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Inter-laboratory comparison of a WDS–EDS quantitative X-ray microanalysis of a metallic glass

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We conducted an inter-laboratory study of a metallic glass whose main component is nickel. Two determinations of the mass fractions of the different elements present within the sample were asked to the participants: one at an acceleration voltage of 15 or 20 kV and another one at 5 kV. We compare the mass fractions obtained from wavelength dispersive (WDS) and energy dispersive spectrometries (EDS) and also try to find an influence of the kind of EDS detector and its entrance window, the background subtraction method, the use or not of standards as well as the quantification method. Both means of WDS and EDS mass fractions are close to the reference values. The dispersion of the results was larger at 5 kV than at 15–20 kV owing to the use of the L lines rather than K lines and to the lowest collected intensities. There is an exception with the case of boron because at the lowest voltage, the excitation condition is more favorable for the production of the K line. It appears that the dispersion of the results is larger with EDS than with WDS, but it was not possible to find a correlation between the large dispersion and one of the considered experimental parameters and quantification factors. Thus, one can think that electron microprobes are inherently better for the determination of mass fractions or that the implementation of quantitative analysis must be optimized for some cases, especially in scanning electron microscopes.

Introduction

Quantitative X-ray microanalysis can be performed either on scanning electron microscopes (SEMs) or electron microprobes (EPMAs), either with wavelength dispersive spectrometry (WDS) or energy dispersive spectrometry (EDS). Then, depending on the experimental constraints, quantitative analysis can be performed either with high (a few 10 keV) or low (a few keV) energy electrons, either with standard materials or without standard. Thus, it is difficult to find some laboratories working in the same conditions. Consequently, the practitioners of quantitative X-ray microanalysis cannot know the reliability of their measurements and quantifications owing to the lack of comparison. Thus, they should rely on samples whose composition is certified by a metrology institute or other quantification methods.

This is why, mainly under the auspices of Groupement National de Microscopie Electronique À Balayage et de Microanalyses,[1] we conducted this inter-laboratory study of a metallic glass, in order for the users to know if they introduce any systematic error in their results or if they use the best-suited experimental conditions and data treatments. The results of the participating laboratories were kept anonymous. This study also points to some inherent difficulty regarding the inaccuracy of some fundamental parameters.[2] Let us note that a recent inter-laboratory study of steel using WDS and EDS at low voltage has given evidence of inaccuracy of mass absorption coefficients for the L lines of the *3d* elements.[3] Let us mention other inter-laboratory comparison studies based on WDS[4] or EDS[5] involving less than ten participants. We would like to emphasize that the authors of the paper are not members of a certification organism and that the aim of this inter-laboratory study is not to evaluate or give a score to the participating laboratories. We only intent to give to the participating laboratories the means to compare their measured values obtained on a well-characterized sample with those of other laboratories working *a priori* in the same or very similar experimental conditions. So, we do not follow the protocol of International Organization of Standardization[6] or International Union of Pure and Applied Chemistry[7] regarding the proficiency testings.

Sample

The pristine sample is a thin tape of a metallic glass with Ni as the major component, whose size is 15 × 2 cm. Its thickness is 0.3 mm, i.e. much larger than the penetration length of the most

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energetic electrons used in this study. It was prepared by melt spinning to avoid its crystallization and thus was amorphous. The amorphous state of the sample was confirmed by electron backscattered diffraction. The mass fraction of the different elements, as determined by inductively coupled plasma mass spectrometry, was B, 3.6%; Cr, 10.4%; Fe, 5.6%; Co, 23.4%; Ni, 50.3%; Mo, 6.7%. Al and Si were found as impurities in the 0.1–0.2% mass fraction range. These values are given with a 4% measurement uncertainty. Owing to the homogeneous nature of the sample, the inductively coupled plasma mass spectrometry determinations requiring the dissolution of the sample, are valid as references for the X-ray analyses. SEM images have shown that the sample is homogeneous at the micrometer scale. A WDS mapping of the Kα emission of B, Cr, Fe, Co and Ni as well as of the Lα emission of Mo has demonstrated the uniform distribution of these elements. Pieces of 5×5 mm were supplied to laboratories interested in participating to this inter-comparison study. Being conductor, no dedicated preparation was required except the cleaning of the surface.

