Statistical evaluation of the analytical method involved in French nuclear glasses leaching rate determination

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Abstract *– Chemical durability studies of nuclear glasses involves a large number of water leaching experiments at different temperatures and pressures on both, glasses doped with fission products and actinides and non radioactive surrogates. The leaching rates of these glasses are evaluated through ICP-AES analysis of the leachate over time. This work presents a statistical evaluation of the analysis method used to determine the concentrations of various vitreous matrix constituents: Si, B, Na, Al, Ca, Li as major elements and Ba, Cr ,Fe, Mn, Mo, Ni, P, Sr, Zn, Zr as minor elements.*
Calibration characteristics, limits of detection, limits of quantification and uncertainties quantification are illustrated with different examples of analysis performed on surrogates and on radioactive leachates in glove box.

INTRODUCTION

The research approach developed at Marcoule since the early 1980s to predict the alteration behavior of high level waste glass packages (mostly R7T7-type glasses) is based on two complementary levels : understanding and ranking of the basic mechanisms driving glass alteration in a given environment of the glass, and constructing and validating predictive models usable for safety assessment of storage or disposable concepts [1].

Both the study of basic mechanisms and validation of models have made use of a considerable amount of water leaching experiments at different temperatures, pH and pressures on both, glasses doped with fission products and actinides and particularly on inactive surrogates, which have been proved to be representative of high level radioactive glass specimens [2].

The leaching rates of these glasses are evaluated through ICP-AES analysis of the leachate over time.

An analytical method was developed on inactive solutions and adapted to radioactive leachates in a glove box in order to determine in a low sample volume (1 to 2 mL) the concentrations of the vitreous matrix constituents : Si, B, Na, Al, Ca, Li as major elements and Ba, Cr ,Fe, Mn, Mo,, Ni, P, Sr, Zn, Zr as minor elements.

This work presents a statistical evaluation of this method : calibration characteristics, limits of detection, limits of quantification and uncertainty evaluations.

BACKGROUND INFORMATION

Leaching Protocol
Leaching experiments are usually conducted in initially pure water. According to the mechanism studied, either static or dynamic tests are realized.

Dynamic test :
This type of test is designed to evaluate the initial alteration rate of a material which is placed in a very diluted aqueous solution. The surface of altered material over leaching solution volume ratio (SA/V) must be low enough to avoid saturation of the solution.

The glass sample is placed in a 316L stainless steel reactor, in continuously deionized flowing water (renewal rate for example $5h^{-1}$) heated at 90°C, 100°C or 150°C for period of maximum 28 days. Solution samples are taken at the following intervals : 1, 3, 7, 14, 21 and 28 days.

Static test :
This test is used to determine the dissolution kinetics in saturation conditions. The SA/V ratio is high (for example $200 \ cm^{-1}$) and is usually obtained with powdered glass samples.

The samples are introduced in a Savillex PTFE container with ultrapure water, which is then placed in an oven regulated at 90°C.

The duration of the test may vary from 28 days to several months or years. Samples are taken at

different intervals : 1, 7, 14, 28, 56, days for example and ultra-filtered to 10,000 dal. (cutoff threshold : circa 2 nm)..

In each kind of test, the overall volume of solution samples should not exceed 10% of the initial volume of leaching solution, the samples volume usually ranges from 1 to 2mL in static tests and are higher in dynamic tests (5mL).
All samples are acidified with HNO_3 (High purity for trace analysis) to 0.1-0.5 mol.L^{-1}.

EXPERIMENTAL

Reagents

Concentrated HNO_3 (14 mol.L^{-1}) for trace analysis were used (PROLABO - Ultrapur). Calibration standards were prepared in Polypropylene volumetric flasks from certified stock solutions (1000 mg.L^{-1}) purchased from SPEX. 18 megohm deionized water produced by a Milli Q Plus from MILLIPORE was used.
A synthetic certified reference solution (called R7T7 reference solution) containing all the elements was purchased from TECHLAB and used as stock solution to prepare samples for repeatability measurements.

ICP system

All measurements were performed with a Jobin Yvon model JY 66 P spectrometer : a multi-photomultiplier detectors based ICP-AES equipped with a 40.68MHz generator.
The operating parameters are : plasma power 1000 W, plasma gas flow 12 L.min^{-1}, auxiliary gas flow 0.1 L.min^{-1}, nebulizer flow 0.4 L.min^{-1}.

R7T7-glass Leachate Analysis Method

The different elements analyzed, the corresponding wavelengths are listed in Table 1. The matrix is 0.1 mol.L^{-1} nitric acid.
All concentration measurements are made by using multi elements five points calibrations : blank, two low and two high values. The calibration ranges in table 1 start with the lowest standard value. Low calibration ranges (0.01-0.5 mg.L^{-1}) are used to analyze low concentration samples. Each measurement is the mean value of four acquisitions of absolute intensities with 10s integration time.

