Occurrence of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb and Zn in Rice (*Oryza sativa L.*) produced in Uruguay

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Uruguay has emerged as medium-size rice producer and Latin America's major rice exporter, and is now amongst the world's top ten. Although it is a great producer of rice, dietary intake surveys in Uruguay showed a consumption of 10Kg per capita/year, lower than the consumption of Asia (81Kg/year), but higher than that in Europe (3Kg/year) and far below Brazil which is the major consumer of the region with a consumption per capita of 39Kg/year.
Since rice is a staple food consumed world wide, its nutritional vs. toxic composition is of special interest. Thus, the knowledge of toxic as well as micronutrient elements is very important. Here is reported the analysis of forty nine samples of rice (*Oryza sativa L.*) cultivated in Uruguay were selected for this study. The samples were in form of brown, milled, parboiled milled and parboiled brown rice.
The amount of all the metal ions studied in this work fall within the typical range of rice around the world.

For the determination of metal ions in rice, Atomic Absorption Spectrometry (AAS) is probably the technique most widely used, because of its versatility, precision and accuracy. AAS determinations are usually made by Flame Atomic Absorption Spectrometry (FAAS) when the concentrations are high enough, and for those elements which low limits of detection are required the determination is performed with a more sensitive technique, then Electrothermal Atomization Atomic Absorption Spectrometry (ETA-AAS) is generally recommended and Cold Vapor AAS (CV-AAS) for Hg analysis.

Experimental:
For the determination of As, Cd, Cr and Pb **by ETA-AAS in samples digested by dry ashing. Dry ashing of rice samples was performed in a multiplace mineralization block (Tecator Digestion System 20, 1015 Digester) ?????**
Microwave oven (Milestone MLS 1200 MEGA) digestion was performed in rice samples in order to analyse Ca, Co, Cu, Fe, K, Hg, Mg, Mo, Mn, Na, Ni and Zn.
For the determination of mercury analyte additions were performed before digestion and the microwave oven digestion.
A Perkin-Elmer® Model 5000 atomic absorption spectrometer equipped with an HGA-500 graphite furnace, MHS-10 hydride generation system, and deuterium background correction was used. Graphite furnace and flame setting are listed in table 1. and 2. respectively.

Table I. Instrumental Conditions and Furnace Program for the Determination of As, Cd, Cr and Pb

	As	Cd	Cr	Pb
Wavelength (nm)	193.7	228.8	357.9	283.3
Spectral Bandwidth (nm)	0.7	0.7	0.7	0.7
Drying (°C)	110	110	110	110
Ashing (°C)	900	250	1200	450
Atomization (°C)	2700	2100	2700	2300
Cleaning (°C)	2700	2700	2700	2700
Sample Injection (µL)	50	10	50	50

Background Correction	D_2 Lamp	D_2 Lamp	D_2 Lamp	D_2 Lamp
Measurement Mode	Peak area/height	Peak area/height	Peak area/height	Peak area/height

Table II. Instrumental parameters for Flame AAS determinations

	Ca[a]	Co	Cu	Fe	K[b]	Mg[a]	Mo	Mn	Na[b]	Ni	Zn
λ (nm)	422.7	240.7	324.8	248.3	769.9	285.2	313.3	279.5	589.0	231.1	213.9
H Slit (nm)	0.7	0.7	0.7	0.2	1.4	0.7	0.7	0.7	0.7	0.2	0.7
Flame type	AAOF	AAOF	AAOF	AAOF	AAOF	AAOF	NOARF	AAOF	AAOF	AAOF	AAOF
Range (mg/L)	0.2-5.0	0.02-1.0	0.003-1.0	0.1-5.0	2.0-30	0.2-4.0	0.2-5.0	0.01-1.0	1.0-8.0	0.1-2.0	0.004-1.0
BG		D_2 Lamp		D_2 Lamp						D_2 Lamp	D_2 Lamp

AAOF=air-acetylene oxidizing flame, NOARF= nitrous oxide-acetylene reducing flame, BG= Background correction.
[a] 0,1% La_2O_3 was used to control the signal depression caused by some elements
[b] 0,1 % CsCl was used as ionization buffer

Results:
The metal ion composition of brown, milled, parboiled milled and parboiled brown rice is listed in table III. and was calculated on wet basis to allow comparison with literature data of the product when purchased.
The concentration of all the elements studied in this survey fall within the typical range of rice from around the world

Table III. Metal content in different forms of rice produced in Uruguay

	Units	Brown	Milled	Parboiled Brown	Parboiled Milled	LOD	Certified reference Material (%)	Recovery (%)
As	µg/Kg	< LOD	< LOD	< LOD	< LOD	50		87±12
Ca	mg/100g	9.1±1.4	15±1.8	10±1.3	10±1.2	0.010	99±10	95.3±8.9
Cd	µg/Kg	3.43±0.68	4.12±0.72	2.30±0.69	3.75±0.66	1.0		106.2±7.7
Co	µg/Kg	57±11	41±15	59.6±8.4	50±10	20		103.3±6.5
Cr	µg/Kg	< LOD	< LOD	< LOD	< LOD	5.0		89.4±8.1
Cu	mg/Kg	1.80±0.16	1.52±0.16	1.45±0.15	1.33±0.16	0.010	95.2±8.4	99.3±4.6
Fe	mg/Kg	7.14±0.64	7.15±0.66	5.90±0.71	4.41±0.77	0.050	89±11	103±10
Hg	µg/Kg	< LOD	< LOD	< LOD	< LOD	1.0		96.3±9.3
K	mg/100g	217.3±4.9	167±5.6	210.6±3.7	167.2±5.8	0.10	99.4±8.4	95.4±5.7

Mg	mg/100g	121±11	46.4±5.5	116±13	45.4±5.9	0.050	91.3±7.7	98.3±8.0
Mo	mg/Kg	0.82±0.21	0.97±0.19		0.52±0.16	0.10		93.4±7.8
Mn	mg/Kg	25.4±2.8	6.55±0.85	6.28±0.88	5.45±0.79	0.010	91±11	95.3±9.9
Na	mg/100g	2.23±0.21	1.20±0.11	0.95±0.11	2.50±0.21	0.40	96.7±7.8	89±12
Ni	mg/Kg	0.62±0.15	0.72±0.13	0.53±0.10	0.613±0.097	0.020		90.3±9.7
Pb	µg/Kg	< LOD	< LOD	< LOD	< LOD	5.0		91.2±5.5
Zn	mg/Kg	12.6±1.0	6.10±0.73	11.6±1.2	5.86±0.75	0.010	102.8±4.4	92.0±9.4

Conclusions:

The methodology employed for the determination of As, Cd, Cr and Pb by ETA-AAS, and Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni and Zn by FAAS and Hg by CVAAS was appropriate and the results obtained were in general as expected.

The data generated show that the concentrations of arsenic, cadmium, lead and mercury in the samples of rice tested are significantly lower that the maximum tolerance limits established by International Organizations. These low levels achieved confirms the good production practices employed. Then the consumption of rice produced in Uruguay presents no health threat.

Apart from this, the concentrations of all the elements determined in this survey fall within the range typical of rice from around the world.