

Determination of Total Strontium in Uruguayan Rice by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

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ABSTRACT

Strontium (Sr) is found naturally as a non-radioactive element and has 16 known isotopes. Naturally occurring Sr is found as four stable isotopes: Sr-84, -86, -87, and -88. Twelve other isotopes are radioactive. Sr-90 is the most important radioactive isotope in the environment, discovered mostly after the nuclear experiments conducted in the 1950s and 1960s.

In the present work, 86 rice samples (*Oryza sativa* L.) and 7 rice husk samples were

digested by dry ashing for the purpose of determining the total Sr levels by ICP-OES. The mean concentrations found were: 0.281 $\mu\text{g g}^{-1}$ for milled, 0.287 $\mu\text{g g}^{-1}$ for parboiled milled, 0.564 $\mu\text{g g}^{-1}$ for brown, 0.73 $\mu\text{g g}^{-1}$ for parboiled brown, and 1.16 $\mu\text{g g}^{-1}$ for paddy rice, and 3.44 $\mu\text{g g}^{-1}$ for the rice husks. Validation of the method was conducted with a certified reference material, NIST CRM 8418 Wheat Gluten, and the recovery obtained ranged from 89–98%.

As the outer layers (aleurone, pericarp) of the grain are removed, the Sr concentration decreases. It can then be assumed that most of the Sr is stored in these layers. Although no extensive data exist for Sr levels in rice, the values obtained are in good agreement with the results reported for Sr in brown rice from Japan (0.25–0.72 $\mu\text{g g}^{-1}$) and with non-contaminated foodstuffs from other parts of the world. Thus, the Uruguayan rice has Sr levels that match non-contaminated samples and its consumption presents no health threat.

INTRODUCTION

In 1790, Adair Crawford and William Cruikshank first detected non-radioactive strontium in the mineral strontianite in Scotland; and metallic strontium was first isolated in 1808 by Sir Humphry Davy (1).

The alkali earth metal strontium has four naturally occurring isotopes: Sr-84, -86, -87, and -88. Only Sr-87 is radiogenic and is produced by decay from the radioactive alkali metal Rb-87 (2). Twelve other isotopes are radioactive and Sr-90 (half-life 28.78 years) is of greatest importance. Like many other radionuclides, it was discovered in the 1940s during nuclear experiments in connection with the development of the atomic

bomb. It is a by-product of the fission reaction of uranium (^{235}U) and plutonium (^{239}Pu) in nuclear reactors and weapons. Therefore, ^{90}Sr is considered one of the most hazardous constituents of nuclear wastes. Large amounts of ^{90}Sr were produced during the nuclear weapons tests in the 1950s and 1960s, and are therefore dispersed worldwide.

In 1986, the world's worst nuclear power accident occurred at Chernobyl in the former USSR (now Ukraine), introducing a large amount of ^{90}Sr into the environment (3). The largest amount of ^{90}Sr was deposited in the Soviet Republics. The rest was dispersed as fallout over Northern Europe and all other parts of the world. Everyone is exposed to small amounts of ^{90}Sr , since it is widely dispersed in the environment and therefore in the food chain (3). Strontium-90 presents a health problem since it sub-

stitutes for calcium in bone, and prevents its removal from the body. (2)

Owing to its chemical and biochemical similarities to calcium, more than 99% of Sr is efficiently incorporated into bone tissue and teeth. Although humans can absorb Sr by inhalation (as a contaminant in dust) or dermal contact, Sr intake through diet (foodstuffs and water) is the most common pathway into humans (4).

Therefore, knowledge about total Sr in foods is of extreme importance to prevent and control contamination; mainly for those foods that are staples for millions of people.

Currently, rice is the predominant staple food for more than half of the world's population. It is used in at least 15 countries in Asia and the Pacific, 10 countries in Latin America and the Caribbean, one country in North Africa, and seven

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countries in sub-Saharan Africa. Moreover, it provides employment for millions of rice producers, processors, and traders all over the world. Recognizing the importance of rice-based systems in the fight against hunger and poverty, the United Nations General Assembly declared 2004 the International Year of Rice under the theme "Rice is Life" (5). Due to its importance, rice plays a fundamental role for world food security as well as for socio-economic development.

Uruguay is Latin America's major rice exporter and now among the world's top ten exporters. Furthermore, Uruguay is the only rice producer that designates 95% of its production to international markets. Therefore, the quality of rice produced in Uruguay is very important and well known all over the planet.

Prior to analysis, rice samples need to be converted into a liquid form. The two most widely used techniques are based on dry ashing or wet digestion. For the purposes of this work, dry ashing was selected as the solubilization technique. It is an inexpensive procedure and provides good detection limits, although it is time-consuming and strict temperature control must be observed to avoid loss of volatile elements. For the determination and quantification of Sr, inductively coupled plasma optical emission spectrometry (ICP-OES) was chosen because of the technique's versatility, precision, and accuracy. In addition, a large number of samples can be processed in a short period of time.

