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GEOCHEMICAL ANALYSIS

Novel Determination of Trace Metals in Geological Materials Employed in Food Products by Microwave Decomposition and Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

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ABSTRACT
A new methodology for the determination of trace metals in geological materials employed in the food industry by single-reaction chamber (SRC) microwave digestion followed by inductively coupled plasma – optical emission spectrometry (ICP-OES) analysis was developed. The presence of toxic elements for human beings, such as As, Cd, Cr, Hg, Ni, and Pb, must be controlled in those materials that are in contact with food. Most regulations require the presence of these elements in these materials in low concentrations, mostly less than 1 mg kg^{-1}, which requires analytical methodologies that can reach these quantification limits. In the optimization of the sample preparation by microwave digestion, different mixtures of acids were used, so that As, Cd, and Hg were decomposed in an inverse aqua regia solution, while extraction of solid sample with aqua regia and HF was needed to determine Cr, Ni, and Pb. The determination of the analytes present in these solutions was carried out by ICP-OES, optimizing the conditions to obtain the best signal-to-noise ratio for each analyte. The study was undertaken using certified reference materials, two samples of clay, and a sample of sepiolite. Quantification limits of 1 mg kg^{-1} were achieved, which meet the legal requirements. The analyzed samples of clays and sepiolite contained values of Cd and Hg that met the requirements although the results for As, Cr, Ni, and Pb were above the limits required for the food industry.

Introduction

Many geological materials are used in the food industry as additives or as processing aids. According to *Codex Alimentarius*, processing aids are substances that are not consumed as food itself, but they are intentionally used in the processing of foods or their ingredients to fulfill a certain technological purpose during food treatment or processing, and they may result in the unintentional but technically unavoidable presence in the final product as residues of the substance or its derivatives provided (Official Journal of the European Union 2008).

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By definition, a food additive is any substance added intentionally to food for its technological properties in controlled quantities, regardless of its nutritional value. A substance admitted as an additive must be well chemically characterized and must pass the toxicological controls established by the health organizations (Ibañez, Torre, and Irigoyen 2003).

Clays and kaolins are used to clarify wines or vegetable oils, as their inner structure interacts easily with the proteins present in wine and vegetable oils that normally cause turbidity. The properties that a geological material should present to be a processing aid are high specific surface, cation exchange capability, charge density, and swelling degree. Other geological materials, such as calcium carbonate or potassium nitrate, are used as additives to enhance properties or to preserve food. These materials are used in human food and in animal feed. (Hung et al. 2014; Yu et al. 2013)

The reason why additives need to be chemically characterized lies in the presence of some elements at trace levels, such as As, Cd, Cr, Hg, Ni, and Pb, that are hazardous for human or animal health, even at low concentrations. According to Castaing (1998), 300,000 t of silicates are used in the European market of animal food, 50%(wt) of which is sepiolite. This huge consumption is due to the multiple applications of this material in animal food. Their binding and anticaking power gives excellent properties to the food. In addition, it also provides better decomposition and fecal consistency and gives gastric protection to animals, which brings about a reduction of dirty eggs and a reduction of ammonia and bad smell emissions. Therefore, toxic elements in food have also to be controlled because, apart from the animal wellness, whatever the animal eats will be transferred to the food products that humans consume.

The presence of As, Cd, Cr, Hg, Ni, and Pb in the human diet leads to serious health issues, so it is important to establish a strict control of the toxic element concentration. The biggest problem derived from heavy metals is that they cannot be eliminated from the body, being defined as "noiseless enemies" by Londoño-Franco, Londoño-Muñoz, and Muñoz-Garcia (2016) as their presence in the human body alters biochemical and physiological processes causing irreparable damage. To avoid pathologies, or even death, by these toxic elements, many regulations establish the maximum concentration allowed of each toxic metal in food additives and processing aids. Regulation (CE) N°1881/2006 (Official Journal of the European Union 2006) establishes the maximum concentrations of Pb, Cd, Hg, and As allowed in food, while Regulations 2008/84/CE (Official Journal of the European Union 2008), UE 231/2012 (Official Journal of the European Union 2012), and Royal Decree 1466/2009 (Official Bulletin from the Spanish Government 2009) state the maximum concentration of toxic metals in food additives and processing aids. In addition, other regulations describe the sampling methods and official analysis control of these metals, such as Regulation (CE) N°333/2007 (Official Journal of the European Union 2007) and (UE) N°2016/582 (Official Journal of the European Union 2016). Finally, Royal Decree 640/2015 (Official Bulletin from the Spanish Government 2015) lists the approved materials that can be used as processing aids for vegetable oil. There is a range of the allowed concentration of each metal depending on the regulation, although the lowest concentrations allowed are $1 \, mg \, kg^{-1}$ for As, Cd, Cr, Hg, and Ni, and $5 \, mg \, kg^{-1}$ for Pb (although for high consumptions, the limit decreases to $1 \, mg \, kg^{-1}$).

