LABORATORIO TECNOLÓGICO DEL URUGUAY

SIM.QM-S11 / SIM.QM-P25

Supplementary Comparison for elements in Yerba mate (*Ilex paraguariensis*)

Study Protocol

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1. INTRODUCTION

Yerba mate (*Ilex paraguariensis*, Aquilfoliaceae) is a native plant which grows in the subtropical regions of South America: Paraguay, Brazil, Argentina and Uruguay. It is consumed as an infusion called “mate” in the beforementioned countries as well as all around the world as tea. Due to safety reasons the mass fraction of arsenic and cadmium is constantly monitored. Besides, the mass fraction of nutrients as sodium and phosphorus is also measured for labeling purposes.

The aim of this comparison is to enable NMIs/DIs to demonstrate their competence in the determination of elements at low and high levels in a vegetal material within the high silica content category.

2. TIMELINE

Sample preparation:	October, 2019
Homogeneity Testing:	April, 2020
Stability Testing:	October, 2020
Distribution of protocol and questionnaire:	December, 2020
Call for participation:	April, 2021
Registration deadline:	May, 2021
Distribution of samples:	July, 2021
Deadline for submission of results:	October, 2021
Preliminary discussion of results:	November, 2021

Table1: Timeline

3. MESURANDS

Analyte and expected mass fraction (on a dry mass basis)

As: 0,02 – 1 mg/kg

Cd: 0,1 – 5 mg/kg

Na: 1 – 100 mg/kg

P: 500 – 5000 mg/kg

4. STUDY MATERIAL

4.1 Preparation

Several packs of yerba mate (*Ilex paraguariensis*) from the sample number batch lot with suspected contamination were purchased from the local market. Determinations were performed and its was confirmed that the sample contain arsenic and cadmium in quantifiable mass fractions. The sample was dried in a convection oven at 100ºC for 4 hours. After that, it was firstly grinded using a knife miller, in a second step using an ultra-centrifugal miller (particle size approx. 80μm) and thorough mixed. The obtained powder was bottled into a glass amber pre-cleaned bottled. Each bottle contains approx. 25 g of material. A preliminary microbiological study studied showed undetectable (< 10 UFM/g) quantities of aerobic mesophilic as well as yeast and mold. Nevertheless, the material was γ-irradiated with a dose of 23 kGy to ensure sterilization.

4.2 Recommended Minimum sample amount

The recommended minimum sample amount for analysis is at least 0,5g.

4.3 Dry mass determination

The dry mass correction determination must be performed on a minimum of three separate portions of 1 g each. Samples must be dried in an air-forced oven at 103±2ºC for 2 hours. After cooling and weighting, introduce the samples again in the oven for one hour and repeat this step until constant mass. Constant mass is achieved when de difference between weights is less than 0,002g. In general, constant mass is attained in the first 3 hours.

4.4 Homogeneity Assessment of Study Material

The homogeneity study was carried out according to ISO GUIDE 35:2017, using one-way ANOVA. Ten bottles were selected: the first one, the last one and the rest by stratified random sampling.
Determination of Cd was performed by ID-ICP-SFMS, As by SA-ICP-SFMS and Na and P by SA-ICP-OES in three subsamples per bottle.

Results of *F*-Test are shown in the following table:

Element	F	F-critical
Arsenic	2,20	2,39
Cadmium	0,96	2,39
Sodium	1,67	2,39
Phosphorus	1,75	2,39

