POSTER 140

QUALITY OF CERAMIC RAW MATERIALS: THE UNCERTAINTY IN CHEMICAL ANALYSES

A.Albertazzi[*1] , G.Bonvicini[1] , A.Tenaglia[1]

[1]Centro Ceramico di Bologna, Bologna, Italy.

Keywords: uncertainty, chemical analysis, sodium oxide, zirconium oxide

Introduction

The estimate of uncertainty in the chemical analyses of ceramic raw materials plays a key role in view of their technical specification, especially for high-performance ceramic tiles (porcelain stoneware). In the present work the uncertainty in the determination of Na2O, Fe2O3, ZrO2 is evaluated.

Materials and Methods

The repeated measure are run :

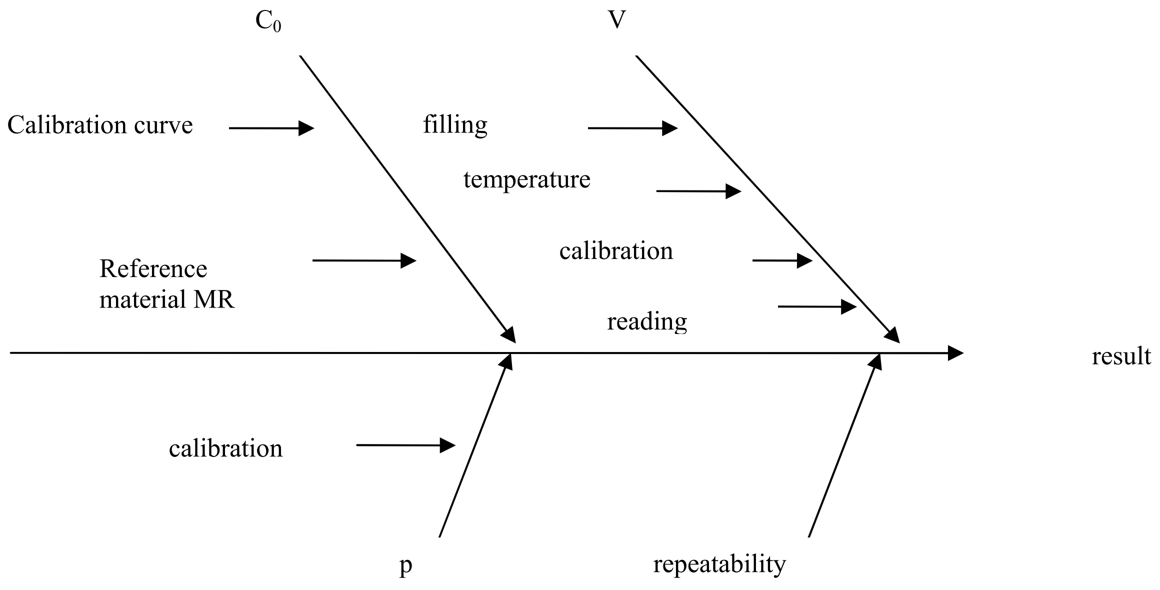
- for Na2O and Fe2O3 by testing a certified reference material -Soda Feldspar (SRM NIST 99a),
- for ZrO2 by testing a sample of a body mix currently used in ceramic tile manufacture.

The chemical analysis is run by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES). The ICP technique works on solution samples, so the materials need preparation before processing. The dissolution of samples is run by two methods: acid digestion by heating a known amount of powder added with HNO3 and HF and acid microwave digestion in H3PO4, HCl and HF. The calibration curves are plotted by 4 points (three standards and a blank solution) for acid digestion and 3 points for microwave dissolution. The analysis is performed at 259.944 nm for Fe, 330.224 nm for Na and 343.824 nm for Zr. The final results are expressed as oxide percentage of the different elements starting from the concentration detected in solution (C_0-mg/l), taking into account the weight (p-g) of the sample treated at the beginning and the volume (V-ml) of the solution using the following equation where f is the stoicheiometric factor to proceed from the element to the corresponding oxide.

$$\frac{C_0}{1000} \times \frac{V}{1000} \times \frac{f}{p} \times 100 = MO_x\%$$

So, taking care of the previous formula, the different contribution to the uncertainty taken in to account are repeatability, weight, volume, reference material and calibration curve as shown in fig.1