The aim of this work was the evaluation of total strontium concentration in samples of paddy, brown, parboiled brown, milled, and parboiled milled rice, as well as in rice husk all cultivated in Uruguay. This study is the first in performing and reporting a survey of Sr levels in Uruguayan rice. The

results are of great significance for Uruguay as it is one of the biggest global exporters of rice.

EXPERIMENTAL

Instrumentation

All analyses were performed using a PerkinElmer® Optima™ 2100 DV ICP-OES (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA), equipped with a dual-view torch, Scott-type spray chamber, and GemTip™ cross-flow nebulizer. A PerkinElmer AS-90 autosampler was used for sampling. The optimum instrumental conditions determined for this study are given in the Table I.

Water purification was carried out using a Milli-Q™ Plus purifier system (Millipore Corporation, Bedford, MA, USA).

Reagents and Solutions

All chemicals used in the sample preparation and analysis were of analytical grade or better.

Working standard solutions of Sr were obtained by appropriate dilution of a Sr stock solution (1000 µg mL⁻¹) (Merck KGaA, Darmstadt, Germany), certified by

TABLE I
Instrumental Operating Conditions

Parameter	Optima 2100 DV
RF Power	1300 W
Nebulizer Flow	0.80 L/min
Auxiliary Flow	0.2 L/min
Plasma Flow	15.0 L/min
Sample Flow	1.50 ml/min
Plasma Height	15 mm
Plasma Viewing	Axial
Processing Mode	Area
Read Delay	30 sec
Rinse Delay	60 sec
Replicates	5
Wavelength	407.771 nm

the manufacturer to ± 1% (w/v) and traceable to the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

All solutions were prepared with ultrapure water with a specific resistivity of 18MΩ·cm obtained by filtering distilled water through a Milli-Q™ Plus purifier system (Millipore Corporation, Bedford, MA, USA) immediately before use.

Procedure

To obtain extensive data for this work, 93 samples were collected from the main rice production areas throughout Uruguay (see Figure 1).

Prior to analysis, approximately 500 g of sample was ground in an analytical mill (Analytical Mill A10, Kinematica GAC, Luzern, Switzerland) and passed through a 1-mm sieve.

The sample (~5 g) was weighed into a beaker resistant to high temperatures and, while continuously shaking the suspension, 5 mL ashing aid solution [10% (w/v) Mg(NO₃)₂ in ethanol] was added. Next, the following temperature program was used: Heating at 125°C until nearly dry, then heating from 125°C to 450°C for 2 hours, and holding at 450°C for 12–14 hours. If white ashes are not obtained after this temperature cycle, 1 mL HNO₃ should be added dropwise (brown fumes should be seen) and then 1 mL 30% H₂O₂ added. Afterwards, repeat the heating cycle until white ashes are observed.

When white ashes occur from the digestion cycle, 5 mL HNO₃ (10%) is added. The solution obtained was homogenized in an ultrasonic bath and then centrifuged.

Duplicate blanks were prepared by adding 5 mL ashing aid solution for the digestion procedure.



Fig. 1. The eight most important areas of rice production in Uruguay (6).

To ensure a high level of analytical reliability, recovery studies were included for each batch to estimate analytical accuracy. The rice samples were spiked with two different amounts (50 and 250 ng) of a certified solution (Merck KGaA, Darmstadt, Germany) and then submitted to the digestion procedure. Each batch also contained a certified reference material (NIST CRM 8418 Wheat Gluten).

Direct calibration against acidified standard solutions was carried out for the determination of total Sr in the solution using the dry ashing treatment. The calibration curve covers the range of 10–2000 ng mL⁻¹.

Measurement of Uncertainty

Evaluation of the measurement of uncertainty associated with a test result is now an essential requirement in many quality systems. The first step in the measurement of uncertainty, in accordance with the recommendations given by EURACHEM/CITAC (EuroAnalytical Chemistry/Co-Operation on International Traceability in Analytical Chemistry) guide (7), is to recog-

nize all possible sources of uncertainty. Then estimate the size of the component associated with each potential source of uncertainty identified. Very useful is the construction of a cause-effect diagram (Ishikawa diagram) where the different contributions to the overall uncertainty associated with the analytical method applied are clearly visualized.

We have distinguished and evaluated the different sources of uncertainty in the quantification of total Sr in rice using ICP-OES by direct calibration. These are as follows: The analytical scale (all solutions were prepared by tared weighing), including repeatability, readability, sensitivity, and linearity of the scale; the density of solutions (density correction must be made since all solutions are prepared gravimetrically); the preparation of the stock and intermediate calibration solutions; uncertainty in the integration of peak area; uncertainty in the chemical calibration (linear least squares fitting procedure was used); the bias, etc.

To calculate the combined standard uncertainty $u_c(y)$ of the analyte concentration, we used the general relationship between $u_c(y)$ of a value y and the uncertainty of the independent parameters x_1, x_2, \dots, x_n on which it depends.

$$u(y) = \sqrt{\sum_{i=1, n} c_i^2 u(x_i)^2}$$

$u(x_i)$ = uncertainty in y arising from the uncertainty in x_i

where y is a function of several parameters x_1, x_2, \dots, x_n

and c_i is:

$$c_i = \frac{\partial y}{\partial x_i}$$

c_i = sensitivity coefficient.

