TRACE LEVEL DETERMINATION OF TOXIC METALS IN GEOLOGICAL MATERIALS BY ICP-OES USED IN THE FOOD INDUSTRY

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1. INTRODUCTION

Many geological material are used in the food industry as <u>additives</u> or as <u>processing aids</u>

- **Clays** and **kaolins** are used for wine and vegetable oil clarification

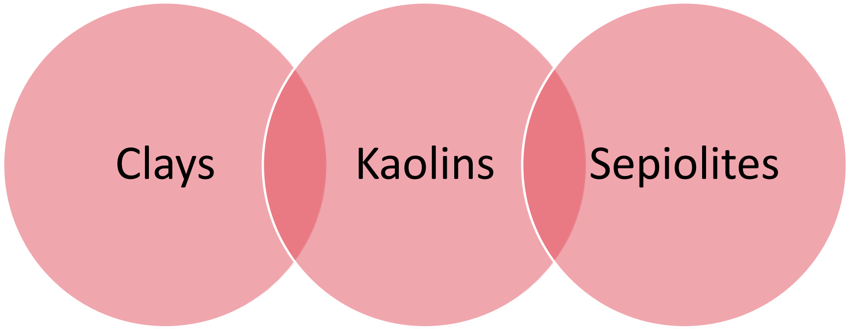
- **Calcium carbonates** and **potassium nitrates** are used as additives for food preservation or enhancement of some properties

[1] N. Worasith, B.A. Goodman, N. Jeyashoke, P. Thiravetyan, *J. Am. Oil Chem. Soc.* 2011; *88*, 2005.

[2] L.F. Londoño-Franco, P.T. Londoño-Muñoz, F.G. Muñoz-García, *Biotecnol. Sect. Agropecu. Agroind*. 2016; *14(2)*, 145.

[3] Jaeckels, N.; Tenzer, S.; Meier, M.; Will, F.; Dietrich, H.; Decker, H.; Fronk, P.; *LWT – Food Science and Technology*, 2017, 75, 335

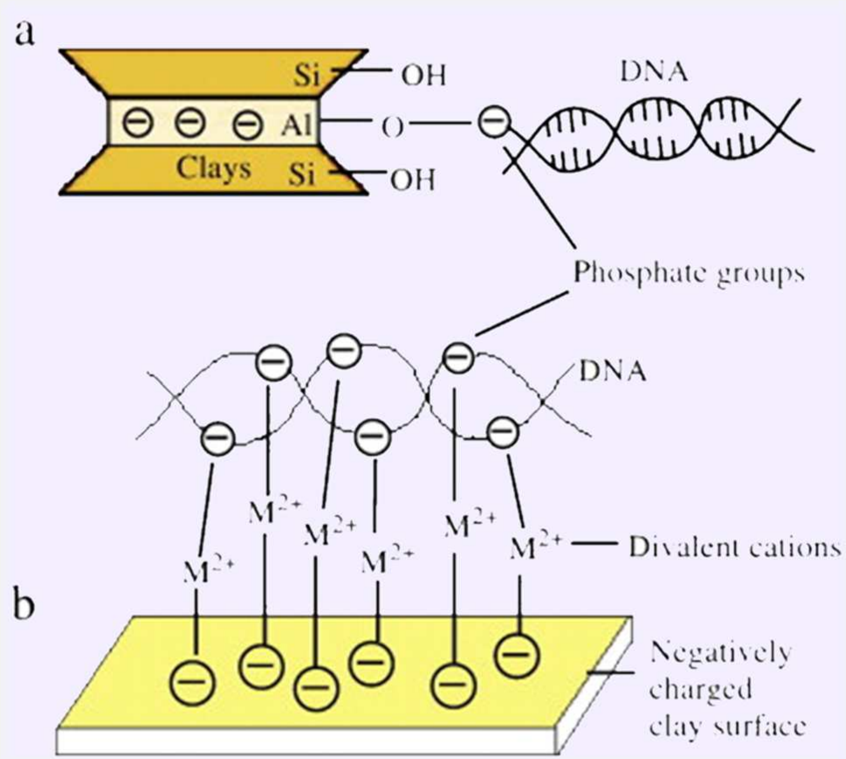
1. INTRODUCTION
1.1 PROCESSING AIDS



The properties that a geological material should present to be used as a processing aid are[4,5]:

- High specific surface area
- Cation exchange capability
- Swelling degree

Mecanism of absorption



[4] S. Servagent-Noinville, M. Revault, H. Quiquampoix, M. H. Baron, *J. Colloid Interface Sci*. (2000), 221, **273**

[5] W. A. Yu, N. Li, D. S. Tong, C. H. Zhou, C. X. Lin, C. Y. Xu, *Appl. Clay Sci.* (2013), 80-81, **443**

1. INTRODUCTION

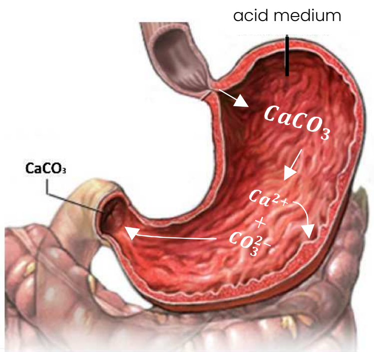
1.2 ADDITIVES

- Calcium carbonate ($CaCO_3$)
  - Used in bakery, drinks, cereals or canned fruit.
  - Improve the digestibility of some food.

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_3O^+ \leftrightarrow HCO_3^- + H_2O$$

$$HCO_3^- + H_3O^+ \leftrightarrow H_2CO_3 + H_2O$$



- Potassium nitrate (KNO_3)
  - Used to prevent meat industry, cheese, etc., from bacteria and fungus

[6] Commission Regulation (EU) No 231/2012 of 9 March 2012 laying down specifications for food additives listed in Annexes II and III to Regulation (EC) No 1333/2008 of the European Parliament and of the Council Text with EEA relevance