Statistical Evaluation

For this purpose, we met the requirements of the French standard XP T 90-210 [3], this procedure

is a way to validate an analytical method, which is a step required by the ISO/IEC 17025 [4, 5].

RESULTS AND DISCUSSION

Linearity

Validation of the linearity model for calibration is achieved via the following design : for each of the sixteen elements, five point calibration sets are obtained by measuring at each concentration level, absolute intensities at the specified wavelength on five different solutions.
For each element, the calibration curve is given by the general equation :

$$y = b_0. + b_1 x \qquad (1)$$

y : the absolute intensity,
x : the concentration of the analyte
b_0, the intercept, b_1 the slope and the standard deviation $s(b_0)$ and $s(b_1)$ are determined by un-weighted least square regression on a set of 25 pairs of values (x_i, y_i).
All models are linear according to the ANOVA and F test in [3].

Limits of Detection and Quantification

As all calibration sets showed that the zero value does not belong to the confidence interval of the intercept, the limit of detection (LOD) are determined by repeated analysis of the blank [3] : ten replicates (HNO_3 0.1 mol.L^{-1}) are used and absolute intensities (y_B) are measured. The prediction value for the LOD signal y_{LOD}, with a prediction value (1-α=1%), is given by :

$$y_{LOD} = \overline{y_B}. + 3s_B \qquad (2)$$

where s_B is the standard deviation of the blank signals. An evaluation of the LOQ signal is given by :

$$y_{LOQ} = \overline{y_B}. + 10s_B \qquad (3)$$

Because the uncertainties in the low part of a calibration range tend to increase, in the R7T7-glass leachate analysis method the concentrations corresponding to these two values are estimated by using a new calibration function near the limit of detection (between 0 and 500 µg.l^{-1}) which leads to new values for b_0, b_1 and $s(b_0)$:

$$LOD = y_{LOD} - \frac{b_{0(LD)}}{b_{1(LD)}} \qquad (4)$$

$$LOQ = y_{LOQ} - \frac{b_{0(LD)}}{b_{1(LD)}} \qquad (5)$$

For each element, the limit of quantification is verified by the repeated analysis of ten replicates of a solution at a concentration level corresponding to the LOQ. The accuracy of the LOQ is verified by the following test :

$$\left|\frac{LOQ - \overline{u_{LOQ}}}{\frac{s_{LOQ}}{\sqrt{n}}}\right| < 10 \qquad (6)$$

besides LOQ will be different from the zero value if the condition below is satisfied :

$$\frac{s_{LOQ}}{LOQ} < 20\% \qquad (7)$$

The different values obtained for the 16 elements are listed in table 1. LOD is obtained by dividing the verified LOQ by three.

Repeatability

In this study, the estimation of repeatability standard deviation s_r is obtained by repeated analysis of ten samples prepared by dilution of the R7T7 reference solution which are representative of real samples. Each sample is analyzed four times. The concentration levels for each element in the solution is equal to the maximum value of the high calibration range.

Uncertainty Estimation

The concentration measurement uncertainties have been evaluated on the basis of the preceding validation study and recommendations of both the Eurachem guide and the French experimental standard XP T 90-220 [6, 7]:

In the case where no dilution is applied to a sample before analysis, the concentration is given by the calibration model :

$$C (in\, mg.L^{-1}) = C_{calibration} \pm U(C)(in\, mg.L^{-1}) \quad (8)$$

$u_T(C)$ is the combined standard uncertainty on C (in mg.L^{-1}) :

$$u_T(C) = \sqrt{u_{sample}(C)^2 + u_{cal}(C)^2 + u_{std}(C)^2} \quad (9)$$

The expanded uncertainty U(C) is obtained by applying a coverage factor of 2 corresponding to a 95% confidence interval :

$$U(C) = 2 \times u_T(C) \qquad (10)$$

TABLE I: Calibration data of the determination of R7T7 elements in solution by ICP-AES - Matrix : HNO$_3$ 0.1 mol.L^{-1}

Element	λ (nm)	Calibration range (mg.L^{-1})	LOD (mg.L^{-1})	LOQ (mg.L^{-1})
Al	396,152	0.2 - 10		
Al	396,152	0.01 - 0.5	0.033	0.100
B	208,959	1 - 20		
B	208,959	0.01 - 0.5	0.007	0.020
Ba	233,520	0.2 - 2		
Ba	233,520	0.01 - 0.5	0.002	0.005
Ca	317,933	0.2 - 10		
Ca	317,933	0.01 - 0.50	0.033	0.100
Cr	267,716	0.2 - 2		
Cr	267,716	0.01 - 0.5	0.003	0.010
Fe	238,207	0.2 - 2		
Fe	238,207	0.01 - 0.5	0.017	0.050
Li	670,776	0.2 - 5		
Li	670,776	0.01 - 0.5	0.033	0.100
Mn	279,482	0.2 - 2		
Mn	279,482	0.01 - 0.5	0.002	0.005
Mo	202,032	0.2 - 2		
Mo	202,032	0.01 -0.5	0.003	0.010
Na	589,592	1 - 10	0.15	0.4
Ni	231,604	0.2 - 2		
Ni	231,604	0.01 - 0.5	0.007	0.020
P	178,297	0.2 - 2		
P	178,297	0.01 - 0.5	0.017	0.050
Si	251,611	1 - 30		
Si	251,611	0.01 - 0.5	0.017	0.050
Sr	407,771	0.2 - 2		
Sr	407,771	0.01 - 0.5	0.002	0.005
Zn	213,856	0.2 - 2		
Zn	213,856	0.01 - 0.5	0.017	0.050
Zr	343,823	0.2 - 2		
Zr	343,823	0.01 - 0.5	0.007	0.020