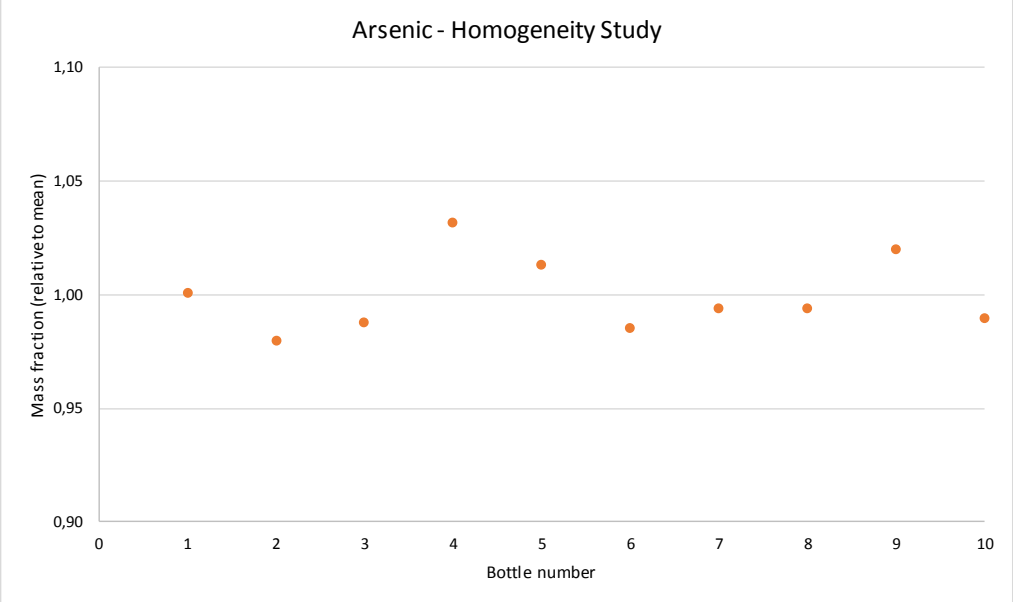
Table 2: Homogeneity *F*-Test Results

It can be concluded that analytes in the sample did not show significant inhomogeneity.

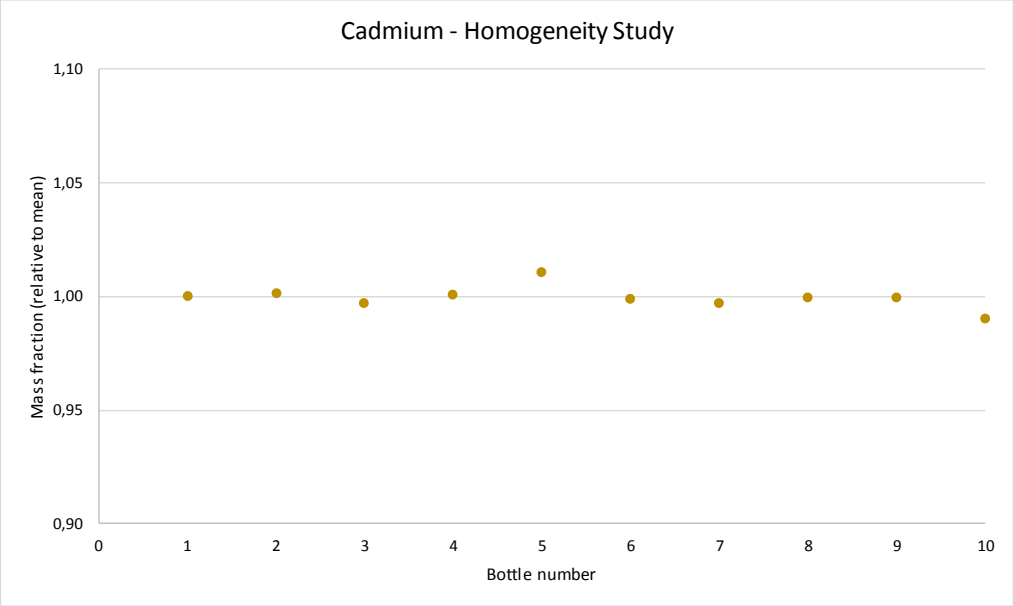
It the next table, variability figures are shown:

ANOVA Estimate	Arsenic	Cadmium	Sodium	Phosphorus
Within-packet, CV_{wth}:	2,9%	0,88%	0,46%	0,54%
Between-packet, CV_{btw}:	2,0%	0,90%	0,28%	0,72%
Total analytical variability, CV:	2,3%	0,89%	0,33%	0,60%