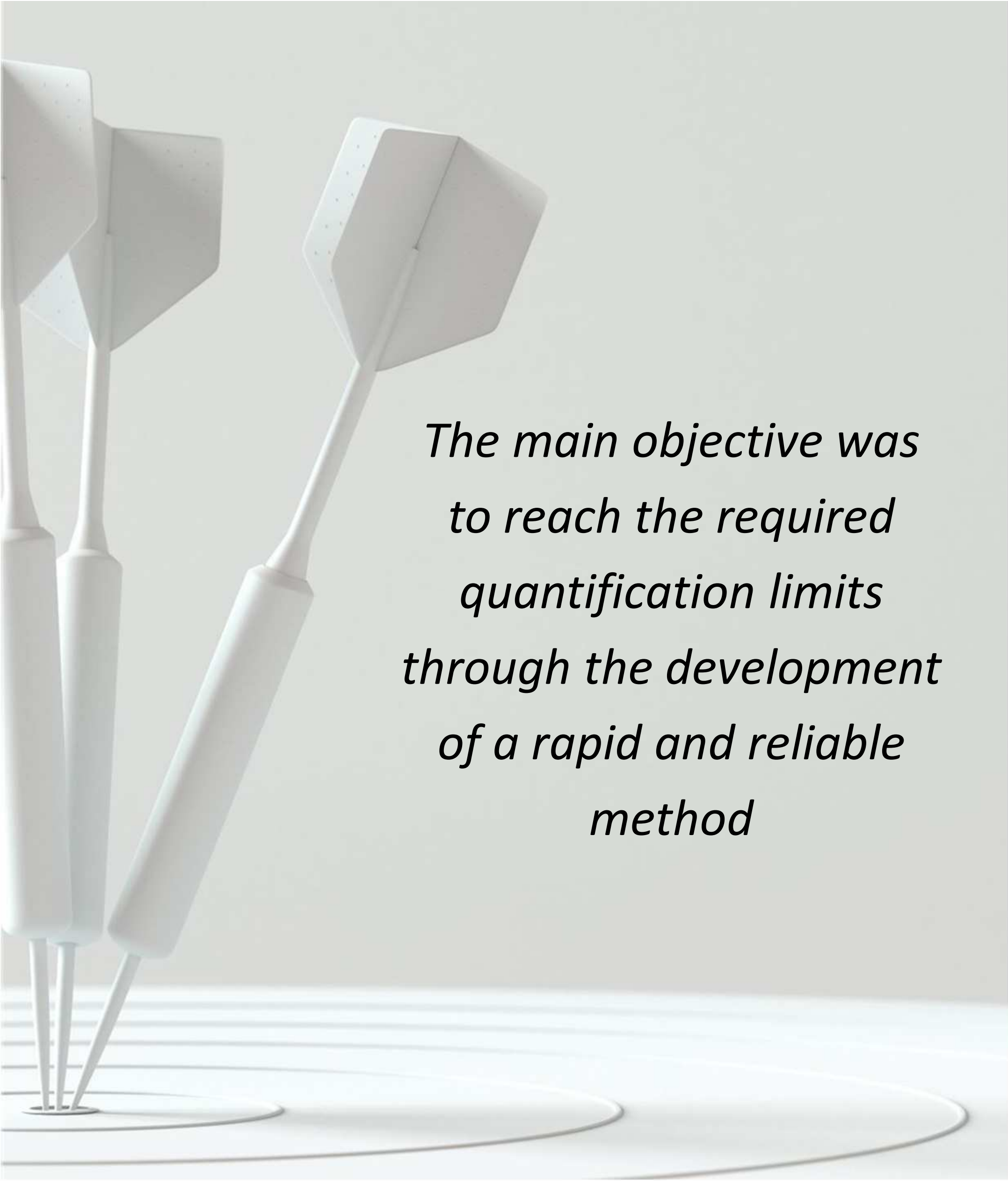
1. INTRODUCTION

1.3. MAXIMUM PERMITTED LEVELS FOR SOME HEAVY METALS PRESENT IN FOOD ADDITIVES AND PROCESSING AIDS

Law Regulation	Additive	As (mg kg^{-1})	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Hg (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})
Regulation (EU) no. 231/2012	$CaCO_3$	3	1	1	-	1	3
	KNO_3	3	-	1	1	1	2
	Bentonite	-	-	-	-	-	-
Royal Decree 640/2015	Kaolinitic clay	3	2	-	1	-	70
	Bentonite	2	-	-	-	-	20
	Other materials used and not included	1	1	-	1	-	5
Directive 2008/84/CE	$CaCO_3$	3	-	-	1	-	5
	KNO_3	3	-	-	1	-	5
	Bentonite	2	-	-	-	-	20
FAO and WHO(*)	$CaCO_3$	3	-	-	-	-	3
	KNO_3	-	-	-	-	-	2
	General limits	Indicated by the manufacturer	1	-	1	-	2 (1 for high consumption)

(*) FAO and WHO Explanatory note evidences for the need to develop a method that avoids the dry-ashing procedure, due to the potential loss of metals and arsenic with high temperatures.

[7] Commission Regulation (EU) No 231/2012 of 9 March 2012 laying down specifications for food additives listed in Annexes II and III to Regulation (EC) No 1333/2008 of the European Parliament and of the Council Text with EEA relevance
[8] Joint FAO/WHO expert commitee on food additives (JECFA), *Limit test for heavy metals in food additive specifications. Explanatory note,* FAO Joint Secretariat, **2002**



The main objective was to reach the required quantification limits through the development of a rapid and reliable method

2. OBJECTIVES

- Reach the quantification limits required
- Decrease the time of analysis to the minimum
- Develop an environmentally friendly control method

3. EXPERIMENTAL PART

3.1. MATERIALS

- Samples

  - Clay 1
  - Clay 2
  - Sepiolite

3. EXPERIMENTAL PART

3.1 MATERIALS

- Certified Reference Materials (CRM)