Laboratories and operating conditions

The number of participating laboratories is 56, involving a total of 69 electron columns and 75 spectrometers. The details are the following:

1. 69 electron columns:
   - 56 SEMs divided into 28 FEG, 27 W and one LaB_6;
   - 13 EPMAs;
2. 75 spectrometers:
   - 57 EDS divided into 37 SDD and 20 Si(Li);
   - 18 WDS installed on 13 EPMAs and five SEMs.

The meaning of the different terms: is FEG, field emission gun; W, tungsten filament gun; LaB_6, lanthanum boride filament gun; SDD, silicon drift detector; Si(Li), lithium drifted silicon diode. We note, with respect to previous inter-laboratory studies initiated by Groupement National de Microscopie Electronique À Balayage et de Microanalyses in 2005 and 2009, that no Ge detector was used in this study, whereas the proportion of SDD is increasing at the detriment of Si(Li) detectors. The number of EPMAs is stable, while the number of WDS apparatus on SEM increases.

The only instruction given to participants was to make an analysis at high voltage, 15 or 20 kV, and another one at 5 kV. The other experimental conditions were left free, but it was asked to specify them. If the user did not know one particular condition, it is noted as undefined. For every different condition, each measurement was repeated at least ten times in a row, changing the location on the sample each time and without new calibration between successive measurements. The laboratories returned the mean value and the standard deviation.

Results

In the following, we use the arithmetic mean and the square root of the variance to present the results. They will be given with one standard deviation, i.e. with a 68% probability to find the consensus value derived from participants in the confidence interval. All the results were accepted provided that the participants gave the details of their experimental treatment and quantifying details as listed in the succeeding text.

EDS analysis at 15 or 20 kV

In this case, the quantification is based on the analysis of the K lines of the *3d* elements and boron and L lines of molybdenum. The expected difficulties regarding this analysis are some interferences: Fe Kβ with Co Kα and Co Kβ with Ni Kα. Let us also mention that the Mo Lα line could be misinterpreted as the S Kα line. The detection and analysis of B Kα emission (185 eV[8]) could also be problematic owing to the very high overvoltage (the ratio of the electron energy to the ionization threshold energy), in the 75–100 range, and to an interference with the intense Mo Mζ line (193 eV[8]). Another problem could originate from the determination of the continuous background, which is generally worse toward the lowest photon energies (<1 keV) owing to the poor transmission of these X-rays through the detector window. With the 57 spectrometers, 64 analyses were performed with the following details:

1. analysis mode: 36 scanning mode, 19 spot mode, one defocused electron beam analysis and eight undefined; this will not be discussed in the following owing to the sample homogeneity;
2. detector: 22 Si(Li) and 42 SDD;
3. entrance window: 59 polymer, three Be and two undefined (but most probably polymer);
4. background determination: 31 model, 20 numerical filter and 13 undefined;
5. standard: 25 from library, 23 without, 14 real and two undefined;
6. quantification method: 22 ZAF method,[9–11] 50 $\varphi(\rho z)$ approach[9,11–14] and 12 undefined.

In these conditions, Cr, Fe, Co, Ni and Mo have been detected and quantified by all the laboratories, whereas only 38 treated Si, 28 Al and 22 B. We present in Table 1 the weight concentrations calculated as the mean of all the measurements.

It appears that the mean of the measured value is quite close to the reference value, even for the boron concentration whose determination was anticipated as challenging. However, the dispersion of the results is quite large, boron showing the widest range of concentration. Within the statistical uncertainty, it has not been possible to observe an influence of the nature of the detector, SDD or Si(Li), the choice of the standard, the method to subtract the continuous background or the quantification method.

Table 1. Mass fraction of the different elements present within the metallic glass sample analyzed at 15 or 20 kV with the energy dispersive spectrometry apparatus. Reference values are compared to the mean of the measured values. The range of the experimental determinations is also given

Element	B	Cr	Fe	Co	Ni	Mo
Reference (wt%)	3.6	10.4	5.6	23.4	50.3	6.7
Experimental mean (wt%)	4.4 ± 3.0	10.5 ± 0.6	5.4 ± 0.4	23.5 ± 0.8	51.4 ± 2.1	7.1 ± 1.4
Experimental range (wt%)	1.2–10.6	9.1–12.5	2.9–5.9	21.3–25.3	45.4–56.9	4.2–14.1

EDS analysis at 5 kV

In this case, the quantification is based on the analysis of the L lines except for boron analyzed with the K line. The expected difficulties arise owing to the strong interferences between the Cr, Fe, Co and Ni lines, the low intensity of the Mo L lines coming from the small overvoltage, 2, and again the B Kα–Mo Mζ interference. The detection and analysis of the B Kα emission should be less problematic because its overvoltage drops to 25. As an example, we show an EDS spectrum in Fig. 1.

