Technological Centre

GLOBAL REPORT

Determination of migration and chemical composition – Ceramic Containers

January | 2019

ànforum

BARRICAS DE PIEDRA

ÍNDICE

1 INTRODUCTION

This report compiles the results corresponding to the assays carried out for ANFORUM BARRICAS DE PIEDRA, with the objective of determining the specific migration, global migration and chemical composition of granite samples.

The following studies have been performed:

- **Chemical composition determination** of granite by X-Ray Fluorescence
- **Global migration** into simulants of interest:
  - Food simulant B: 4% acetic acid in water (w/v)
  - Food simulant C: 20% ethanol in water (W/w)

  Simulants and percentages have been selected as indicated in "RD 891/2006 of 21st of July, approving the sanitary technical standards applicable to ceramic objects for food use", and in annex III of "Commission Regulation (EU) nº 10/2011 of 14th of January 2011 on plastic materials and articles intended to come into contact with food", considering the specific case that "food contained" is wine.

- **Specific migration of heavy metals of interest (Pb/Cd)** into a simulant consisting of 4% acetic acid dissolution.

  Assays have been performed under the parameters established by the standard of the "RD 891/2006 of 21st of July, approving the sanitary technical standards applicable to ceramic objects for food use". Metal Pb and Cd quantification has been carried out using Inductive Coupling Plasma - Quantitative Mass Spectrometry.

- **Pb, Cd, Cu, Ag, K, Mg, B, Br, Na, Ca, Zn, Hg specific migration** in interest simulants:
  - Food simulant B, consisting of 4% acetic acid dissolution
  - Food simulant C, consisting of 20% ethanolic dissolution

  Simulants and percentages have been selected based on indicated in "RD 891/2006 of 21st of July, approving the sanitary technical standards applicable to ceramic objects for food use", and in annex III of "Commission Regulation (EU) nº 10/2011 of 14th of January 2011 on plastic materials and articles intended to come into contact with food", considering the specific case that "food contained" is wine. Selected element quantification has been carried out using Inductive Coupling Plasma - Quantitative Mass Spectrometry.

- **Specific migration in wine sample.** Migration assays have been performed using the wine sample. Final evaluation of sulphate, methanol, ochratoxin A and ethyl carbamate has been carried out.

As indicated for the performance of migration assays, different standards have been considered, such as those listed below:

- Commission Regulation (EC) nº 1935/2004 of the European parliament and of the council of 27th of October 2004, on materials and articles intended to come into contact with food;
- Commission Regulation (EC) nº 2023/2006 of 22nd of December 2006, on good manufacturing practice for materials and articles intended to come into contact with food; RD 891/2006 of 21th of July, approving the sanitary technical standards applicable to ceramic objects for food use; and
- Commission Regulation (EU) nº 10/2011 of 14th of January 2011 on plastic materials and articles intended to come into contact with food.

2 SAMPLES

Different samples of granite specimens have been received for the different types of analysis performed. In the table below the samples received and the use assigned to them are broken down.

Table 1. Samples received for the performance of different migration and chemical composition studies.

Sample Code CETIM	Description	Offer	Determination
20171124_1	18 Granite test samples 10x2.5x1 cm	OF17-0039	Pb/Cd Migration in Acetic Acid Global Migration in Acetic Acid Specific Migration in Acetic Acid
20171124_2	10 Granite test samples 7x7x2 cm	OF17-0039	Granite Chemical Composition Wine Migration
2011724_3	6 Granite test samples 10x10x2 cm	OF17-0039	Radon Determination
20171211_1	1 Wine bottle*	OF17-0039	Wine Migration
20171211_2	1 bottle	OF17-0039	Wine Migration
20171211_3	1 bottle	OF17-0039	Wine Migration
20171215_1	4 Granite test samples 6.2x6.2x2 cm	OF17-0039	Radon Determination
20180418_1	1 Granite test sample	OF18-0020	Granite Chemical Composition
20180418_2	1 Granite test sample	OF18-0020	Granite Chemical Composition
20180418_3	1 Granite test sample	OF18-0020	Granite Chemical Composition
18ME49	18 Granite test samples 10x2.5x1 cm	OF18-0071	Global Migration in Ethanol Specific Migration in Ethanol Granite Chemical Composition

*Aging wine on Lías- Santiago Roma. Selection 2017. Cuba 17. 01.12.17

Pre-treatment of samples

All the samples were preconditioned in desiccator prior to the performance of the corresponding studies. The time of preconditioning was continuous until the obtention of constant weight in successive weighed samples.