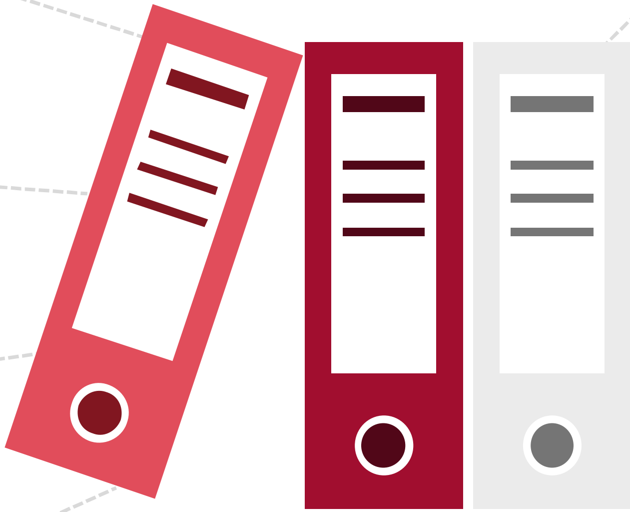
Database consulted

Bundesanstalt für Materialforschung und –prüfung **(BAM)**

Bureau of Analysed Samples Ltd. **(BAS)**

CANMET Materials

Institute for Reference Materials and Measurements **(IRMM)**



National Institute of Standards and Technology **(NIST)**

Central Geological Laboratory of Mongolia **(CGL)**

International Association of Geoanalysts **(IAG)**

National Research Centre for Certified Reference Materials **(GBW)**

SA Bureau of Standards, Republic of South Africa **(SABS)**

3. EXPERIMENTAL PART

3.1 MATERIALS

- Certified Reference Materials (CRM)

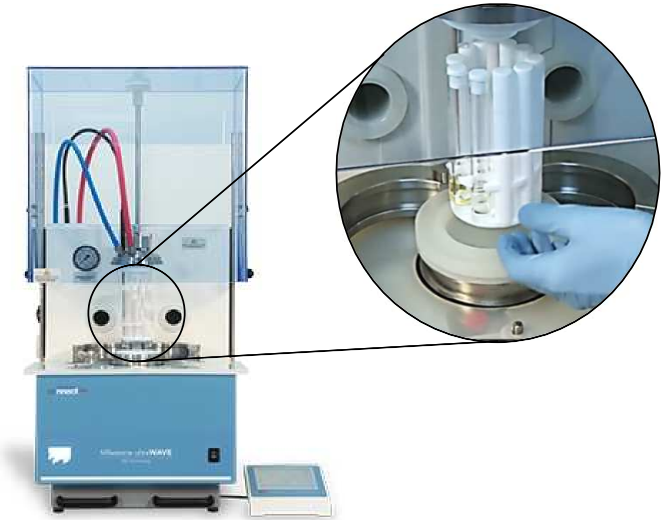
Certified Reference Materials		Pb (mg·Kg-1)	Ni (mg·Kg-1)	Cr (mg·Kg-1)	Cd (mg·Kg-1)	Hg (mg·Kg-1)	As (mg·Kg-1)
Interlaboratory Test for the Analysis of geological samples (GeoPT) organised by IAG (International Association of Geoanalysts) (United Kingdom)	GeoPT-24 (Londmyndian greywacke, OU-10)	26.9±0.9	17.7±0.5	34±1.2	2.8±0.4	-	-
	GeoPT-36a (Metal-rich sediment, SdAR-M2)	808±13	48.75±0.97	49.6±1.6	-	1.436±0.096	75.82±4.34
	GeoPT-40A (Calcareous organic-rich shale, ShTX-1)	6.05±0.58	74.92±2.56	29.65±0.26	2.02±0.12	-	15.05±0.84
Central Geological Laboratory of Mongolia (CGL) (Mongolia)	Granite (MGT-1)	24.81±0.69	5.76±0.28	182±7	(0.13)	-	2.28±0.24
	Basalt MBL-D	5.66±0.41	163±21	188±15	-	-	-
	Mercury Soil-2 (MS-2)	-	-	-	-	1.52±0.08	-
	Mercury Soil-3 (MS-3)	-	-	-	-	2.75±0.19	-
National Research Centre for Certified Reference Materials GBW (China)	GBW 07401 Soil	98±6	20.4±1.8	62±4	4.3±0.4	0.032±0.004	34 ± 4
	GBW 07103 Soil	31±3	2.3±0.8	3.6±0.9	0.029±0.009	0.0041±0.0012	2.1±0.4
	GBW 07405 Soil	552±29	40±4	118±7	0.45±0.06	0.29±0.03	412±16

3. EXPERIMENTAL PART

3.2 INSTRUMENTATION

SAMPLE PREPARATION

UltraWAVE



MEASUREMENT OF ANALYTES

ICP-OES

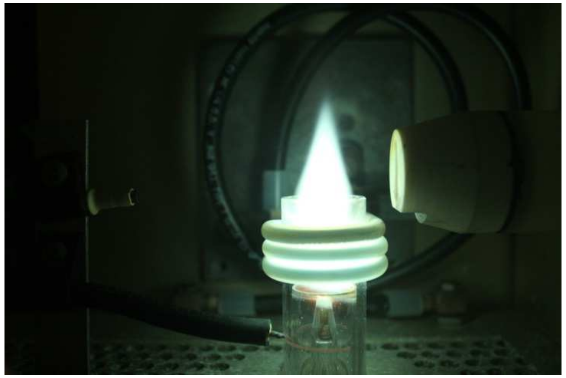
3. EXPERIMENTAL PART

3.3 DEVELOPMENT OF THE METHOD

Optimization of the sample preparation

- Sample weight
- Type and mixture of acids
- Addition of HF
- Volume of acid
- Digestion temperature
- Digestion time