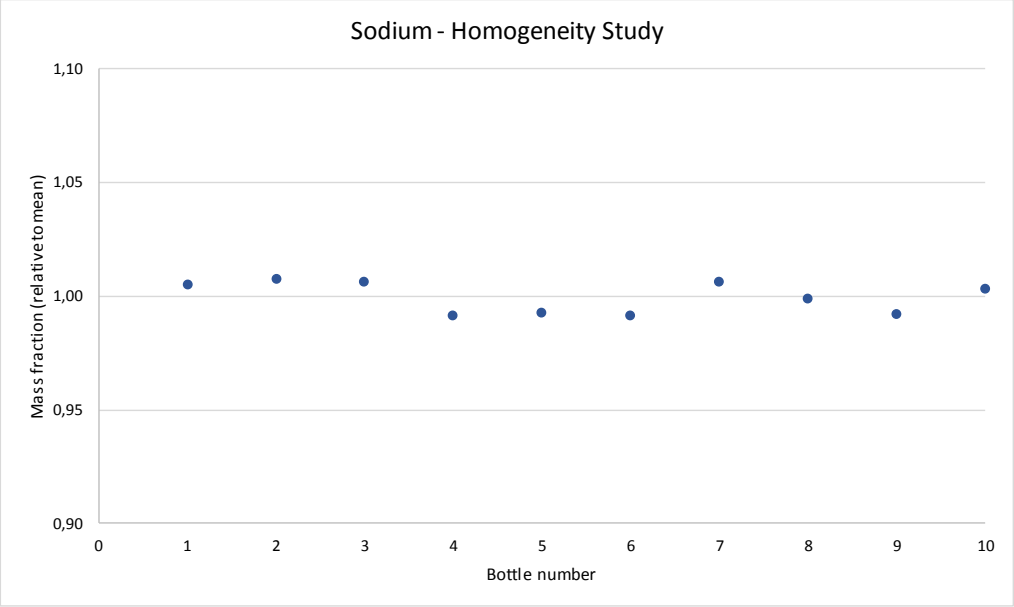
Table 3: Homogeneity ANOVA Results



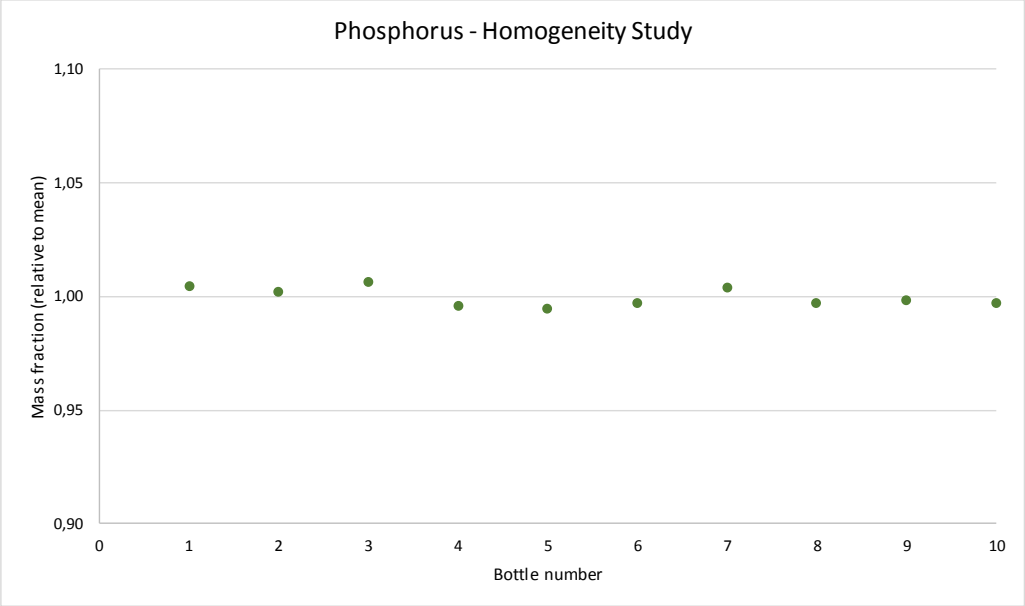
Graph 1: Homogeneity - Arsenic results per bottle