In this case, only 43 analyses have been performed. All have detected Ni and Mo but only 42 Co, 41 Cr, 37 Fe and 21 B. This is most probably due to some deconvolution misinterpretation but could also come from poor quality spectra and then a faulty automatic identification procedure. The determined concentrations are given in Table 2. Once again, there is a fair agreement between the mean of the measured values and the reference ones. However, with respect to the analysis at 15–20 kV, the accuracy of the results is lower and their dispersion larger. There is an exception for the case of boron owing to the improved ionization of B K level with a 25 overvoltage. For Ni and Mo concentrations, two aberrant measurements have been taken out of the dataset. One is particularly surprising as it gives calcium as the major element, whereas no Ca peak was observed on the EDS spectrum. Most probably, this was caused by a lack of control of the background subtraction by the laboratory and to a poor spectrum quality because of low count, although it should be easy to treat such a case as the background is very flat in this energy range and with this sample. This points out the interest of really studying any spectra and not only push on the ‘quant’ button and let the software operate automatically.

The different considered parameters do not have a significant influence on the results, except for the method used to remove the background. When the numerical filter is used, the accuracy of the measurements is better, and their dispersion is lower, see Table 2. It should also be noted that among the six laboratories, which were not able to quantify iron, five were modeling the background (the sixth did not mention which subtraction method was used). However, this looks more like a faulty deconvolution procedure owing to the low Fe concentration and to the presence of nearby Co and Ni lines (Fig. 1).

WDS analysis at 15 or 20 kV

On EPMAs, the analysis of the different emission lines was carried out by using a Ni/C (12 times) or a Mo/B4C (once) multilayer for B Kα, PET (pentaerythritol, seven times) or LiF (lithium fluoride, five times) crystal for Cr Kα, an LiF crystal for Fe, Co and Ni Kα and a PET crystal for the Mo Lα. One user gave undefined conditions. The participants detected all the elements.

The operating conditions for the WDS spectrometers on SEM are presented in Table 3. It can be seen that only two laboratories were able to detect boron. Sometimes, Kα or Lα lines were used by the different laboratories to measure the same element. We could have expected the use of a coupling of WDS and EDS measurements where EDS analyzed the major elements and WDS the minor ones, but this was not carried out by the participants in this interlaboratory study. A specific study involving coupling of EDS and WDS should be proposed to test the capabilities of such an approach.

Table 4 shows the mass fraction deduced from the measurements on the EPMAs and WDS spectrometers on SEMs, in comparison to the reference concentrations. The procedures used for matrix corrections were the ZAF method[9–11] or the φ(ρz)

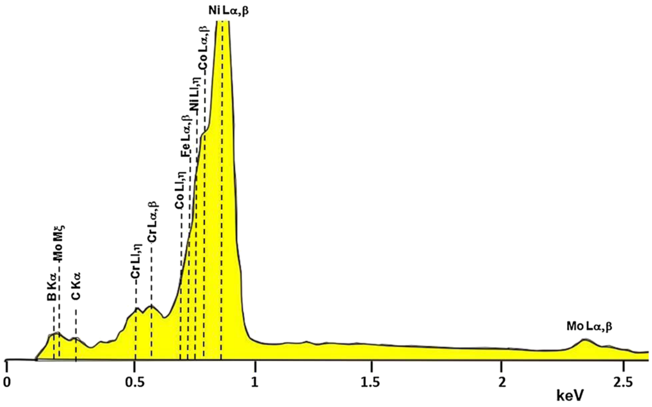

Figure 1. Energy dispersive spectrometry spectrum of the metallic glass sample obtained at 5 kV.