Some authors have described methods to characterize geological materials, such as clays, kaolins, or calcium carbonates, focusing upon the determination of the major elements. Other authors have developed methods to determine these minor toxic elements in food, but few authors have described methods for the determination of these elements in geological materials intended for food additives or processing aids (Gazulla et al. 2004; Jayabun, Pathak, and Sengupt 2020; Quadro et al. 2019; Roomiani, Mashayekhi, and Ghaeni 2016; Mohammed, Mohammed, and Mohammed 2017).

There are different techniques to determine the concentration of these elements, such as atomic absorption spectrometry (AAS), inductively coupled plasma – optical emission spectrometry (ICP-OES), inductively coupled plasma – mass spectrometry (ICP-MS), and wavelength dispersive x-ray fluorescence spectrometry (WD-XRF). AAS, ICP-OES, and ICP-MS require the analytes in liquid form, while WD-XRF just requires minimal sample preparation. However, WD-XRF cannot determine some elements at trace levels in some materials, as AAS and ICP-OES are more effective in these cases. Regarding AAS, As and Hg determination need a hydride generation module which is highly effective for these elements at trace levels, but this technique is time-consuming as sample preparation, calibration curves, validation standards, and samples need to be freshly prepared due to the low concentrations handled. Besides, this procedure uses the following reagents: sodium borohydride, sodium hydroxide, hydrochloric acid, potassium iodide, ascorbic acid, and potassium permanganate. Sodium borohydride and potassium permanganate are quite toxic.

In a previous work, a WD-XRF methodology was optimized to decrease the quantification limits to trace levels in the required elements according to the regulations. These quantification limits were achieved for Pb or Cd, while for the values for Hg, Ni, and Cr were still too high to accomplish the strictest requirements (Gazulla et al. 2021).

When developing the quantification method, there are many methods based on the fusion of the sample at high temperatures with different fluxes (carbonates, borates, etc.). These methods are unsuitable for the determination of Hg due to its high volatility. Another method in the literature performs acid decomposition at atmospheric pressure and elevated temperatures, although this method is also unsuitable for Hg. In addition, methods have described the decomposition of the sample using a microwave oven, but in this approach the sample mass is usually small and as a result achieving low quantification limits becomes challenging (Roomiani, Mashayekhi, and Ghaeni 2016; United States Environmental Protection Agency 1996; Senior et al. 2016; Cooperative work of the German Society for Fat Science (DGF)) 2001; Lozano 2016; Quadro et al. 2020). Although there are many methods in the literature, they are tedious and require the use of high acid quantities or thermal treatments at high temperatures which are not environmentally friendly. Thus, there is a special interest in designing a method to determine the desired elements with the required quantification limits in the minimum time and using the minimum quantity of harmful reagents. Besides, the sample preparation must be chosen considering that if the decomposition method uses an open-air system or needs the addition of reagents during the decomposition process itself, contamination or analyte loss may occur, both of which are undesirable (Ferreira et al. 2015).

The need of having a rapid and accurate method to monitor the concentrations of As, Cd, Cr, Hg, Ni, and Pb at trace levels in geological materials used in the food

industry, such as clays, kaolins, sepiolites, and calcium carbonates, resulted in the set-up of a new methodology. The development was addressed by optimizing sample preparation in a single chamber reaction using microwave radiation with analysis by ICP-OES.

