;

• modification of the profile of the radiation source due to various factors (the size of the discharge spectrum, the configuration of the stand, magnet sizes, etc.)

If the loading procedures are respected by the operators, and the equipment used is in optimal working conditions, then these errors given by the measuring optics are insignificant. In order to be able to make an assessment of the uncertainty budget due to the optical geometry of the spectrometers, only specialists who use special equipment should be called upon.

4. Errors due to the fluctuation of the electronics for measuring the intensity of the spectral line and processing the electrical signals (CCDs + PC)

The errors of the measuring electronics are negligible under normal operating conditions of the device[1,4]. These can be evaluated through repeatability tests with chemically and structurally homogeneous samples, respectively with certified standards.

5. Errors due to the contamination state of the argon in which the electrical discharge occurs

Contamination of argon (Ar) with oxygen, nitrogen, water vapor and hydrogen, etc. but especially with oxygen and water vapor it introduces large measurement errors because it favors the oxidation of the deposition zone on the sample surface and reduces the vaporization efficiency. This influencing factor is reduced to an insignificant level by using spectrally pure argon (purity ≥ 99.998) or by purifying argon using filter cartridges, filtering installations of the type "BOC rare gas purifier", "KASpurifier for argon", etc. [1]

Note. The condition of the argon used affects (in most cases) the accuracy of the measurements, so special attention must be paid to the acquisition of spectral Ar.

Evaluation of uncertainty due to Ar can be performed using standard Ar certified for spectrochemical use. The uncertainty due to Ar is minimized by using an appropriate Ar type.

The previously specified influence factors (1÷4) introduce a standard deviation of the form:

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

To perform the calculation of s^2, it is necessary to evaluate the standard dispersions s_1^2 ....s_5^2, each of which is formed by the dispersions of the factors that influence them. Thus, s_1^2 is evaluated with the following 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^2_{os} – is the standard dispersion grouped with structural homogeneity

s^2_{oc} – is the standard dispersion grouped with chemical homogenization

s^2i – is the standard dispersion grouped by the number of inclusions

s^2_{cp} – is the standard deviation grouped with the percentage of compounds and precipitates

s^2_{pm} – is the standard dispersion grouped with the metal processing mode

s^2_{cont} – is the standard dispersion grouped with the degree of contamination of the sample

s^2_{gd} – is the standard dispersion grouped by the percentage of dissolved gases

s^2_m – is the standard dispersion grouped with the degree of magnetization of the sample.

3. EXPERIMENTAL RESULTS

According to the law of error propagation, the reproducibility of the measured values is determined by the errors of individual processes respectively:

$$S_M^2 = S_P^2 + S_A^2 + S_E^2 + S_R^2 \qquad (3)$$

where:

S_M = dispersion of measured values

S_P = dispersion due to the sample (processing, preparation, etc.)

S_E = dispersion due to the excitation source of the optical emission

S_O = the error due to the optics of the device

S_R = the error due to the recording system

The error introduced by the sample (homogeneity, sample preparation, etc.) can be kept to minimum values using appropriate sampling techniques. Currently, electronic systems have very small recording errors. The excitation error S_E and the error due to optics S_O respectively the error due to the discharge distance (distance between the electrodes) are of major importance.

If the source of radiation produced by electric discharge is replaced by a light source that is constant then the reproducibility should be $S \leq \pm 0.05\%$. Errors due to individual downloads never appear explicitly, but are implicitly found in S_E. A good reproducibility is necessary, but it is not a sufficient condition for a good device facility. This is an eminently statistically determined variable.