Table 3. Operating conditions for wavelength dispersive spectrometry/scanning electron microscopes apparatus for the analysis at 15 or 20 kV: choice of the crystal or multilayer noted ‘Multi’, and of the analyzed line. TlAP is the thallium acid phthalate crystal

	B	Cr	Fe	Co	Ni	Mo
Labo1	—	TlAP Lα	TlAP Lα	TlAP Lα	TlAP Lα	TlAP Lα
Labo2	—	TlAP Lα	TlAP Lα	TlAP Lα	TlAP Lα	EDS
	—	EDS	TlAP Lα	TlAP Lα	TlAP Lα	EDS
	—	EDS	EDS	TlAP Lα	TlAP Lα	EDS
Labo3	—	LiF Kα	LiF Kα	LiF Kα	LiF Kα	PET Lα
Labo4	Multi Kα	LiF Kα	LiF Kα	LiF Kα	TlAP Lα	PET Lα
Labo4	Multi Kα	LiF Kα	LiF Kα	LiF Kα	LiF Kα	PET Lα

EDS, energy dispersive spectrometry; LiF, lithium fluoride; PET, pentaerythritol.

Table 2. Mass fraction of the different elements present within the metallic glass sample analyzed at 5 kV with the energy dispersive spectrometry apparatus. Reference values are compared to the mean of the measured values. The range of the experimental determinations is also given. The lines ‘Model’ and ‘Filter’ give the concentrations determined by using a model or a filter to remove the background

Element	B	Cr	Fe	Co	Ni	Mo
Reference (wt%)	3.6	10.4	5.6	23.4	50.3	6.7
Experimental mean (wt%)	3.1 ± 2.0	10.5 ± 3.8	3.9 ± 2.8	22.8 ± 5.3	54.0 ± 4.7	6.0 ± 1.9
Experimental range (wt%)	0.5–7.7	0–20.8	0–9.4	0–31.7	45.3–64.3	3.3–14.6
Model (wt%)	3.4 ± 2.4	11.4 ± 3.6	3.5 ± 3.2	21.7 ± 3.9	55.1 ± 4,9	6.2 ± 2.5
Filter (wt%)	3.5 ± 1.7	10.6 ± 2.4	4.9 ± 1.9	25.2 ± 2.3	52.9 ± 3.4	5.9 ± 1.5

Table 4. Mass fraction of the different elements present with the metallic glass sample analyzed at 15 or 20 kV with the electron microprobe and WDS spectrometer on SEM. Reference values are compared to the mean of the measured values. The range of the experimental determinations is also given

	Element	B	Cr	Fe	Co	Ni	Mo
	Reference (wt%)	3.6	10.4	5.6	23.4	50.3	6.7
Electron probe	Experimental mean (wt%)	3.8 ± 0.7	10.4 ± 0.2	5.4 ± 0.1	23.3 ± 0.3	50.6 ± 0.8	6.7 ± 0.3
	Experimental range (wt%)	2.5–5.1	10.1–10.6	5.2–5.7	22.5–23.6	49.5–52.2	6.0–7.1
WDS/SEM	Experimental mean (wt%)	3.4 ± 0.9	10.1 ± 1.7	5.2 ± 0.7	23.3 ± 0.3	54.7 ± 4.3	6.3 ± 1.0
	Experimental range (wt%)	2.8–4.0	7.3–12.0	4.0–5.9	19.7–25.6	50.6–61.7	4.7–7.0

SEM, scanning electron microscopes; WDS, wavelength dispersive spectometry.

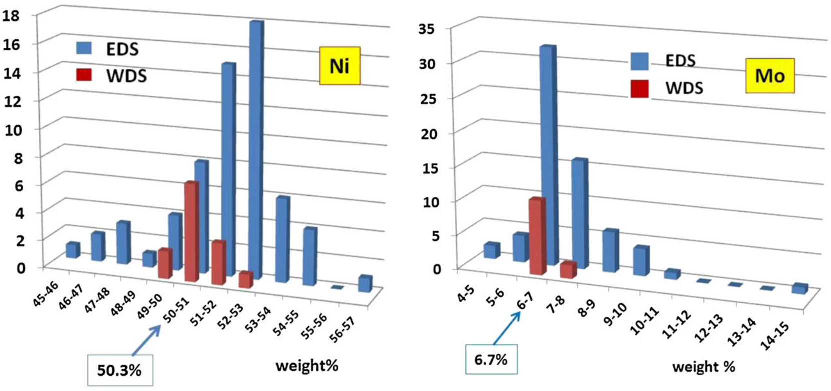

Figure 2. For Ni and Mo, dispersion of the mass fractions deduced from EDS and wavelength dispersive spectometry WDS measurements. The values in rectangular boxes correspond to the reference mass fractions.