Materials and methods

Instrumentation

All measurements were performed with an Agilent 5100 SVDV inductively coupled plasma – atomic emission spectrometer equipped with a vertical torch with a 1.4 mm internal diameter injector, solvent resistant tubing, and a double pass cyclonic spray chamber. The instrument uses a solid-state RF (SSRF) system operating at 27 MHz to deliver a stable and robust plasma and operates at a power of 1.5 kW. It is possible to operate with axial and radial plasma viewing although in this study all measurements were performed with the axial mode to improve the quantification limit. An Echelle polychromator ensures a better resolution and maximum stability and reproducibility in the emission lines. It is also equipped with a charge-coupled device (CCD) detector with simultaneous measurement from 177 to 785 nm.

An inert system consisting of a concentric nebulizer OneNeb, a spray chamber, and a fully demountable torch kit, all made of PTFE, was used to measure solutions made with HF. Solutions without HF were monitored with a different nebulizer, spray chamber, and torch made of quartz.

Acid extractions were carried out using an UltraWAVE microwave oven from Milestone based on the single reaction chamber (SRC) technology, equipped with five TFM vessels of 40 mL. The SRC consists of a large 1 L pressurized stainless steel reaction chamber that can operate at high temperatures and pressure, which also serves as the microwave cavity. A base load of 140 ml of deionized water with 5 ml of nitric acid were added to the reaction SRC so that all samples were under the same temperature and pressure. The chamber was pressurized to 40 bars with nitrogen which seals each vial and prevents sample solutions from splashing or boiling, thus avoiding cross-contamination or loss of volatiles (Nóbrega et al. 2012; Druzian et al. 2016). The use of the single reaction chamber allows the decomposition of all materials with different sample preparation conditions at the same time.

A Mettler-Toledo model XA105 balance with a sensibility of 0.1 mg was used for preparing all working standards and samples.

Reagents, standards, and reference materials

The following standard solutions were used to construct the calibration curves for ICP OES determination: standard solutions of 1000 mg L^{-1} of As and Cr, both from Fluka, and standard solutions of 1000 mg L^{-1} of Cd, Hg, Ni, and Pb from Merck.

Multielement standard solution of 100 mg·L^{-1} from Sigma-Aldrich was used for validation of Pb, Cr, Ni, and, Cd curves, while a multielement standard solution of 100 mg·L^{-1} from Merck was used for validation of Hg and As.

Table 1. Sample preparation variables and their investigated ranges.

Variable studied	Range studied
Sample weight (g)	0.1 − 2
HNO$_3$/HCl ratio	1/3 − 3/1
Addition of HF (g)	Yes (1 g) / No
Total volume of acids (g)	10 − 12
Final weight dilution (g)	25 − 50
Temperature of decomposition (°C)	220 − 260
Decomposition time (min)	10 − 40

All acids used were for trace analysis. Nitric acid 69%, hydrochloric acid 37%, and hydrofluoric acid 40% from Panreac were used to extract the analytes in the SRC digestor. Boric acid from Merck was used to neutralize the hydrofluoric acid.

The development of the method was carried out using the following certified reference materials with different matrices and concentrations to ensure accuracy: GBW07401 Soil, GBW07103 Soil GBW07405 Soil from the National Research Center for Certified Reference Materials GBW (China); GeoPT-24 (Londmyndian graywacke, OU-10), GeoPT-36a (Metal-rich sediment, SdAR-M2), GeoPT-40A (Calcareous organic-rich shale, ShTX-1) from the Interlaboratory Test for the Analysis of Geological Samples (GeoPT) organized by the International Association of Geoanalysts (IAG) (United Kingdom); and Granite MGT-1, Basalt MBL-D, Mercury Soil-2 (MS-2), and Mercury Soil-3 (MS-3) from the Central Geological Laboratory of Mongolia (CGL).

Samples

Different samples were selected to ensure that the developed method was robust. The values obtained by the new method were compared with those obtained by the WD-XRF protocol developed in a previous work (Gazulla et al. 2021). Two clays (identified as Clay 1 and Clay 2), which may be used in the wine and oil industry, and a sepiolite, which may be used in animal feed for swine, were chosen to carry out this study.

