DETERMINATION OF HEAVY ELEMENTS AT TRACE LEVEL IN CERAMIC RAW MATERIALS

M.F. Gazulla, M. Rodrigo, M.J. Ventura, M. Orduña, C. Andreu

Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las Industrias Cerámicas (AICE). Universitat Jaume I. Castellón. Spain.

1. INTRODUCTION

In ceramic raw materials that are going to be in contact with food, the quantities of certain heavy metals such as Pb, Cd, Cr, Ni, Hg, and As need to be known with precision as they are harmful to health, and their concentrations must not exceed the allowed maximum limit values, which lie between 1 and 2 mg·kg^{-1}[1-2]. Major and minor elements are usually determined by wavelength-dispersive X-ray florescence (WD-XRF) spectroscopy, a technique that reaches the required quantification limits. However, in trace analysis, other analysis methods need to be considered to enable the limits set in applicable legislation to be reached.

The study seeks to develop a methodology for Pb, Cd, Cr, Ni, Hg, and As analysis, using WD-XRF[3-4] and inductively coupled plasma optical emission spectrometry (ICP-OES) techniques, in which the quantification limits required are reached in the shortest possible time, so that this method can be used as a control method.

2. EXPERIMENTAL DEVELOPMENT

The development of a new method consists of two clearly differentiated parts: sample preparation and analyte measurement. In developing the work, sample preparation for WD-XRF measurement was optimised by using different binders: N-butyl methacrylate, stearic acid, mannitol, and other commercial additives such as Spectroblend® and Licowax C®, studying the forming conditions of the corresponding pellets.

In sample preparation for ICP-OES measurement, a Milestone UltraWAVE™ microwave system was used. The following variables were studied: amount of sample, HNO_3/HCl ratio, need for HF addition, final dilution of the sample, digestion time and temperature. On the other hand, measurement conditions were optimised to reach the required quantification limits in both WD-XRF and ICP-OES measurement. The WD-XRF measurement was carried out using a PANalytical AXIOS wavelength-dispersive X-ray fluorescence spectrometer, while the ICP-OES measurement was performed with an Agilent 5100 spectrometer.

To assure result accuracy, 25 different reference materials from different commercial suppliers, such as NIST, BAS, GBW, CGL, and GeoPT, were used. In addition, a series of geological materials were also analysed: a kaolin, a clay, and a sepiolite.

3. RESULTS

Tables 1 and 2 detail the results obtained in the analysis of 8 reference materials and three unknown samples by the methods developed for WD-XRF and ICP-OES.

	As			Cd			Cr		
	Cert	**ICP-OES**	**WD-FRX**	**Cert**	**ICP-OES**	**WD-FRX**	**Cert**	**ICP-OES**	**WD-FRX**
GeoPT-24	-	-	-	2.8	3.1	4	34	33	33
GeoPT-36A	75.8	76.9	74	5.1	5.0	5	49.6	49	54
GBW 07401	34	36	33	4.3	4.6	4	62	66	64
GBW 07405	412	391	410	0.45	<1	<1	118	112	116
GBW 07103	2.1	2.4	3	0.029	<1	<1	3.6	3.3	5
CGL-008	2.28	1.8	3	0.13	<1	1	182	178	181
	Hg			**Ni**			**Pb**		
	Cert	**ICP-OES**	**WD-FRX**	**Cert**	**ICP-OES**	**WD-FRX**	**Cert**	**ICP-OES**	**WD-FRX**
GeoPT-24	-	-	-	17.7	18.2	19	26.9	25.7	28
GeoPT-36A	1.436	1.3	<3	48.75	47.7	49	808	715	810
GBW 07401	0.032	<1	<3	20.4	21.7	19	98	101	97
GBW 07405	0.29	<1	<3	40	37	39	552	518	547
GBW 07103	0.0041	<1	<3	2.3	1.93	<3	31	29	32
CGL-008	-	-	-	5.76	5.37	7	24.81	26	24
CGL-305	2.75	1.4	4	-	-	-	-	-	-
CGL-304	1.52	2.6	<3	-	-	-	-	-	-

Table 1 *Results (mg·kg-1) of the analysis of some reference materials by the two newly developed methods*

	Kaolin		Clay		Sepiolite	
	ICP-OES	**WD-FRX**	**ICP-OES**	**WD-FRX**	**ICP-OES**	**WD-FRX**
As	3	3	4	3	3	5
Cd	<1	<1	<1	<1	<1	<1
Cr	25	28	39	43	42	4
Hg	<1	<3	<1	<3	<1	<3
Ni	1	<3	2	3	10	12
Pb	99	104	63	75	39	40

Table 2 *Results (mg·kg-1) of the analysis of three geological materials by the two newly developed methods*

On the one hand, good agreement was observed between the certified values of the analysed reference materials and the results obtained by both ICP-OES and WD-XRF. On the other hand, analysis of the unknown materials showed there were no noticeable differences between the two methods, though it may be noted that the ICP-OES method exhibited lower quantification limits for Hg and Ni.

4. CONCLUSIONS

In the WD-XRF method, the following quantification limits were reached: As – 2 $mg\cdot kg^{-1}$, Cd – 1 $mg\cdot kg^{-1}$, Pb – 1 $mg\cdot kg^{-1}$, Hg – 3 $mg\cdot kg^{-1}$; and Ni – 3 $mg\cdot kg^{-1}$. The ICP-OES method with preliminary sample digestion by the UltraWAVE microwaves reached quantification limits of 1 $mg\cdot kg^{-1}$ for all elements. Both methods are respectful of the environment because they require no major use of solid and/or acid reagents or high temperatures.

One of the differences to be borne in mind is analysis time, this being 40 min for the WD-XRF method and about 2 hours for the ICP-OES method. Use of one method or the other will depend on the quantification limit required and the available time for carrying out the determination.

5. REFERENCES

[1] Londoño-Franco, L.F.; Londoño-Muñoz, P.T.; Muñoz-García, F.G. Los riesgos de los metales pesados en la salud humana y animal. *Biotecnol. Sect. Agropecu. Agroind.*, 14(2), 145, 2016.

[2] Worasith, N.; Goodman, B.A.; Jeyashoke, N.; Thiravetyan, P. Decolorization of rice bran oil using modified kaolin. *J. Am. Oil Chem. Soc;* 88, 2005, 2011.

[3] Gazulla, M.F.; Rodrigo, M.; Ventura, M.J.; Orduña, M.; Andreu, C. Development and validation of a WD-XRF method for quantitative trace analysis: Application in the food industry. *X-ray Spectrom.*, 50, 197-209, 2021.

[4] Gazulla, M.F. (2-6 Agosto 2021). Determination of Pb, Cd, Ni, Cr, Hg, and As at trace levels in geological materials used in the food industry. 70th annual Denver X-ray Conference.

6. ACKNOWLEDGEMENTS

This study was co-funded by the Autonomous Government of Valencia through the Valencian Institute for Business Competitiveness (IVACE) under project IMDDEA/2021/5, and by the European Regional Development Fund (ERDF) under the Operational ERDF programme for the Valencia Region 2014-2020.