3 METHODOLOGY

The methodology followed in the studies is compiled below.

3.1 GRANITE TEST SAMPLES CARACTERIZATION

For the analysis of the granite test samples two types of characterization have been considered:

3.1.1 Granite Chemical Composition Determination

For the **granite chemical composition** determination, the next methodology has been followed:

- Sample preparation: samples have been milled to adequate size for its analysis (‹ 63 µm), mixed with inert wax (20% weight) and compacted in pill form.
- Assay method: multi-element vacuum analysis (multi-res). Results are semi-quantitatively analysed.
- Standards used: internal standards of the spectrophotometer.
- Instrumental equipment: Fluorescence spectrophotometer model S4 Pioneer (Bruker-AXS), Muffle Carbolite, Analytical balance XP-205 (Mettler-Toledo).

3.1.2 Radon Determination

Determination of the radon concentration in the received granite samples has been carried out.

Radon concentration measurements in continuous were carried out with a multiparameter monitor for the measurement of radon gas AlphaGuard DF2000 (serial number 033) from Bertin, with manufacturer's calibration certificate traceable to three international standards. Experimental assays of the materials were performed in a gas-tight nylon chamber.

3.2 MIGRATION ASSAYS

Migration assays have been performance by test sample immersion in the selected food simulant or in the real sample (depending on the study). Migration assays have been evaluated under certain conditions of time and temperature according to the assays performed and the standard selected. Detailed specifications of each assay are compiled below.

Al the assays were performed, at least, in triplicate and with the corresponding associated blanks performance.

3.2.1 Global Migration

In order to carry out migration assays and, since there is a lack of specific regulations for ceramic containers, *Regulation (EU)10/2011 of the Commision of 14th January of 2011* was taken as reference. This Regulation addresses plastic materials and objects intended to make contact with food. However, although it may differ in the nature of the container, is related to food containers. *RD 891/2006 of 21st of July 2006*, which approves the sanitary technical standards applicable to ceramic objects for food use, was also taken as reference.

Table 2 below shows the compilation of the parameters under which the global migration assays have been carried out in the different simulants selected.

Table 2. Global Migration Assays.

Simulant	Procedure	Conditions	Analysis
4% acetic acid dissolution	Granite test sample immersion in simulant (assay performed in triplicate and with a blank without granite test sample)	40ºC ± 2ºC 10 days	Dryness evaporation of the simulant and gravimetric analysis.
20% ethanol dissolution			

Figure 1.Global migration assay after dryness evaporation. From left to right: blank and three samples results after assay with granite test samples (samples 1, 2 y 3).

3.2.2 Specific Migration of Heavy Metals of Interest Pb and Cd

The performance of Pb and Cd migration assays was conducted based on *RD 891/2006 of 21st of July 2006*, which approves the sanitary technical standards applicable to ceramic objects for food use.

The conditions considered for this are:

Table 3.Specific Migration Assays of Heavy Metals of Interest (Pb/Cd).

Simulant	Procedure	Conditions	Analysis
4% Acetic acid dissolution	Granite test sample immersion	22ºC ± 2ºC 24 hours	ICP-MS quantitative of Magnetic Sector ELEMNT2 of ThermoFinnigan

3.2.3 Specific Migration of Elements of Interest

Specific migration studies for food simulants B and C have been carried out determining the following elements: Cu, Ag, K, Mg, B, Br, Na, Ca, Zn, Hg, Cd and Pb.

Two types of migration assays have been carried out depending on the simulant used. The following table shows the parameters under which this specific migration assays have been carried out.

Table 4.Specific Migration Assays of Elements of Interest.

Simulant	Procedure	Conditions	Analysis
4% acetic acid dissolution	Granite test sample immersion in simulant (assay carried out in triplicate and with a blank without granite test sample)	40ºC ± 2ºC 10 days	ICP-MS quantitative of Magnetic Sector ELEMNT2 of ThermoFinnigan
20% ethanol dissolution			

3.2.4 Specific Migration of Wine Sample

Analysis of typical components of wine have been carried out to determine its quality. In particular, methanol, ochratoxin A and ethyl carbamate have been evaluated. For a correct result, these compounds should not be modified for the wine container. For its determination, specific migration studies of granite test samples have been carried out in the wine and have been compared to wine samples subjected to the same assay conditions, but without granite test samples.