Experimental procedure

The experimental development was carried out by optimizing the sample preparation by the SRC digestor UltraWAVE and the measurement conditions by ICP-OES.

Optimization of the sample preparation

The selection of the variables of study was undertaken to reach the complete extraction of the analytes in the minimum volume to achieve the required quantification limits. For this purpose, the use of the maximum sample weight in the minimum dilution volume was intended. Besides, sample preparation time was also studied to decrease it to make the procedure suitable as a control method. Table 1 shows the studied variables and their range of values.

The optimization and ensuring of the accuracy of the sample preparation method developed was carried out using certified reference materials.

Traditional decomposition methods recommend the use of hydrofluoric acid to obtain a complete decomposition of geological samples, but its use implies serious issues as it attacks glass and is extremely harmful. This recommendation derives from the need to fully decompose the sample, as hydrofluoric acid is used to decompose silicates. In this study, the optimization was carried out trying not to use hydrofluoric acid to extract the analytes.

However, during the conduction of the different experiments, complete recovery of Ni, Cr, and Pb was not achieved using only HNO_3 and HCl in the extraction process, probably because they are part of a mineralogical phase that does not decompose only with the aforementioned acids, concluding that HF was needed to completely extract Ni, Cr, and Pb. Apart from the use of HF, a different (sample):(mixture of acids) ratio was also needed. These findings resulted in the design of two sample preparation processes: one for As, Hg, and Cd with no use of HF, and another for Ni, Cr, and Pb with HF addition, being optimized to use the minimum quantity. A sample mass of 0.2 g in 9 g of a mixture of acids was needed to provide the complete extraction of Ni, Cr, and Pb. However, with this solid:liquid ratio, the desired quantification limits for As, Hg, and Cd were not obtained, a reason why two different decomposition conditions were needed.

Optimization of the measurement conditions

The conditions were optimized by monitoring the response after changing power, nebulizer flow, plasma flow, auxiliary flow, and pump rate.

Among the analytes selected in this work, Hg was the most difficult to determine by ICP-OES due to its high volatility, although the literature reported mercury at trace levels by ICP-OES in blood, urine, or mushroom, which are different from the matrices considered in this work (American Standard Test Method (ASTM) 2020; Enrico et al. 2020; Wilhelm and Bloom 2000; PS Analytical 2020).

Plasma power and plasma flow are related to plasma temperature. Higher plasma power leads to higher temperatures whereas higher plasma flow decreases the torch temperature. For these reasons, the conditions for Hg used lower plasma power and higher plasma flow to decrease the temperature. Regarding the nebulizer gas flow and peristaltic pump rate, they are related to the sample quantity that arrives at the torch so higher values of these parameters were used to increase the number of analyte atoms passing through the torch.

ICP OES calibration

Calibration standards were prepared by making stepwise dilutions with pure water of the stock standards to prepare calibration curves with the appropriate concentrations that allow the determination of the analytes. Regression analysis was carried out to characterize the linearity of the calibration curves.

Validation

Validation was carried out by analyzing certified reference materials decomposed using the optimized sample preparation methodology. The reported results are the mean of

three replicates. To evaluate the quality of the developed method, the differences between the certified and experimental values were compared with the related uncertainty. The difference between the two values was determined by:

$$\Delta_m = \left| c_{\exp} - c_{cert} \right| \tag{1}$$

where Δ_m is the absolute value of the difference between the experimental and certified value, $c_{\exp}$ is the obtained experimental concentration, and c_{cert} is the certified value of the analyte.

Δ_m is compared with its expanded uncertainty ($U_{\Delta m}$) which is determined by:

$$U_{\Delta_m} = 2 \cdot u_{\Delta_m} \tag{2}$$

where U_{Δ_m} is the expanded uncertainty, u_{Δ_m} is the uncertainty of Δ_m and 2 is the coverage factor (k), which corresponds approximately to the 95% confidence level.

$$u_{\Delta_m} = \sqrt{u_{\exp}^2 + u_{cert}^2} \tag{3}$$

where u_{Δ_m} is the combined uncertainty of the certified and the experimental value, $u_{\exp}$ is the uncertainty of the measured value, and u_{cert} is the uncertainty related to the certified value.

If $\Delta_m \leq U_{\Delta m}$, there is no significant difference between the measured and the known values.