approach.[9,11–14] Both kinds of measurements give concentrations close to the reference ones. However, EPMA is more precise and also leads to less dispersed results. This result could be related to several EPMA technical designs and specificities, especially beam current stability and accuracy of the sample Z-positioning with respect to the geometry of WDS spectrometers. As a consequence, the composition of the sample is determined to a few tenths of percent. With respect to the EDS determination, more precise results are obtained by WDS regarding the determination of the boron concentration, the concentration of the other elements being correctly evaluated by both WDS and EDS techniques. However, with respect to the dispersion of the results, EDS gives the worse results, as is illustrated in Fig. 2 where the EDS and EPMA quantifications of Ni and Mo are compared. These results clearly illustrate the interest of WDS compared to EDS for the accuracy of quantitative X-ray measurements in electron microscopy and for the quantification of light elements.

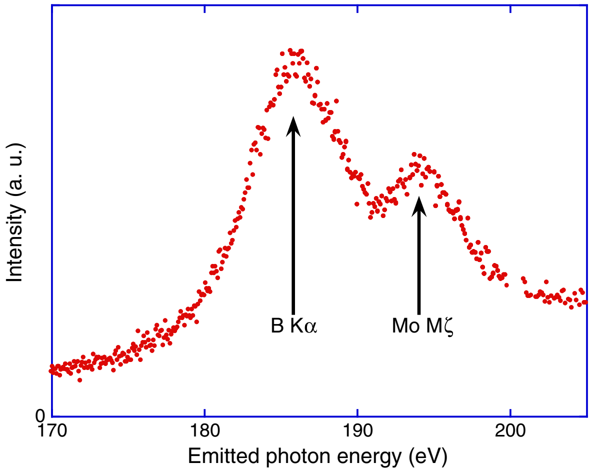

Figure 3. Wavelength dispersive spectrometry spectrum of the metallic glass sample in the range of the B Kα emission. It is obtained with an electron microprobe working at 5 kV and working with a Ni/C multilayer.

WDS analysis at 5 kV

With this operating condition, only 7 EPMA analyses and 3 WDS/SEM analyses were carried out. Among the three last ones, only one quantified boron. As in EDS, the Lα line of the transition metals was used for quantification, the acceleration voltage being too low to allow exciting K shells of *3d* and *4d* elements. As can be seen in Fig. 3, owing to the improved spectral resolution in WDS analysis, the intensity maximum of the B Kα and Mo Mζ emissions are well separated. This makes it easier for the boron quantification. The mass fractions of the different elements are given in Table 5. Owing to the small number of analyses, the dispersion of the results is not given. As was observed in the EDS case, the standard deviation on the mass fraction increases when the acceleration voltage decreases, except for boron.

It appears at 5 kV with WDS on SEM and with a microprobe that the boron and molybdenum concentrations are well evaluated, the one of iron is under-evaluated but within the uncertainty, whereas the cobalt and nickel ones are overestimated. The determination for chromium is correct with the EPMA and underestimated with the WDS/SEM. The origin of the

Table 5. Mass fraction of the different elements present within the metallic glass sample analyzed at 5 kV with the electron microprobe and WDS spectrometer on SEM. Reference values are compared to the mean of the measured values. Boron value obtained by WDS on SEM is given without standard deviation because only one determination was performed

	Element	B	Cr	Fe	Co	Ni	Mo
	Reference (wt%)	3.6	10.4	5.6	23.4	50.3	6.7
Electron micro-probe	Experimental mean (wt%)	3.7 ± 0.5	10.0 ± 1.3	4.8 ± 1.3	26.0 ± 2.6	56.8 ± 6.1	7.1 ± 0.9
WDS/SEM	Experimental mean (wt%)	2.5	7.7 ± 1.8	5.3 ± 2.2	26.3 ± 3.3	60.7 ± 3.4	6.8 ± 0.3

SEM, scanning electron microscopes; WDS, wavelength dispersive spectometry.

overestimation of the Co and Ni concentration can be due to some problem in the correction factors, particularly owing to a large uncertainty in the mass absorption coefficients when using the L lines, as recently emphasized in Llovet *et al.*[3] Indeed, from the measured intensity on the sample, a k-ratio is determined by dividing it by the intensity of the standard. Then, the mass fraction is deduced from the k-ratio thanks to a mathematical model taking into account matrix, absorption and fluorescence effects, which are not the same in the studied sample and in the reference. The problem of uncertainty in mass absorption coefficients does not exist for the 20 kV analysis with K lines.