Graph 2: Homogeneity - Cadmium results per bottle



Graph 3: Homogeneity - Sodium results per bottle



Graph 4: Homogeneity - Phosphorus results per bottle

4.5 Stability Assessment of Study Material

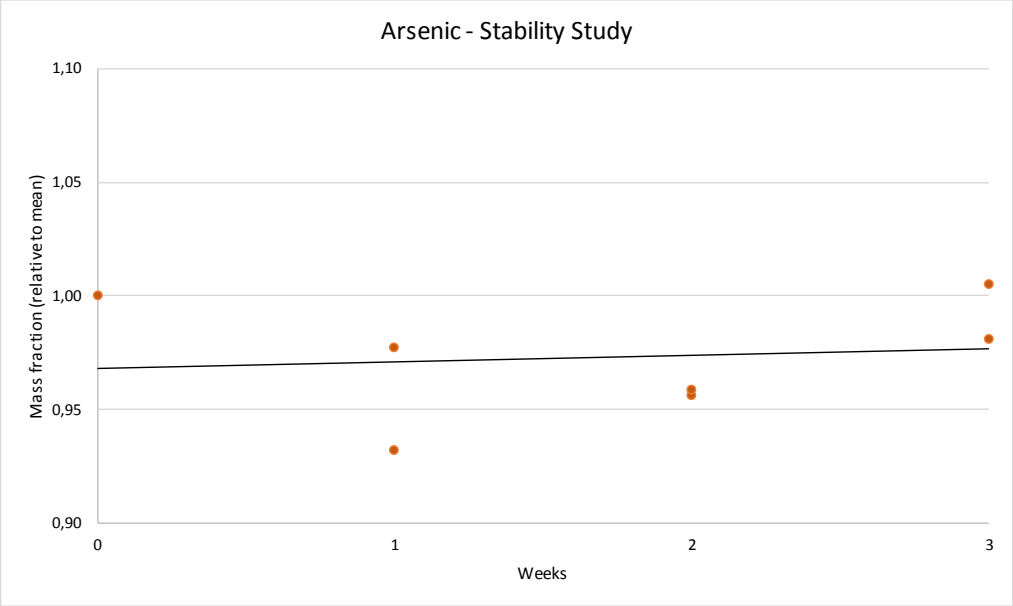
To evaluate a possible sample's instability during transportation due to temperature effect, an isochronous study designed for a period of three weeks at 40 °C was carried out. Two bottles were removed from the oven each week. Determination of Cd was performed by ID-ICP-SFMS, As by SA-ICP-SFMS and Na and P by SA-ICP-OES on three subsamples per bottle.

The following acceptance criteria was applied:

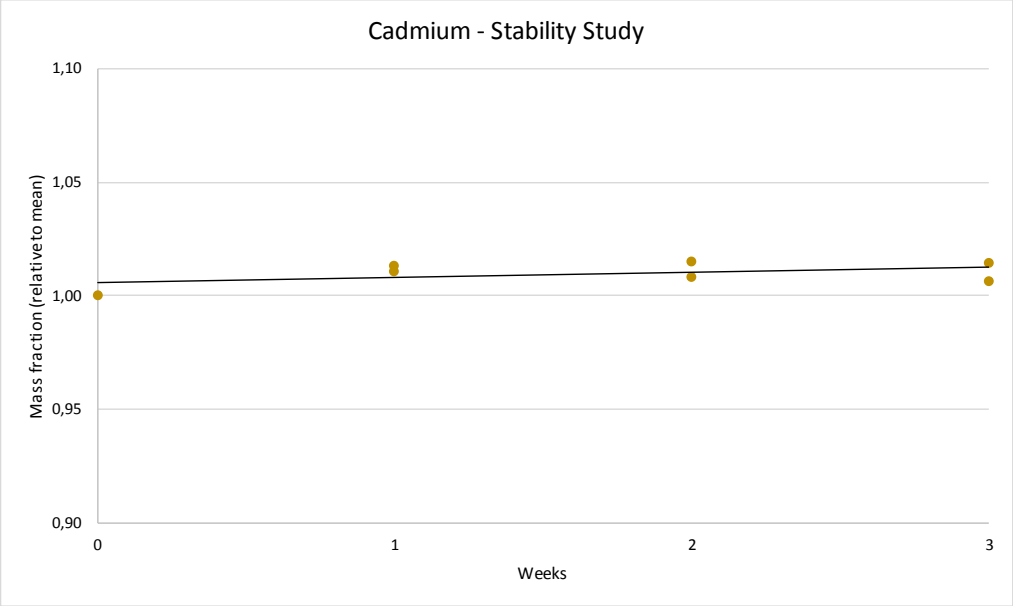
$|b| < t_{0,95};n-2*s'b$, where

- b, slope
- s'b, slope uncertainty
- n, number of time intervals

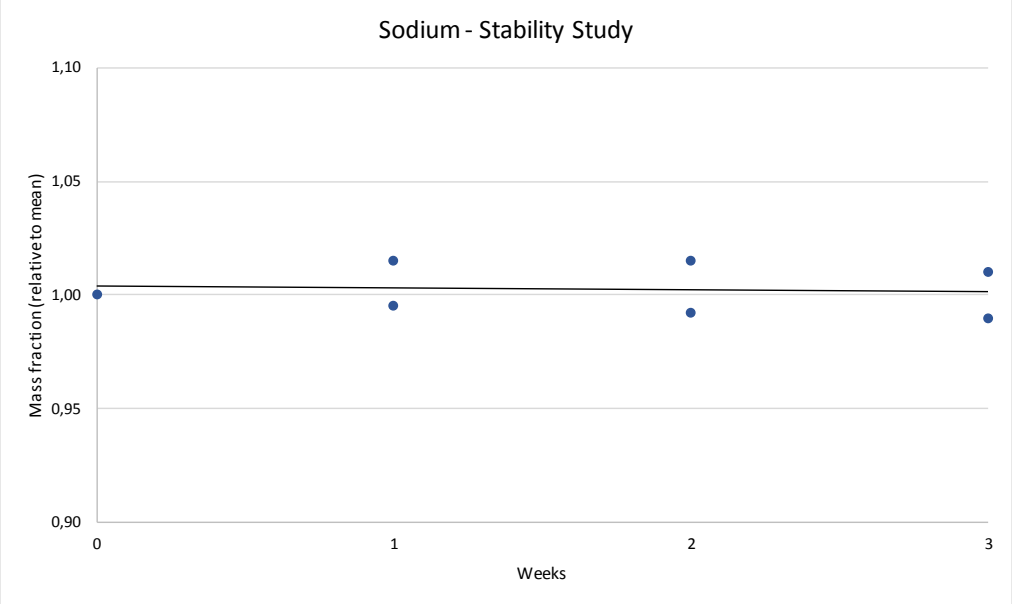
It can be concluded that analytes in the sample did not show significant instability after being exposed at 40°C for 3 weeks.