The uncertainty (U) of the results were determined by:

$$U = k \cdot u_{method} \tag{4}$$

where u_{method} is the combined uncertainty of the method calculated by:

$$u_{method}^2 = u_{V_R}^2 + u_{V_L}^2 + u_R^2 \tag{5}$$

where u_{V_R} is the uncertainty of the certified value, u_{V_L} is the uncertainty of the measurement of the certified reference material, and u_R is the uncertainty of the measurement of the sample. The values of u_{V_L} and u_R were calculated by the expression, $\frac{s}{\sqrt{n}}$ where s is the standard deviation of the measurement and n is the number of measurements.

The coverage factor k is determined from the Student's t-distribution corresponding to the appropriate degrees of freedom and 95% confidence.

The limit of quantification (LOQ) of the method, which expresses the quantifiability of an analyte, was calculated according to the IUPAC guidelines as ten times the standard deviation of the measurement (Gazulla et al. 2010; Currie 1995):

$$LOQ = 10 \cdot s \tag{6}$$

where s is the standard deviation.

Results and discussion

Optimization of sample preparation

Sample preparation was optimized by changing the variables in Table 1 to achieve the lowest quantification limit using the maximum sample weight permitted by the preparation process and applying the lowest dilution factor.

Two sample preparation processes were developed for the analytes to obtain the required quantification limits.

Decomposition method 1: As, Cd, and Hg

Different experiments were carried out modifying the variables within the range shown in Table 1. The best results were obtained with 1 g of sample, 9 g of HNO_3, and 3 g of HCl, submitting the mixture to decomposition at 260 °C and a maximum pressure of 85 bars for 40 minutes in the UltraWAVE. The obtained solution was diluted with pure water to a final weight of 40 g.

Decomposition method 2: Cr, Ni, and Pb

Different proportions of HNO_3 and HCl were tested but complete recovery was not achieved in any case. Only when HF was added to the mixture of HNO_3 and HCl complete recovery of Cr, Ni, and Pb was obtained.

In order to use the minimum quantity of HF, sample weight had to be diminished to 0.2 g. The best results were obtained by mixing 0.2 g of the sample with 2 g of HNO_3 and 6 g of HCl, adding 1 g of HF, and submitting the mixture to decomposition at 260 °C and a maximum pressure of 85 bars for 40 minutes in the microwave. After decomposition, 0.35 g of boric acid were added to neutralize the HF, allowing it to react at 160 °C for 20 minutes. The resulting solution was diluted to a final weight of 30 g with pure water.

The use of the microwave oven permits the analysis of more than one sample and/or conducts both decomposition methods simultaneously, which makes the preparation faster compared to traditional processes.

Optimization of the ICP-OES conditions

The conditions were optimized for each element to obtain the quantification limit required. No common conditions could be used for all analytes. The Cr, Ni, and Pb decomposition uses HF so, a special PTFE nebulizer, nebulizer chamber, and torch are needed for the measurement. On the other hand, As, Cd, and Hg are decomposed without HF and hence are analyzed with a conventional quartz system, although they cannot be simultaneously determined as Hg is quite volatile and needs special measurements conditions. Table 2 shows the optimum conditions for each element.

Of special note are the conditions for Hg. Lower plasma power and higher plasma flow were established to be able to reach the desired quantification limit. In addition, higher nebulizer gas flow and pump rate were required to obtain better sensitivity.

Table 2. Optimum measurement conditions for each element by ICP-OES and correlation coefficients of the calibration curves.

	As	Cd	Hg	Cr	Ni	Pb
Plasma Power (kW)		1.4		1.2		1.5		
Plasma Flow (L/min)		13.5		15.0		12.0		
Nebulizer Gas Flow (L/min)		0.70		0.85		0.80		
Peristaltic Pump Rate (rpm)		12		15		10		
Analytical line (nm)	188.890 (I)	214.439 (II)	184.887 (I)	283.563 (II)	231.604 (II)	220.353 (II)
Correlation coefficient (R^2)	0.99990	0.99995	0.99987	0.99995	0.99994	0.99998

Calibration

Four lines of each element were selected to provide the most sensitive and interference-free analysis. The lines for As and Hg were atomic (I), while ionic (II) transitions were employed for Cd, Cr, Ni, and Pb. After calibration, all calibration curves showed excellent linearity as shown in Table 2.