Optimization of the measurement conditions



- Plasma power
- Plasma flow
- Nebulizer flow
- Peristaltic pump speed

4. RESULTS

4.1 OPTIMISATION OF SAMPLE PREPARATION

Variables and range studied

Variable studied	Range studied
Sample weight (g)	0.1 - 2
Nitric / Hydrochloric acid ratio	1/3 – 3/1
Addition of HF (ml)	Yes (1 ml) / No
Dilute to weight / final weight dilution (g)	25 - 50
Temperature of digestion (ºC)	220 - 260
Digestion time (min)	15 - 45

Discussion after the experiments for sample preparation optimisation

Sample weight (g)	Acid mixture	Comments
1,0	9 ml HNO_3 + 3 ml HCl	Not all the analytes are extracted with this condition
0,2	2 ml HNO_3 + 6 ml HCl + 1 ml HF	The quantification limits needed for all the analytes are not reached

→ There is not a unique digestion condition that permits de analysis of all the analytes with the requires quantification limits

→ ***Necessity to have different digestion conditions for different elements***

4. RESULTS

4.1 OPTIMISATION OF SAMPLE PREPARATION

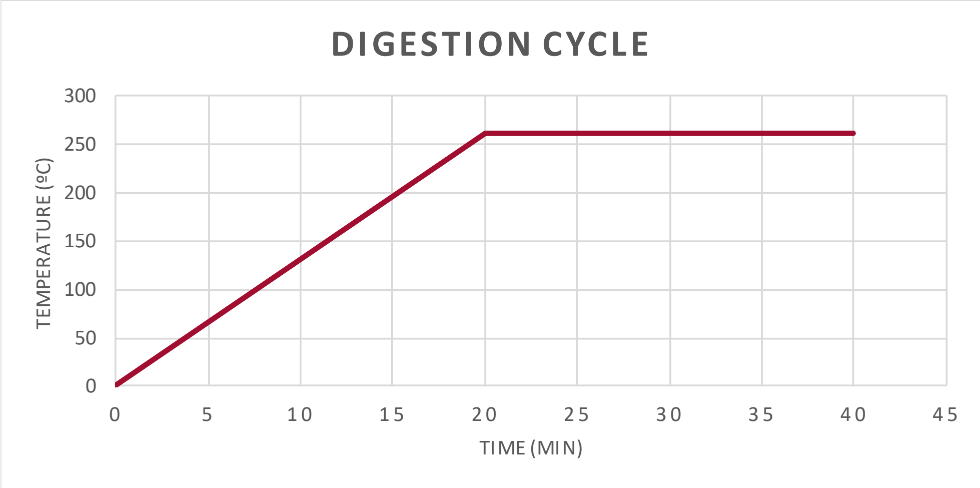
DIGESTION METHOD 1 – As, Cd, and Hg

Elements	Sample weight (g)	Acid mixture	Final weight (g)
As, Cd, and Hg	1,0	9 ml HNO_3 + 3 ml HCl	40

DIGESTION METHOD 2 – Pb, Cr, and Ni

Elements	Sample weight (g)	Acid mixture	Final weight (g)
Pb, Cr, and Ni	0,2	2 ml HNO_3 + 6 ml HCl + 1 ml HF(*)	40

(*) Need of addition of 0.35 g of H_3BO_3 to neutralize the HF



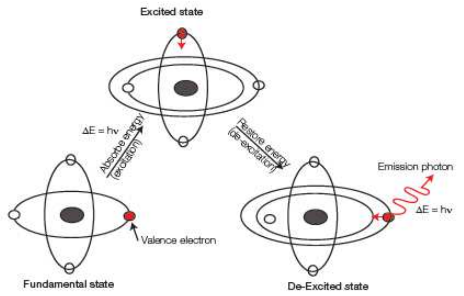
Digestion temperature – 260ºC

Digestion time – 40 min

"Same digestion cycle (time and temperature) but different acid mixtures"