Determination of $u_{sample}(C)$:
We have used the repeatability standard deviations s_r obtained in the validation study. These values correspond to the maximum levels of the calibration ranges. This approach is valid because real samples are very similar to the R7T7 reference solution and the repeatability was found constant over the calibration range in the linearity study. But this value should be verified for low concentrations near the LOQ.

Determination of $u_{cal}(C)$:
The uncertainty due to the experimental part of the calibration is obtained by using the standard deviation of the predicted values for concentrations at a given level, in the linearity statistical design.

Determination of $u_{std}(C)$:

This uncertainty due to bias on the material accuracy is affected to the standard concentrations in the linearity model. For each calibration standard C_{std}, prepared with a volume V_{stock} of standard stock solution C_{stock} and diluted to the final volume V_{final} in a flask, the standard uncertainty is given by the following equation :

$$u_{std}\left(C_{std}\right) = C_{std} \times \sqrt{\left[\frac{u(C_{stock})}{C_{stock}}\right]^2 + \left[\frac{u(V_{final})}{V_{final}}\right]^2 + \left[\frac{u(V_{stock})}{V_{stock}}\right]^2} \quad (11)$$

For each value x the uncertainty is given by a tolerance interval "±a ": standard stock solution are certified with C_{stock} ±0.6%, pipettes used to deliver V_{tock} are calibrated with the maximum allowed deviation between ±0.5% and ±2%, and class B 100 mL±0.2 mL flasks are used for final dilution. Thus the standard uncertainties u(x) are calculated assuming rectangular distributions :

$$u(x) = \frac{a}{\sqrt{3}} \quad (12)$$

Results

The contributions of the different parameters are shown in figure 1 for different elements at their maximum concentration levels.
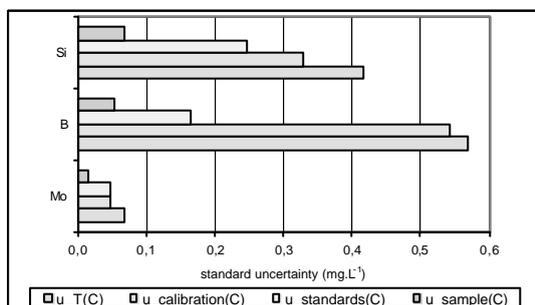

Fig. 1. Uncertainties in Si, B, Mo determination at 30, 20 and 2 mg.L^{-1} respectively

This graph clearly shows that contribution to uncertainty is due to the calibration and the standards.

The relative combined standard uncertainties calculated for the different elements present in a typical R7T7 leaching solution are reported on figure 2: they are all below 4% for minor elements (at $2\,\text{mg.L}^{-1}$) . Uncertainties on other major elements except Boron at 20 mg.L^{-1} are all below 2%.

The corresponding relative expanded uncertainties vary between 6% and 8% for minor elements (at 2 mg.L^{-1}) and Boron (at 20 mg.L^{-1}) and are near 4% for the other major elements : Al, Ca, Li Na and Si at concentrations varying
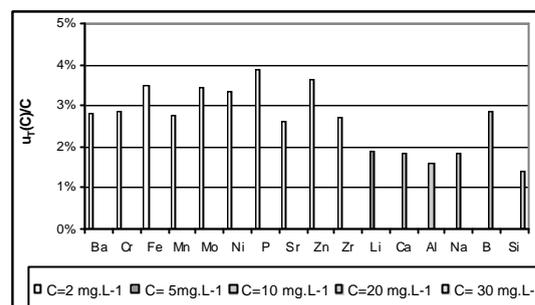
from 5 to 30 mg.L^{-1}.

Fig. 2. Relative combined standard uncertainties for a typical R7T7-leaching solution analysis.

CONCLUSION

Measurement uncertainties have longer been estimated on the basis of the analysts experience. With this study in compliance with EN ISO 17025 principles, we demonstrate, the fitness for purpose of the analytical method used as a basis to predict the alteration behavior of French high level waste glass. This work represents calculations on a great amount of measurements (about 1.5 thousand). It will be completed by repeatability tests on low concentration values and will be continued to estimate expanded uncertainty of the leaching rates encountered on radioactive materials.

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