The migration procedure employed has been the same previously described for the case of global and specific migration, but using wine instead of food simulant. Based on this, the conditions employed have been the following:

Table 5.Specific Migration Assays for wine: sulphates determination, ochratoxin A, ethyl carbamate and methanol.

Simulant	Procedure	Conditions	Analysis
Wine provided by the enterprise	Granite test sample immersion in simulant and compared with wine blank without test sample	40ºC ± 2ºC 10 days	Sulphates (gravimetric method) Ochratoxin A Ethyl carbamate Methanol

A specific migration procedure has been carried out in duplicate and with additional blank.

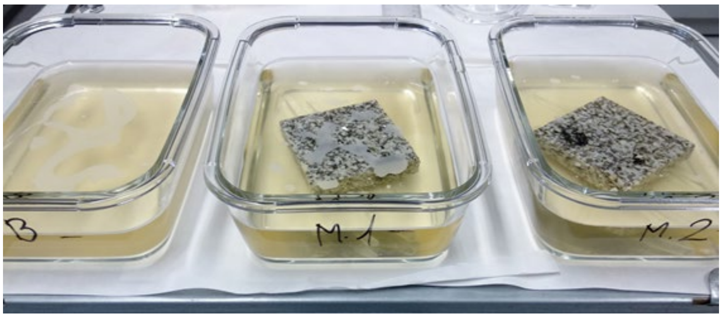

Figure 2. Migration assay in wine.

The particular analysis-procedures for each component are compiled below.

3.2.4.1. Sulphates determination

Sulphates determination (K_2SO_4) has been carried out by gravimetric techniques.

3.2.4.2. Ochratoxin A determination

Ochratoxin A determination has been carried out by using high performance liquid chromatography (HPLC) by immunoaffinity.

3.2.4.3. Ethyl carbamate determination

Ethyl carbamate determination has been carried out by gas chromatography coupled to mass spectrometry (GC/MS).

Basis

It is done by injecting:

- Direct sample diluted to 40% vol. (dry extractive lower than 20 g/L),
- An extractive obtained with ether,
- An extractive obtained after an adsorption process with dichloromethane in a solid phase extraction column,

in a chromatograph coupled to mass spectrometer with ionization source by electronic impact, in acquisition mode SIM (selected ion monitoring) or FS (full scan).

Reactives

- Ethyl carbamate
- Internal standard: propyl carbamate, butyl carbamate or deuterated ethyl carbamate
- Pure ethanol
- Ultrapure water
- Dichloromethane
- Ether
- Sodium sulphate

Sample preparation

Samples are diluted to 40% vol. with water or ethanol.

Spirits procedure with dry extractive < 20 g/L

A solution is prepared in 10 mL flask to inject in the chromatograph:

- adding 200 µL of internal work, which concentration is 10 mg/L,
- use a volumetric flask to reach the indicated volume with the calibration solution or with the sample diluted to 40% vol.

Internal standard concentration of this solution (200 µg/L) can be adjusted in function of ethyl carbamate concentration of the medium employed.

Calculation

The responsive factor (RF) is employed. This factor is obtained from the reference solution:

$$RF = \frac{A_{PI}/C_{PI}}{A_{SP}/C_{SP}}$$

where:

A_{PI} is the pic area corresponding to internal standard, and C_{PI} is its concentration;

A_{SP} is the pic area corresponding to ethyl carbamate of standard solution, and C_{SP} is its concentration.

Once calculated RF, samples concentration is calculated:

$$C = F_{conc.} \times RF \times C_{PI} \times \frac{A}{A_{PI}}$$

where: C is the sample concentration, A is the pic area, and $F_{conc.}$ is the concentration factor of an occasional dilution.

4 RESULTS

Results evaluation has been carried out considering that the International organization of the vineyard and the wine fixes the acceptable limits as follows:

Table 6. Acceptable limits of the parameters considered for the assays.

Parameter	Maximal concentration
Cadmium	0.01 mg/L
Methanol	250-400 mg/L depending on the type of wine
Ochratoxin A	2 µg/L
Lead	0.15 mg/L
Sulphates	1-2.5 g/L depending on the type of wine
Ethyl carbamate	180 µg/L
Boron	80 mg/L
Bromine	1 mg/L
Copper	1 mg/L
Silver	<0.1 mg/L
Sodium	80 mg/L
Zinc	5 mg/L

The results obtained for each of the studies performed are compiled below.