Validation

The validation of the methodology was undertaken by the measurement of several reference materials with certified or known values of the analytes. Table 3 shows the results obtained with their uncertainty, together with the certified or known values.

The obtained results were in good accordance across the studied range. The values for As, Cr, Ni, and Pb were diverse, ranging from few mg·kg^{-1} to values higher than 100 mg·kg^{-1}, which denoted quantitative extraction exceeding 98%. The values for Hg and Cd were lower since geological materials contain these elements in minute concentrations.

To objectively compare the obtained results with the known values, the difference between both (Δ_m) was compared with the related uncertainty ($U_{\Delta m}$). The results of this comparison are presented in Table 4.

Table 4 shows good agreement between the results obtained by the developed methodology for analyzed reference materials. Since $\Delta_m < U_{\Delta m}$ in all elements, thus the method is validated.

After validation of the methodology with the analysis of certified reference materials, the quantification limits of the method were determined. Quantification limits of 1 mg·kg^{-1} were obtained for all analytes when the sample is prepared in the SRC microwave digestor using two decomposition methods and the resulting solutions analyzed by ICP-OES using the optimized conditions for each element. These quantification limits met the requirements for food additives.

The methodology was also validated by analyzing samples of unknown composition by the developed method and comparing the results with those obtained by an independent technique, WD-XRF, developed in a previous study (Gazulla et al. 2021). The results are shown in Table 5.

There were no significant differences in the results between these methodologies, thus validating the new methodology using microwave preparation and ICP-OES analysis. The quantification limits for Ni, Cr, Hg, and As are lower by ICP-OES than by WD-XRF and meet the requirements established in the strictest regulations.

Table 3. Analysis of the reference materials by the developed methods.

| | Decomposition method 1 | | | | | | Decomposition method 2 | | | | | |
| | As (mg·kg⁻¹) | | Cd (mg·kg⁻¹) | | Hg (mg·kg⁻¹) | | Cr (mg·kg⁻¹) | | Ni (mg·kg⁻¹) | | Pb (mg·kg⁻¹) | |
	Certified	Measured	Certified	Measured	Certified	Measured	Certified	Measured	Certified	Measured	Certified	Measured
GeoPT-24	–	–	2.8 ± 0.4	3.1 ± 1.0	–	–	34 ± 1.2	33 ± 4	17.7 ± 0.5	18 ± 3	26.9 ± 0.9	26 ± 3
GeoPT-36A	75.82 ± 4.34	76.9 ± 5.3	5.1 ± 0.2	5.0 ± 1.0	1.436 ± 0.096	1.3 ± 1.0	49.6 ± 1.6	49 ± 5	48.75 ± 0.97	48 ± 5	808 ± 13	800 ± 68
GBW07401	34 ± 4	36 ± 4	4.3 ± 0.4	4.6 ± 1.0	0.032 ± 0.004	<1	62 ± 4	66 ± 5	20.4 ± 1.8	22 ± 3	98 ± 6	101 ± 10
GBW 07405	412 ± 16	391 ± 30	0.45 ± 0.06	<1	0.29 ± 0.03	<1	118 ± 7	112 ± 10	40 ± 4	37 ± 4	552 ± 29	518 ± 30
GBW 07103	2.1 ± 0.4	2.4 ± 1.0	0.029 ± 0.009	<1	0.0041 ± 0.0012	<1	3.6 ± 0.9	3.3 ± 1.0	2.3 ± 0.82	1.5 ± 1.0	31 ± 3	28 ± 3
Granite (MGT-1)	2.28 ± 0.24	1.8 ± 1.0	(0.13)[a]	<1	–	–	182 ± 7	178 ± 15	5.76 ± 0.28	5.0 ± 1.0	24.81 ± 0.69	26 ± 3
Mercury Soil-2 (MS-2)	–	–	–	–	1.52 ± 0.08	1.4 ± 1.0	–	–	–	–	–	–
Mercury Soil-3 (MS-3)	–	–	–	–	2.75 ± 0.19	2.6 ± 1.0	–	–	–	–	–	–