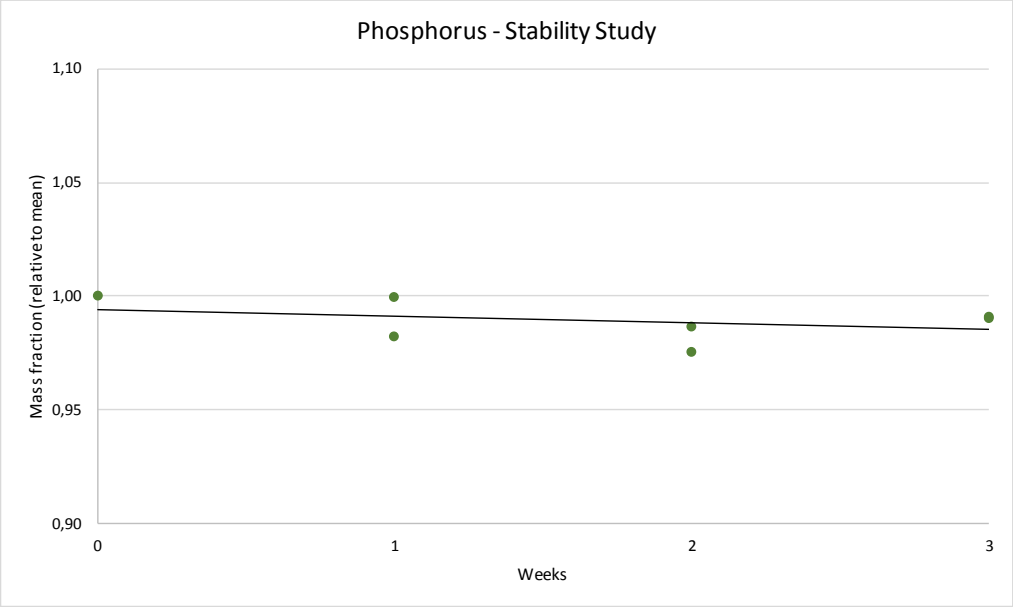
Graph 5: Stability study – Arsenic



Graph 6: Stability study - Cadmium



Graph 7: Stability study – Sodium



Graph 7: Stability study - Phosphorus

Long term stability studies will be carried out during the comparison schedule. Bottles which are storage at room temperature will be selected. Determination will be performed and data will be evaluated as for short-term stability studies.

5. Instructions and sample distribution

A bottle containing 30 g of material will be sent to participants. A temperature label indicator will be attached the bottled to establish whether or not the maximum temperature has been reached during transportation. The material must be storage at room temperature, between 18 and 25 °C. Participants will be asked to return the sample receipt form that will be provided in due time.

6. Reporting of results

The final results should be returned to the coordinator lab using the supplied reporting template.
All participants must include:

- Final results and uncertainty budget, reported as mg/kg on a dry mass basis, from at least 5 independent replicate measurements.
- A detailed description of the sample preparation methods, analytical techniques, calibration approach and any correction applied.

7. Use of SIM.QM-SXX in support of calibration and measurement capability (CMC) claims

7.1 How far the light shines

Successful participation in this supplementary comparison will help demonstrate capabilities for the determination of elements in plants and other high silica content related materials.
It will support CMCs in the groups:

- Arsenic: Metalloids and semi-metals at mass fraction levels above 20 µg/kg.
- Cadmium: Transition elements at mass fraction levels above 50 µg/kg.
- Phosphorus: Non-metals (except: C, O, N) at mass fraction levels above 50µg/kg.
- Sodium: Alkali and alkaline earth elements at mass fraction levels above 50µg/kg.

7.2 Core Capability table

Analyte groups	Matrix challenges						Calibration materials and solutions
	Water/aqueous	High Silica content (e.g. Soils, sediments, plants, ...)	High salts content (e.g. Seawater, urine, ...)	High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, ...)	Difficult to dissolve metals (Autocatalysts, ...)	High volatile matrices (e.g. solvents, fuels, ...)	
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)		Na					
Transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ag, Cd, Ta, W, Au, Hg, Al, Ga, In, Tl, Pb, Po)		Cd					
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)							
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)		As					
Non-metals (P, S, C, N, O)		P					
Halogens (F, Cl, Br, I)							
Rare Earth Elements (Lanthanides, Actinides)							
Inorganic species (elemental, anions, cations)							
Small organo-metallics							
Proteins							
Nanoparticles							

Low level (e.g. below 50 µg/kg)

High level (e.g. above 50 µg/kg)

8. Contact Details

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9. References

International Organization for Standardization. (2017). Reference materials – Guidance for characterization and assessment of homogeneity and stability (ISO/GUIDE 35).