4.1 GRANITE TEST SAMPLE CHARACTERIZATION

In the next sections, the results obtained for each procedure carried out are shown.

4.1.1 Chemical Composition Determination

Chemical composition determination of granite has been performed by using a fluorescence spectrophotometer model S4 Pioneer (Bruker-AXS), Muffle Carbolite, Analytical balance XP-205 (mettler-Toledo), thought a multi-element vacuum analysis.

The next table compiles all the results obtained from the determinations of chemical composition of granite test samples conducted. Next, Table 3 includes a comparison of the composition determinations conducted for the granite test samples with the results obtained in previous analysis of the same sample typology is carried out.

Table 7.Chemical composition determination of granite by fluorescence spectrophotometry for all the offers, expressed in %.

Sample		SiO_2	Al_2O_3	K_2O	Na_2O	CaO	P_2O_5	MgO	TiO_2	BaO	Rb_2O	MnO	ZnO	ZrO_2	SrO	CuO
20171124_2_Sample1 [OF17-0039]	%	68.6	16.6	6.7	3.8	0.92	0.62	0.39	0.23	<0.020	0.044	0.028	---	0.013	0.011	0.008
	Typical Deviation	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
20171124_2_Sample2 [OF17-0039]	%	72.7	14.7	5.6	3.3	0.77	0.53	0.34	0.2	<0.020	0.037	0.025	---	0.012	0.009	0.007
	Typical Deviation	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
20180418_1 [OF18-0020]	%	68.2	16.7	7.0	3.4	1.2	0.42	0.48	0.39	0.065	0.046	0.019	0.016	0.023	0.02	0.006
	Typical Deviation	0.1	0.1	0.1	0.1	0.1	0.01	0.01	0.01	0.002	0.001	0.001	0.001	0.002	0.001	0.001
20180418_2 [OF18-0020]	%	68.5	16.4	7	3.2	1.2	0.42	0.52	0.4	<0.020	0.048	0.016	0.016	0.024	0.022	0.008
	Typical Deviation	0.1	0.1	0.1	0.1	0.1	0.01	0.01	0.01	<0.020	0.001	0.001	0.001	0.001	0.001	0.001
20180418_3 [OF18-0020]	%	68.7	16.4	6.7	3.4	1.2	0.43	0.46	0.37	0.067	0.045	0.014	0.014	0.023	0.02	0.007
	Typical Deviation	0.1	0.1	0.1	0.1	0.1	0.01	0.01	0.01	0.002	0.001	0.001	0.001	0.001	0.002	0.001
18ME49_Sample11 [OF18-0071]	%	69.8	15.7	7.0	3.1	1.0	0.5	0.5	0.3	<0.020	0.045	0.018	0.013	0.021	0.016	---
	Typical Deviation	0.1	0.1	0.1	0.1	0.1	0.01	0.01	0.01	<0.020	0.001	0.001	0.001	0.001	0.001	---