[a]Value in brackets is informative

Table 4. Comparison of the results obtained with the new methodology with the certified value, comparing $\Delta_m = |c_{exp} - c_{cert}|$ with $u_{\Delta_m} = 2.\sqrt{u_{exp}^2 + u_{cert}^2}$

	Decomposition method 1						Decomposition method 2					
	As (mg·kg^{-1})		Cd (mg·kg^{-1})		Hg (mg·kg^{-1})		Cr (mg·kg^{-1})		Ni (mg·kg^{-1})		Pb (mg·kg^{-1})	
	Δm	U$_{\Delta m}$	Δm	U$_{\Delta m}$	Δm	U$_{\Delta m}$	Δm	U$_{\Delta m}$	Δm	U$_{\Delta m}$	Δm	U$_{\Delta m}$
GeoPT-24	–	–	0.3	2.1	–	–	1.0	8.4	0.3	6.1	0.9	6.3
GeoPT-36A	1.1	13.7	0.1	2.0	0.1	2.0	0.6	10.5	0.8	10.2	8	119
GBW07401	2	11	0.3	8.2	–	–	4	13	1.6	7.0	5	23
GBW 07405	34	83	–	–	–	–	6	24	3	11	34	83
GBW 07103	0.3	2.2	–	–	–	–	0.3	2.7	0.8	2.6	3	8
Granite (MGT-1)	0.5	2.1	–	–	–	–	4	33	0.8	2.1	1.2	6.2
Mercury Soil-2(MS-2)	–	–	–	–	0.1	2,0	–	–	–	–	–	–
Mercury Soil-3(MS-3)	–	–	–	–	0.15	2.04	–	–	–	–	–	–

Table 5. Comparison between the limit of quantification (LOQ) and the results obtained by WD-XRF and the developed ICP-OES method for the analysis of three samples.

	LOQ		Clay 1		Clay 2		Sepiolite	
	WD-XRF	ICP-OES	WD-XRF	ICP-OES	WD-XRF	ICP-OES	WD-XRF	ICP-OES
As (mg kg^{-1})	1	1	3 ± 2	4 ± 1	3 ± 2	3 ± 1	5 ± 2	3 ± 1
Cd (mg kg^{-1})	3	1	<1	<1	<1	<1	<1	<1
Cr (mg kg^{-1})	2	1	43 ± 3	39 ± 4	28 ± 2	25 ± 3	45 ± 3	42 ± 5
Hg (mg kg^{-1})	1	1	<3	<1	<3	<1	<3	<1
Ni (mg kg^{-1})	3	1	3 ± 1	2 ± 1	<3	1 ± 1	12 ± 4	10 ± 2
Pb (mg kg^{-1})	2	1	73 ± 5	67 ± 5	104 ± 10	99 ± 10	40 ± 3	39 ± 4

The methodology developed in this study requires a total analysis time of 90 min, including sample preparation and measurement. The microwave permits the simultaneous analysis of two samples, which is sufficiently rapid to be used as a control method. In addition, this approach is more environmentally friendly than other standardized techniques such as HG-AAS for Hg and As because fewer harmful reagents are used. Regarding the sample preparation, the use of the microwave for decomposition does not require temperatures of 1000 °C, such as alkaline fusion procedures.

Conclusions

1. A new, robust, and fast quality control methodology has been developed to ensure the absence of heavy metals that are hazardous for humans in food.
2. The method based on new microwave technology for analyte extraction permits the determination of all investigated heavy metals in approximately 90 min which makes it useful as a control method.
3. Two decomposition methods for sample preparation were optimized to completely extract all analytes and reach the quantification limits required. One method was for As, Cd, and Hg and the other for Cr, Ni, and Pb.
4. The optimization of the measurement conditions was also critical to reach the required quantification limit for mercury with no need of hydride generation

and made ICP-OES suitable when the requirements are $1\,mg{\cdot}kg^{-1}$ for all elements.

5. The developed methodology is environmentally friendly as it decreases the quantities of toxic reagents needed to carry out the sample preparation and there is no need to use decomposition processes that involve high temperature.

Disclosure statement

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