The reproducibility of the spectrometers is generally related to the type of material analyzed as shown in the example (table 1and fig. 1)

Table1. Reproducibility obtained with the Foundry Master spectrometer on the MRC BAS 658 cast iron sample

Nr. crt. testing	C	Si	Mn	S	P
1	3,32	2,07	0,523	0,053	0,220
2	3,34	2,08	0,515	0,054	0,229
3	3,33	2,10	0,535	0,051	0,232
4	3,31	2,10	0,528	0,058	0,230
5	3,30	2,13	0,531	0,053	0,239
6	3,34	2,05	0,524	0,055	0,221
7	3,34	2,10	0,522	0,053	0,243
8	3,35	2,11	0,519	0,053	0,219
9	3,32	2,08	0,519	0,057	0,219
10	3,33	2,08	0,523	0,058	0,227
Medie	**3,33**	**2,09**	**0,524**	**0,055**	**0,228**
SD	**0,0147**	**0,0214**	**0,0057**	**0,0023**	**0,0080**
RSD	**0,4**	**1,0**	**1,1**	**4,2**	**3,5**

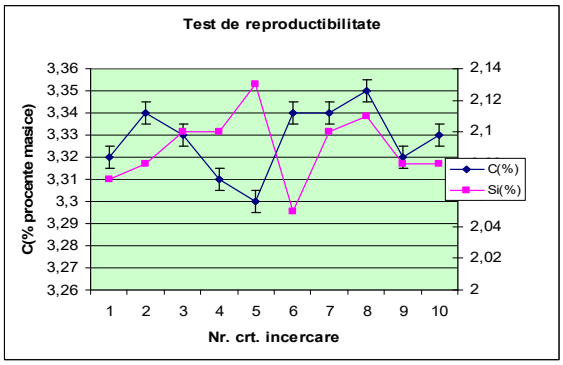


Figure. 1. Graphic representation of the results of the determinations made for elements C and Si

Repeatability

The repeatability of the concentration measurement, expressed as the relative experimental standard deviation, upon commissioning an atomic absorption spectrophotometer, must be less than or equal to that specified by the manufacturer. In operation, it must not exceed ± 2 % in the case of atomization in the flame and, respectively, ± 5 % in the case of atomization in the oven.

The repeatability of the concentration measurement, expressed as relative experimental standard deviation, when commissioning an inductively coupled plasma optical emission spectrometer, must be less than or equal to that specified by the manufacturer. In operation, it must not exceed ± 2 %.

The repeatability of concentration measurement, expressed as relative experimental standard deviation, when commissioning an X-ray fluorescence emission spectrometer, must be less than or equal to that specified by the manufacturer. In operation, it must not exceed ± 5 %.

As previously defined, the repeatability of the spectrometer establishes the degree of agreement between the results of successive measurements performed under the same measurement conditions on a suitable metal sample.

Repeatability is performed using the same measurement procedure, the same observer, the same spectrometer, used in the same conditions, the same place. The repetition of measurements is carried out in a short period of time.

Repeatability is expressed quantitatively according to the characteristics of the scattering of the measurement results. An example of a study of the repeatability of Ni determination from a high alloy steel will be presented. Thus, in Table 2 are presented the results obtained in 27 tests carried out under identical conditions and in Table 3 their grouping. In fig. 2 and fig 3 show the frequency distributions that highlight or not the random nature of the errors that influenced the meters.

Note. Type A uncertainty is evaluated, respectively by statistical methods.The way of processing the data from Table 2 is presented in Table 4.

Table 2. The results of the repetitive spectrochemical test

No.	1	2	3	4	5	6	7	8	9
C (%)	9.71	9.82	9.86	9.89	9.92	9.94	9.96	9.99	10
Nr.crt.	10	11	12	13	14	15	16	17	18
C (%)	10.02	10.05	10.06	10	10.08	10.1	10.1	10.11	10.12
Nr.crt.	19	20	21	22	23	24	25	26	27
C (%)	10.16	10.17	10.21	10.23	10.26	10.27	10.29	10.3	10.33

C-concentration

Table 3. Frequency distributions of Ni concentrations in AISI 316 stainless steel

Center of the Interval	Interval	absolute frequency	relative frequency (%)
9.75	9.7-9.79	1	4
9.85	9.8-9.89	2	8
9.95	9.9-9.99	4	16
10.05	10-10.09	5	20
10.15	10.1-10.19	6	24
10.25	10.2-10.29	5	20
10.35	10.3-10.39	2	8