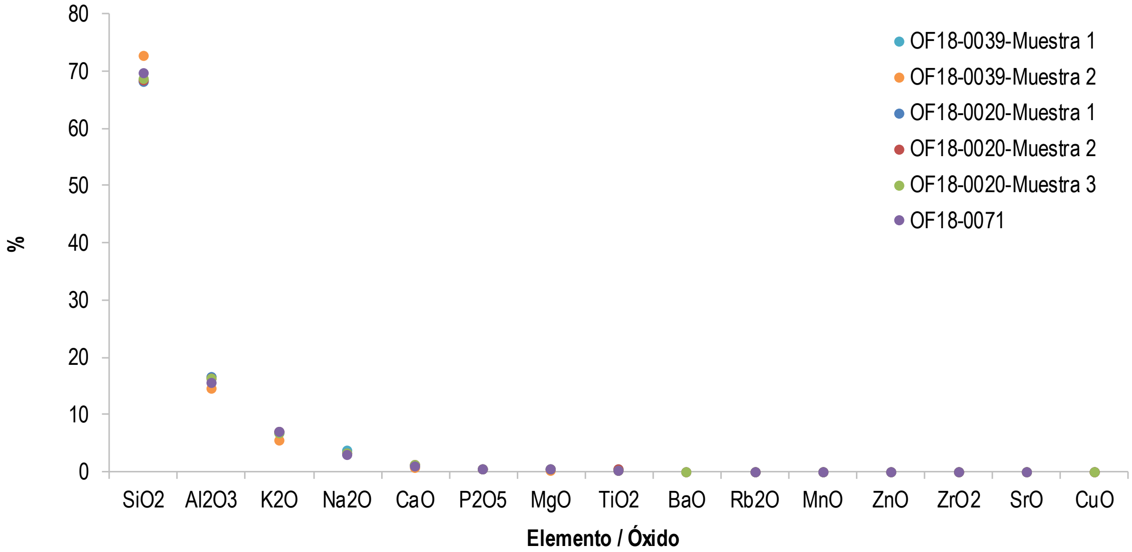

Figure 3. Graphic representation of the determination of the granite chemical composition for all the samples analysed up to now.

4.1.2 Radon Determination

The measurements of radon concentration in continuous mode have been carried out, as indicated previously, employing a multiparameter monitor and a gas-tight nylon chamber.

The results obtained are compiled in the following table:

Table 8. Determination of the exhalation concentration of granite gas radon expressed as (Bq/m² *s)

Offer	Sample	^{222}Rn (Bq/m² *s) Exhalation
OF17-0039	*20171215_1_Sample1*	1.13 E-04 ± 7.75 E-05

4.2 GLOBAL MIGRATION

Global migration determination is carried out by gravimetric methods, as previously indicated.

Table 9 summarizes all the data and results about global migration carried out in two kinds of simulant:

- OF17-0039: Food simulant type B (4% acetic acid dissolution)
- OF18-0071: Food simulant type C (20% ethanol dissolution)

Global migration results are expressed for individual samples and as average with standard deviation.

Table 9. Results of the global migration determination expressed as average for individual test samples.

Offer	Sample	Weight test sample assayed (g)	Global migration ($mg_{migrated}/mg_{simulant}$)	Global migration ($mg_{migrated}/Kg_{sample}$)
OF17-0039	*Blank*	---	---	---
	20171124_1_Sample4	70.76240	0.34615	826.71
	20171124_1_Sample5	67.62929	0.330178	825.09
	20171124_1_Sample6	69.02584	0.33136	811.29
OF18-0071	*Blank*	---	---	---
	18ME49_Sample1	65.82896	$3.48x10^{-05}$	$9.11x10^{-05}$
	18ME49_Sample2	66.82852	$2.91x10^{-05}$	$7.48x10^{-05}$
	18ME49_Sample3	66.39710	$2.91x10^{-05}$	$7.53x10^{-05}$

Table 10. Results of the global migration determination.

Offer	Simulant		Global migration ($mg_{migrated}/mg_{simulant}$)	Global migration ($mg_{migrated}/Kg_{sample}$)
OF17-0039	**4% Acetic Acid**	*Average*	0.33590	821.03
		Standard Deviation	0.00890	8.4729
OF18-0071	**20% Ethanol**	*Average*	$3.10x10^{-05}$	$8.04\ x10^{-05}$
		Standard Deviation	$3.28\ x10^{-05}$	$0.93\ x10^{-05}$

4.3 SPECIFIC MIGRATION OF HEAVY METALS OF INTEREST

The next table compiles the results of the migration assays of lead and cadmium, obtained by Magnetic Sector ICP-MS ELEMENT2 of Thermo Finningan after specific migration.

Table 11. Results of Cd and Pb determination by ICP-MS.

Offer	Sample	Weight test sample (g)	Cd (µg/L)	Pb (µg/L)
OF17-0039	*Blanco*	---	< 0.1	0.5
	20171124_1_SAMPLE1	70.61564	2.8	25
	20171124_1_SAMPLE2	66.88589	1.6	24.7
	20171124_1_SAMPLE3	69.69582	1.8	24.6
	Average	---	***2.1***	***24.8***
	Error	---	*0.643*	*0.208*

As compiled in table 6, limits of maximal concentration established for these compounds are **10 µg/L** for the cadmium and **150µg/L** for the lead. Therefore, the results obtained are lower than established limits in all the cases.