Discussion and conclusion

From this inter-laboratory study, it appears that the dispersion of the mass fractions is rather large. This shows the utility of such a study as we demonstrate that the implementation of quantitative analysis must be optimized for some cases. For example, in the WDS/SEM analysis, there was no combined analysis where EDS could be used to determine the concentration of the major elements. However, the value resulting from the mean of all the determinations is always in good agreement with the reference value.

We found that the EPMAs give better results than EDS spectrometer, both from the point of views of accuracy (Table 6) and dispersion of measurements. Owing to small number of WDS systems on SEMs, it is difficult to obtain a conclusive comparison with EPMAs and EDS systems. None of the envisaged experimental and quantification factors can be regarded as the responsible of the better performances of EPMAs over EDS. To illustrate this point, we present in the Table 6 a comparison of the means of the uncertainties of the EDS and WDS quantifications made at 20 kV. Each laboratory calculates its standard deviation from the ten measurements made for each determination; then, the mean is calculated by taking into account all the laboratory values. Then, we calculate the ratio of this mean to the reference mass fraction to obtain what we call the relative standard deviation. Proceeding this way, it can be seen that WDS technique is twice more precise than the EDS one. Thus, one can think that electron probes are inherently better for the determination of mass fractions. These types of analysis show also that EDS analysis is not as straightforward as sometime expected and that users need good training to fully exploit their equipment and results. As seen, the best results are coming from WDS. This can be explained by several reasons including the following:

1. A WDS spectrum is generally easier to treat. Indeed, its shape generates a better resolution, a better signal/noise ratio and a more flat background, so all these facilitate identification and quantification.
2. As WDS is a technique that requires standards analysis, it could be possible that WDS users are more aware of the quantification process than some EDS users and then can give more accurate or less disperse results.

However, we can expect that following some recommendations of Newbury and Ritchie,[15] such as examine every analysis, understand the particular procedures of the standardless analysis and try to know how the commercial programs provide their results, then the quality of the EDS results could approach the one obtained through WDS.

Although most of the WDS analysis gave results close to the reference values of the chemical composition, there was a problem with the analysis at 5 kV, which leads to an overestimation of the Co and Ni mass fractions. This raises the question of the accuracy of the fundamental parameters, particularly of the mass absorption coefficient of *3d* elements when the L lines are used[3] but also how the quantification programs are working. For example regarding this last point, in the EDS analysis at 15 or 20 kV, it appears that some quantification programs return too high values of the k-ratios but that the deduced mass fractions are correct. This suggests that these programs do not use the ‘conventional’ definition of the k-ratio. Then, comparison between k-ratio determinations performed

Table 6. For the EDS and WDS determinations of the mass fractions, mean values of the uncertainties and calculation of the ratio of this mean to the reference value. The ratios are the relative standard deviations

Element	Reference mass fraction (wt%)	Mean value of the EDS standard deviation	EDS ratio (%)	Mean value of the WDS standard deviation	WDS ratio (%)
Cr	10.4	0.11	1.06	0.05	0.48
Fe	5.6	0.08	1.43	0.04	0.71
Co	23.4	0.18	0.77	0.11	0.47
Ni	50.3	0.2	0.40	0.23	0.46
Mo	6.7	0.13	1.94	0.07	1.04

EDS, energy dispersive spectrometry; WDS, wavelength dispersive spectometry.

on different systems can be more or less illusory. Thus, we point out the necessity to obtain information from EDS and WDS suppliers regarding the data treatment procedures in their quantification programs.

The full analysis of the results of this inter-laboratory test can be found (in French) at the following address: http://www.gn-meba.org/ech_tests.htm.

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