4. RESULTS

4.2 OPTIMISATION OF MEASUREMENT CONDITIONS



	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

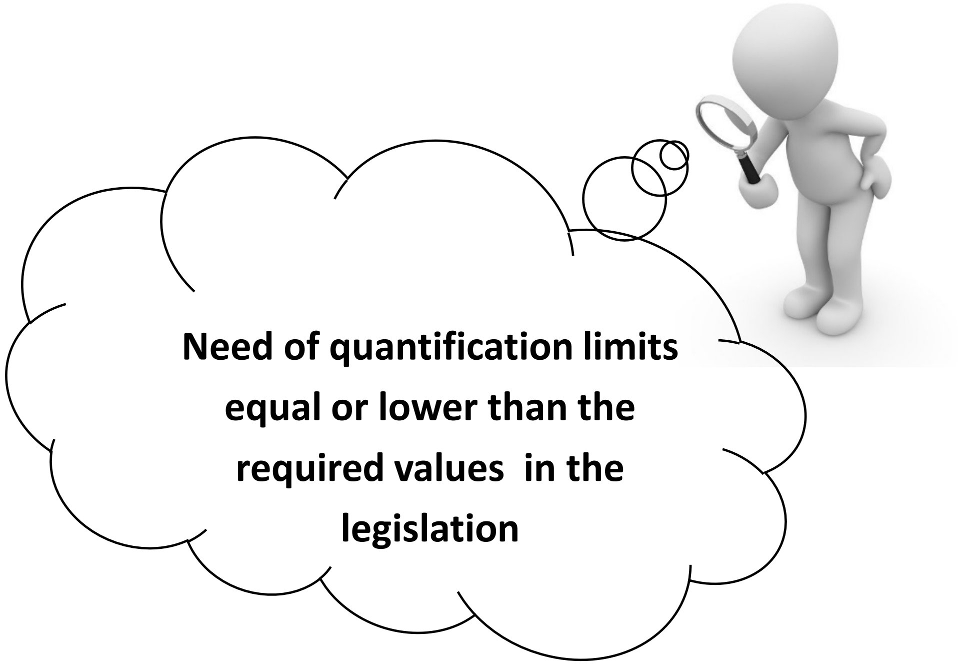
Time used in the process of measurement by ICP-OES (including calibration, validation, and measurement of all the analytes)	30 min

Being able to measure such low quantities of Hg by ICP-OES, without the necessity of using hydride generation, is challenging

4. RESULTS

4.3 VALIDATION

Detection limit (L_D)	Quantification limit (L_Q)
$L_D = 3{,}29s$	$L_Q = 10s$
s = standard deviation	



Uncertainty (U)	Method uncertainty (u_{method})
$U = k \cdot u_{method}$	$u_{method} = u^2_{V_R} + u^2_{V_L} + u^2_R$
k = 2	$\boldsymbol{u_{V_R}}$ = uncertainty of the certified value $\boldsymbol{u_{V_L}}$ = uncertainty of the measurement of the CRM $\boldsymbol{u_R}$ = uncertainty of the measurement of the sample

4. RESULTS

4.3 VALIDATION

- In order to compare the results obtained either with the certified value of the CRM or with values obtained by an independent technique, the difference between both (Δ_m) was compared with the related uncertainty ($U_{\Delta m}$)

$$\Delta_m = |c_m - c_{cert}|$$

$$u_{\Delta m} = \sqrt{u_m^2 + u_{cert}^2}$$

$$U_{\Delta m} = 2u_{\Delta m}$$

Δ_m= absolute value of the difference between the measured and the known value (certified or measured by an independent technique)

c_m = measured value by ICP-OES

c_{cert} = certified value or value measured by an independent technique

$u_{\Delta m}$ = combined uncertainty of the measured value and of the certified/measured by other technique value

u_m= uncertainty of the measured value by ICP-OES

u_{cert}= uncertainty of the certified value or value measured by an independent technique

Goodness of the method → $\Delta_m \leq U_{\Delta m}$

[9] T. Linsinger. Comparison of a Measurement Result with the Certified Value, https://ec.Europa.eu/jrc/sites/jrcsh/files/erm_application_note_1_en.pdf (accessed: Sept 2020)