4.4 SPECIFIC MIGRATION

After specific migration assays, quantitative determination of Cu, Ag, K, Mg, B, Br, Ag, Na, Ca, Zn, Hg, Cd and Pb has been carried out by Magnetic Sector ICP-MS ELEMENT2 of Thermo Finnigan.

The nest tables compile the results of specific migration assays carried out in two types of simulant:

- OF17-0039: Simulant of dissolution of 4% acetic acid
- OF18-0071: Simulant of dissolution of 20% ethanol

The results of specific migration are expressed for individual samples and as average with standard deviation.

Table 12. Results of specific migration: Quantitative determination of metals expressed as µg/L for individual samples.

Offer	Sample	Ag	B	Ca	Cd	Cu	Hg	K	Mg	Na	Pb	Zn	Br
OF17-0039	***Blank***	<5.0	35	272	<0.25	<1.25	0.126	36	<50	178	<0.5	31	<50
	20171124_1_Sample7	<5.0	55	31417	9.9	58.4	<0.050	3219	6432	1862	57	952	<50
	20171124_1_Sample8	<5.0	67	29244	6.6	51.3	<0.050	3325	6397	2132	80	823	<50
	20171124_1_Sample9	<5.0	29	31021	6.7	51.0	<0.050	3235	5894	1880	81	817	<50
OF18-0071	***Blank***	<5.0	19	<75	<0.25	<1.25	<0.05	33	<50	85	<0.5	<5.0	<50
	18ME49_Sample6	<5.0	47	398	<0.25	<1.25	<0.05	536	226	567	<0.5	<5.0	<50
	18ME49_Sample7	<5.0	35	446	<0.25	<1.25	<0.05	501	236	564	<0.5	<5.0	<50
	18ME49_Sample8	<5.0	32	397	<0.25	<1.25	<0.05	583	226	622	<0.5	<5.0	<50

Table 13. Results of specific migration: Quantitative determination of metals measured as average µg/L and standard deviation between granite samples.

Offer	Sample	Ag	B	Ca	Cd	Cu	Hg	K	Mg	Na	Pb	Zn	Br
OF17-0039	*Average*	<5.0	50.3	30560.7	7.7	53.6	<0.05	3259.7	6241	1958	72.7	864	<50
	Standard deviation	<5.0	19.4	1157.3	1.9	4.2	<0.05	57.1	301.0	150.9	13.6	76.3	<50
OF18-0071	*Average*	<5.0	38	414	<0.25	<1.25	<0.05	540	229	584	<0.5	<5.0	<50
	Standard deviation	<5.0	7.9	28.0	<0.25	<1.25	<0.05	41.1	5.77	32.6	<0.5	<5.0	<50

Table 14 below shows acceptable limits for most of the parameters considered in the migration assays. The comparative of the results obtained for specific migration of the different metals in the food simulants considered, with the previous acceptable limits, reveals that all the metals are under the acceptable limits of the International Organization of the vineyard and the wine (OIV).

Table 14. Comparative of the results obtained with OIV's acceptable limits and with normal values of concentration.

Metals	Normal Values (µg/L)	ENONATURA Acceptable Limits (µg/L)	Results (µg/L)	Results (µg/L)
Ag	3-10	<100	<5.0	<5.0
B	18000-30000	80000	50.3	38
Ca	37000-139000	---	30560.7	414
Cd	1-10	10	7.7	<0.25
Cu	10-280	1000	53.6	<1.25
Hg	<1-1.4	---	<0.050	<0.05
K	300000-1400000	---	3259.7	540
Mg	30000-77000	---	6241	229
Na	6400-44800	80000	1958	584
Pb	<1-100	150	72.7	<0.5
Zn	5000	5000	864	<5.0
Br	200-4000	1000	<50	<50

Note: normal values listed in the table are based in the bibliographic search conducted about recommendations of the parameters carried out in wine.

4.5 MIGRATION IN WINE AS SIMULANT

Compounds of greatest interest for the Enterprise in the wine contained in a granite receptacle are:

- Sulphates
- Ochratoxin A
- Ethyl carbamate
- Methanol

Sample standards used for this assay have been the ones indicated in the next table:

Table 15. Data of the assay carried out.