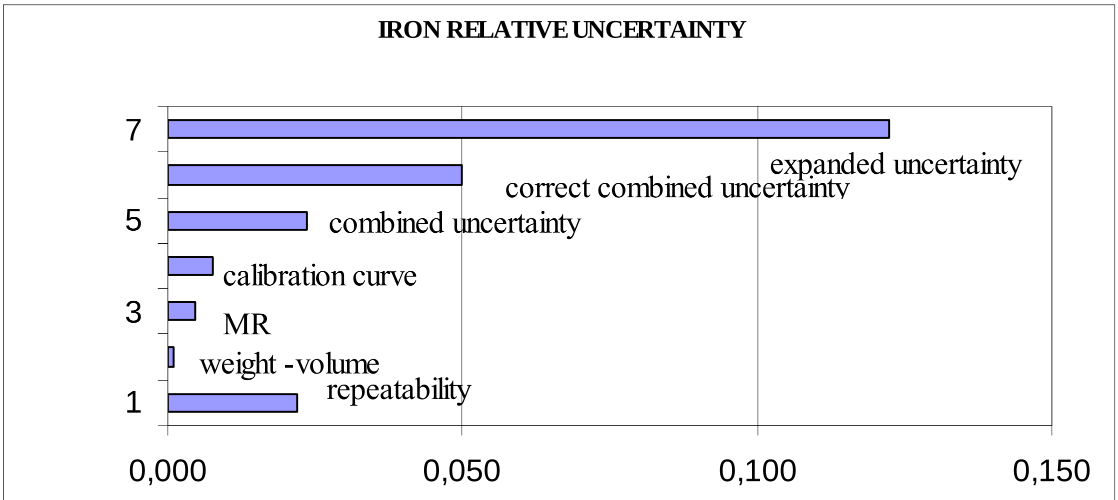
Fig 1 –cause and effect diagram



Results

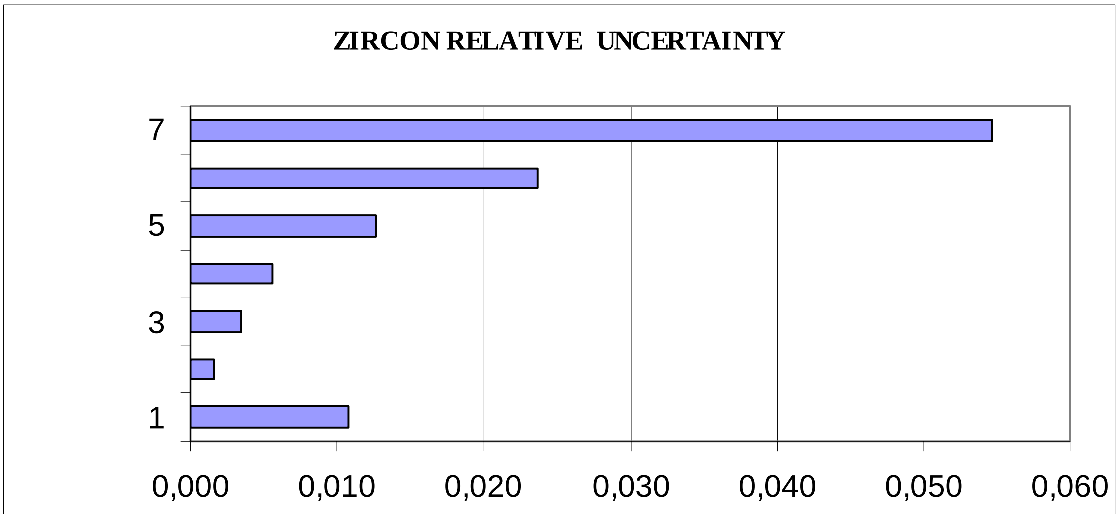
Taking care of all the uncertainty contributions above indicated the following results are obtained – Fe2O3= (0,065 ± 0,008)% ZrO2= (1,77 ± 0,10)% Na2O = (6,20 ± 0,32)% as shown in the following three figures.

Fig 2- uncertainty of iron Fe2O3= (0,065 ± 0,008)%



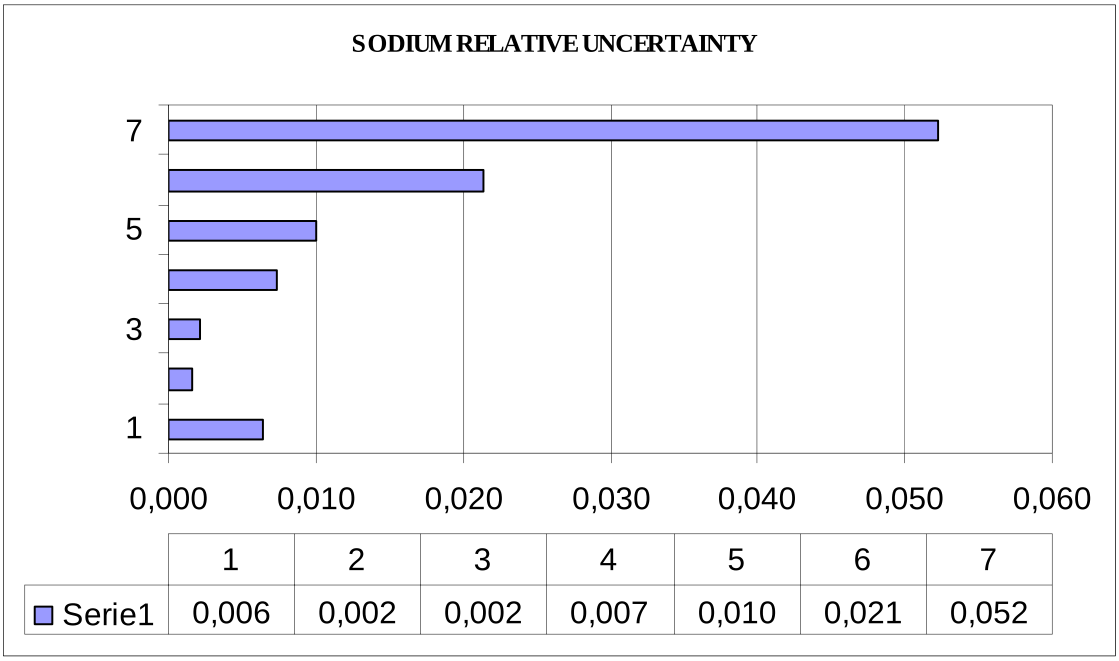
	1	2	3	4	5	6	7
Serie1	0,022	0,001	0,005	0,008	0,024	0,050	0,122