4. RESULTS

4.3 VALIDATION

4.3.1 Measurement of the CRM by the new methodology by ICP-OES using UltraWAVE® for analyte extraction

	DIGESTION METHOD 1						DIGESTION METHOD 2					
	As ($mg \cdot kg^{-1}$)		Cd ($mg \cdot kg^{-1}$)		Hg ($mg \cdot kg^{-1}$)		Cr ($mg \cdot kg^{-1}$)		Ni ($mg \cdot kg^{-1}$)		Pb ($mg \cdot kg^{-1}$)	
	Cert	Exp	Cert	Exp	Cert	Exp	Cert	Exp	Cert	Exp	Cert	Exp
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)**	<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	-	-	-	-	-	-

4. RESULTS

4.3 VALIDATION

4.3.2 Calculation of the goodness of the method

	DIGESTION METHOD 1						DIGESTION METHOD 2					
	As ($mg \cdot kg^{-1}$)		Cd ($mg \cdot kg^{-1}$)		Hg ($mg \cdot kg^{-1}$)		Cr ($mg \cdot kg^{-1}$)		Ni ($mg \cdot kg^{-1}$)		Pb ($mg \cdot kg^{-1}$)	
	Δ_m	$U_{\Delta m}$	Δ_m	$U_{\Delta m}$	Δ_m	$U_{\Delta m}$	Δ_m	$U_{\Delta m}$	Δ_m	$U_{\Delta m}$	Δ_m	$U_{\Delta m}$
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	-	-	-	-	-	-

For all the elements analysed, $\Delta_m < U_{\Delta_m}$ ➡ There are no significant differences ➡ Methodology validated

4. RESULTS

4.3 VALIDATION

4.3.3 Comparison between the results obtained by ICP-OES and WD-XRF

There are no significant differences between the values obtained

The main difference between the two techniques is the quantification limit

	Clay 1		Clay 2		Sepiolite	
	WD-XRF	ICP-OES	WD-XRF	ICP-OES	WD-XRF	ICP-OES
As (mg kg^{-1})	3 ± 2	4 ± 1	3 ± 2	3 ± 1	5 ± 2	3 ± 1
Cd (mg kg^{-1})	<1	<1	<1	<1	<1	<1
Cr (mg kg^{-1})	43 ± 3	39 ± 4	28 ± 2	25 ± 3	45 ± 3	42 ± 5
Hg (mg kg^{-1})	<3	<1	<3	<1	<3	<1
Ni (mg kg^{-1})	3 ± 1	2 ± 1	<3	1 ± 1	12 ± 4	10 ± 2
Pb (mg kg^{-1})	75 ± 5	63 ± 5	104 ± 10	99 ± 10	40 ± 3	39 ± 4

[10] Gazulla, M.F.; Rodrigo, M.; Ventura, M.J.; Orduña, M.; Andreu, C.; *X-Ray Spectrometry*, (2021), **50**, 197-209

4. RESULTS

4.4 OBJECTIVE ACHIVEMENT

Objective 1. Reach the quantification limits required

Element	L_Q(mg kg^{-1})
As	1
Cd	1
Cr	1
Hg	1
Ni	1
Pb	1

Objective 2. Decrease the time of analysis to the minimum

Total sample preparation time: 60 min
Total measurement time: 30 min
Total analysis time: 90 min (less than 2h)

Objective 3. Develop an environmentally friendly control method

Use of little quantity of acids and no need of digestion or extraction processes at high temperature

5. CONCLUSIONS

- A new robust and fast quality control method has been developed to ensure the absence of heavy metals in food that are hazardous for humans.

- The method based on a new microwave technology for analyte extraction permits the determination of all the heavy metals studied in a relatively short time.

- A sample preparation method for ICP-OES was optimized, depending on the group of elements to be measured: one for As, Cd, and Hg and another for Cr, Ni, and Pb

5. CONCLUSIONS

- ICP-OES method is suitable as long as the requirements are 1 ppm for all the elements.

- The methodology developed is environmentally friendly, as decreases the amount of acids needed to carry out the sample preparation, and there is no need to use digestion processes at high temperatures.

6. ACKNOWLEDGEMENTS

6. ACKNOWLEDGEMENTS

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