Offer	Granite test sample	Weight (g)	Wine Sample	Simulant (mL)
OF17-0039	*Blank*	---	Aging over Lías. Santiago Roma. Selection 2017. Cuba 17	500
	20171124_2_Sample3	246.97	Aging over Lías. Santiago Roma. Selection 2017. Cuba 17	500
	20171124_2_Sample4	252.13	Aging over Lías. Santiago Roma. Selection 2017. Cuba 17	500

Below, the results corresponding to the analyses are compiled.

4.5.1 Sulphates

Sulphates determination (K_2SO_4), carried out gravimetrically, showed the next results for the samples studied.

Table 16. Results of the sulphates determination.

Offer	Sample	Sulphates (g/L)
OF17-0039	Blank	<1.5
	20171124_2_Sample3	< 1.5
	20171124_2_Sample4	< 1.5

According to the World Health Organization (WHO), the maximum acceptable concentration is between 1-2.5 g / L. Therefore, quantified values are quantitatively lower than that limit.

4.5.2 Ochratoxin A

Ochratoxin A determination, carried out by immunoaffinity by HPLC, showed the next results for the samples evaluated:

Table 17. Results of the ochratoxin A determination.

Offer	Sample	Ochratoxin A (µg/L)
OF17-0039	Blank	< 0.05
	20171124_2_Sample3	< 0.05
	20171124_2_Sample4	< 0.05

According to the World Health Organization (WHO), the maximum recommended concentration of ochratoxin A is 2 µg/L, so the quantified values are quantitatively lower to that limit.

4.5.3 Ethyl Carbamate

Ethyl carbamate determination has been carried out by gas chromatography coupled with mass spectrometry (GC/MS), as indicated in the section 3 on this report. Below, the results obtained are compiled.

Table 18. Results of ethyl carbamate determination.

Offer	Sample	Ethyl carbamate (µg/L)
OF17-0039	Blank	< 15
	20171124_2_Sample3	< 15
	20171124_2_Sample4	< 15

According to the World Health Organization (WHO), this carcinogenic and genotoxic agent should not exceed **180 µg/L.**

4.5.4 Methanol

Methanol determination, carried out by gas chromatography, showed the next results:

Table 19. Results of the methanol determination.

Offer	Sample	Methanol (mg/L)
OF17-0039	**Blank**	48
	20171124_2_Sample3	48
	20171124_2_Sample4	41

According to the World Health Organization (WHO), methanol presents the next maximum concentration depending on the type of wine:

- **400 mg/L** → for red wine
- **250 mg/L** → for White and rosé wine

5 CONCLUSIONS

The different determinations carried out, which partial conclusions have been compiled throughout the previous sections, have revealed that the compounds of interest are within acceptable limits according to OIV or within normal values for wine.

For specific cases as **radon,** there are not normative or interesting values to establish a comparative.

The conclusions obtained in the fulfilment of determinations of migration, composition and other compounds of interest, indicates that the analysed parameters are below the acceptable limits of OVI's wine substances, and the conclusion of **acceptable limits** for the samples can be established.

Global and specific migration assays deserve special mention, which have been determined under two types of simulants (4% acetic acid and 20% ethanol). The results obtained for both simulants indicate that analysed compounds of interest are within acceptable limits according to OIV or within normal values for wine.

In the light of these results, and based on the normative, such as the *Regulation 1935:2004 of the European parliament and of the council of 27th of October 2004, on materials and articles intended to come into contact with food*, it is estimated that the evaluated barrels could be considered as **inert materials**. The fundaments considered in this case are that:

- The stone and, specifically granite, has been historically one of the selected materials to use in systems of wine elaboration.

- The Regulation of reference establishes in Paragraph 3 that the underlying principle of the whole legal framework is that "*any material or article intended to come into contact directly or indirectly with food must be sufficiently inert to preclude substances from being transferred to food in quantities large enough to endanger human health or to bring about an unacceptable change in the composition of the food or a deterioration in its organoleptic properties*". Based on the analysis carried out, those provisions are satisfied.

- In addition, and, due to the definition of both concepts and the nature of the stone, it should not be considered as active or intelligent material.

On this basis, the suitability of considering the stone as inert material is established.

Rosalía Noguerol Cal
Manager
Advanced Materials Area
M: +34 604007585
T: +34 881 105 624 (Ext. 1)
rnoguerol@cetim.es

CETIM Technological Centre

Parque Empresarial de Alvedro, calle H, 20.
15810 Culleredo, A Coruña, Spain

+34 881 105 624 | info@cetim.es | www.cetim.es