Fig 3- uncertainty of Zircon ZrO2= (1,77 ± 0,10)%



	1	2	3	4	5	6	7
Serie1	0,011	0,002	0,003	0,006	0,013	0,024	0,055

Fig 4 - uncertainty of sodium $Na_2O = (6{,}20 \pm 0{,}32)\%$



Discussion

It is well known that Fe_2O_3 (and more generally iron oxides) contaminates raw materials giving color problems after firing. The feldspars at present in use in ceramic tile manufacture have an iron content of 0.1÷0.2%. For "superwhite porcelain stoneware" the iron concentration has to be significantly lower (less than 0.05%). The uncertainty associated with the analytical method enables to obtain results that fit the practical/industrial purposes.

As far as porcelain tile body composition is concerned, white products are characterized by quite high amount of zircon sand which is used as whitener. Because of the use of zircon bearing products that contain traces of natural radioisotopes and have a specific activity generally two orders of magnitude higher than the average value in the earth's crust, the ceramics industry is included in the list of possible activities to be subject to regulation. In its Recommendation RP112 the European Union suggested a criterion to ensure the compliance with the maximum allowable doses for the exposed individuals. Also the People's Republic of China, in the documents "Limit of radionuclides in building materials" (GB 6566) and "Implementation rules for compulsory certification of decorative products and fitment products" (CNCA-12C-050:2004) adopted limits that should not be exceeded by ceramic tiles. The increasing of ZrO_2 amount from 3% to 5% is responsible for the significant increasing in radioactivity bringing the exceeding of the limit as indicated for the sample 2 in the following table 1.

Table 1 – Radioactivity levels and Zircon content

	Radioactivity level requirements for class A According to CNCA-12C-050:2004		ZrO_2
	Internal exposure index $I_{Ra} \leq 1.0$	External exposure index $I_{\gamma} \leq 1.3$	%
Sample 1	0.8	0.6	2.54
Sample 2	**1.4**	**1.1**	**5.18**
Sample 3	0.2	0.3	0.07
Sample 4	0.2	0.4	0.13
Sample 5	0.9	0.8	3.19

Also for ZrO_2 , obtained uncertainty is appropriate for the purpose of raw material characterization.

As regards Na2O the calculated widened uncertainty does not completely fit with the fixed goal.
The chemical analysis of two feldspar samples, one of them having production problems, finds the following Na2O values: 9.47±0.49% and 8.90±0.46%. These results look like two different values, but they have an overlapping of their uncertainty ranges. Consequently work is in progress to find new operating conditions with the purpose of obtaining better (lower) uncertainty values.

Conclusion

The data presented in this poster reflects the fragmentariness typical of service to the industries; this kind of work needs a lot of attention to the problems of production and the skill to understand and individuate the suitable type of analyses which can indicate the solution to the problem. The detailed description of the different phase of a chemical analyses has the aim to explain that there are a lot of different parameters that may be varied to achieve the suitable answer, in other words the results with the suitable uncertainty.

References

1. S.Righi,L.Bruzzi, "L'industria ceramica e la nuova normative Europea in materia di radioprotezione". CERAMICAACTA 12, n°5-6, 74-84. (2000)

2. EC "Radiological protection principles concernine the natural radioactivity of building materials " Radiatio Protecion 112, 1999

3. GB 6566, 2001 "Limit of radionuclides in building materials"

4. Ref.No.CNCA-12C-050:2004 "Inplementation rules for compulsory certification of decorative products and fitment products"

5. EURACHEM/CITAC Guide "Quantifying uncertainty in analytical measurement- second edition" 2000

6. ARPA Emilia Romagna " Linee guida per la validazione dei metodi analitici e per il calcolo dell'incertezza di misura" Bologna 2003