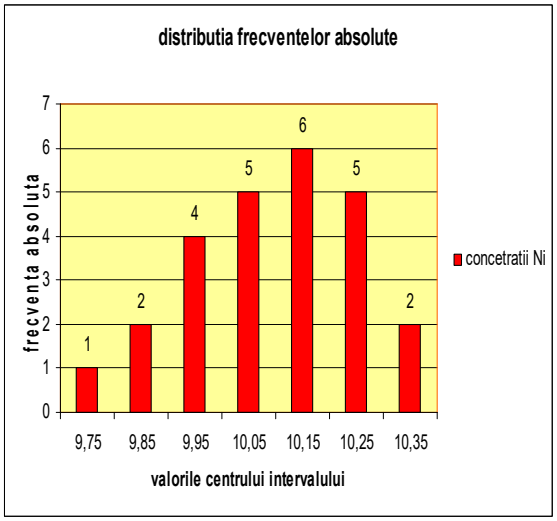


Figure 2. Histogram of absolute frequencies

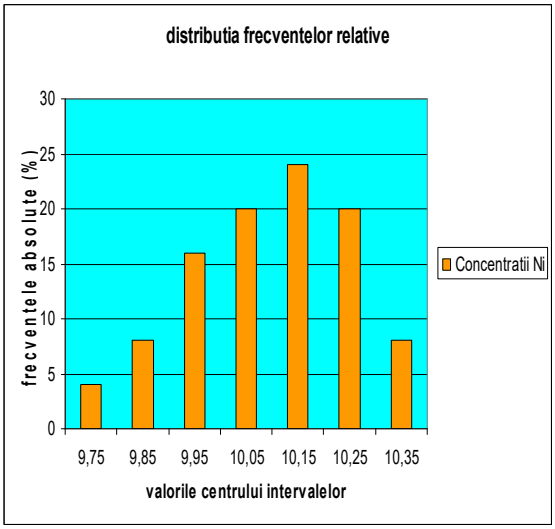


Figure 3. Histogram of relative frequencies

Table 4. Example of calculation of statistical parameters of repeatability determination of Ni concentration in a NiCr AISI 316 steel sample

Nr.crt.	Concetration	Deviation	Squared Deviation
1	9.71	-0.365	0.1332
2	9.82	-0.255	0.0650
3	9.86	-0.215	0.0462
4	9.89	-0.185	0.0342
5	9.92	-0.155	0.0240
6	9.94	-0.135	0.0182
7	9.96	-0.115	0.0132
8	9.99	-0.085	0.0072
9	10.00	-0.075	0.0056
10	10.02	-0.055	0.0030
11	10.05	-0.025	0.0006
12	10.06	-0.015	0.0002
13	10.08	0.005	0.0000
14	10.10	0.025	0.0006
15	10.10	0.025	0,0006
16	10.11	0.035	0,0012
17	10.12	0.045	0,0020
18	10.16	0.085	0,0072
19	10.17	0.095	0,0090
20	10.21	0.135	0,0182
21	10.23	0.155	0,0240
22	10.26	0.185	0,0342
23	10.27	0.195	0,0380
24	10.29	0.215	0,0462
25	10.30	0.225	0,0506
26	10.33	0.255	0,0650
Medium value	10.075	ASD	0,1610
		RDS	1,598
	Medium ASD		0.032
The result of the test		10.08	C_{min}
Degree of confidence 96%	Deviation + -	0.06	C_{max}

4. CONCLUSIONS

From what is shown in this article, it is clear that spectrochemical experiments are affected by a relatively large number of influencing factors that generate errors and, implicitly, contribute to the existing uncertainty in a way that is difficult to estimate. From these considerations it follows that it is more advisable to use the standard uncertainty of type A weighted with an appropriate factor depending on the degree of test desired.

The laboratory must take into account these factors in the development of testing and calibration methods and procedures, in the training and qualification of personnel and in the selection and calibration of the equipment it uses.

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