Once the combined standard uncertainty was determined, the expanded uncertainty U was obtained by multiplying the $u_c(y)$ with a coverage factor k .

$$U = ku_c(y)$$

The coverage factor, k , depends on the value of the Student's t -test for the number of degrees of freedom for the confidence level of 95%.

RESULTS AND DISCUSSION

The results obtained in this work are shown in Table II. The total Sr contents were calculated on a wet basis to allow a comparison with the literature data of the product when purchased.

The methodology employed for the determination of Sr was appropriate, as can be inferred from the recovery studies performed on spiked samples, which ranged from 89–95% for the lowest concentration of Sr (50 ng) and from 91–98% for the highest concentration of Sr (250 ng). In addition, the recovery of Sr from the certified reference material (NIST CRM 8418 Wheat Gluten) was between 89.5 and 98.1±6.3%.

TABLE II
Total Sr Content in Milled (long and short grain), Parboiled Milled, Brown (long and short grain), Parboiled Brown, and Paddy Rice, and in Rice Husk

Rice Type	Grain	Total Sr Concentration ($\mu\text{g g}^{-1}$)			n	LOD (ng g^{-1})	Spike Recovery (%)
		Min.	Max.	Mean			
Milled	Long	0.190±0.039	0.421±0.063	0.281±0.048	11	5	91±12 95±11
Parboiled Milled	Long	0.135±0.026	0.439±0.028	0.287±0.027	14	5	91.6±8.9 91.3±9.4
Milled	Short	0.160±0.028	0.351±0.054	0.247±0.041	13	6	89±13 89±12
Brown	Long	0.354±0.057	0.78±0.11	0.564±0.085	13	5	95.4±11.2 93.2±8.7
Parboiled Brown	Long	0.638±0.088	0.80±0.11	0.73±0.11	14	7	94.5±9.1 93±10
Brown	Short	0.554±0.089	0.605±0.097	0.578±0.092	14	6	91±12 98.2±5.7
Paddy	Long	0.97±0.14	1.41±0.19	1.16±0.16	7	7	92±10 92±11
Husk	-	2.88±0.39	3.91±0.51	3.44±0.47	7	7	90±13 93.4±9.9

Although not much data was found for the total Sr content in rice, the values obtained in the rice samples analyzed in this study are in good agreement with those reported in rice samples from Japan (8). They found levels of total strontium in brown rice ranging from 0.25 to 0.72 $\mu\text{g g}^{-1}$ (as can be seen in Table III).

Table III shows the average concentration of total Sr in common natural materials. For instance, the average concentration of Sr in crustal rocks is 370 $\mu\text{g g}^{-1}$, while in soils it is 240 $\mu\text{g g}^{-1}$, but can fall below 10 $\mu\text{g g}^{-1}$ or exceed 1000 $\mu\text{g g}^{-1}$. For hydrological samples (seawaters, rivers, rain) the overall mass content of Sr ranges from 0.01 to 7600 $\mu\text{g L}^{-1}$ and for biological samples (wood, roots) from 8-2500 $\mu\text{g g}^{-1}$ (9).

TABLE III
Average or Ranges of Sr Concentrations in Different Natural Materials (1, 4, 8-12)

Material	Sr ($\mu\text{g g}^{-1}$)	Material	Sr ($\mu\text{g L}^{-1}$)
Average Crust	370	Seawater	7600
Soil Minerals	240	Spring Water	20-100
Sandstone	20	Rain	1-400
Low-Ca Granite	100	Wines from:	
High-Ca Granite	440	Chile	532
Basalt	465	California	1924
Wood	8-2500	Madeira	939
Roots (Spruce)	20	Australia	1879
Conifer Needles	2-20	South Africa	722
Rice from Japan	0.25-72	Bordeaux	275

In the samples studied here, logical values of Sr were obtained from the rice's husk to the milled rice. The removal of the outer layers of the rice shows a reduction in the Sr content. Paddy rice (rice which has retained its husk after threshing) presented the highest values of Sr ($0.97\text{--}1.41\ \mu\text{g g}^{-1}$). The complete elimination of the husk from the paddy rice produces brown rice; therefore, it is reasonable that the Sr content in brown rice is lower ($0.35\text{--}0.78\ \mu\text{g g}^{-1}$) than in paddy rice. With the milling process of brown rice, total removal of husk and bran is performed; consequently, this type of rice presented the lowest value of Sr ($0.281\ \mu\text{g g}^{-1}$).

It is generally accepted that as greater amounts of rice bran are removed from the grain during milling and polishing, more vitamins and minerals are lost (13). In the rice samples analyzed in this work, the milling process seems to have great influence on the Sr levels.

Since the Sr concentration in rice samples is highly affected by processing (milling and polishing), it can be said that most of the Sr is situated in the external layers of the grain (aleurone and pericarp).

On the other hand, prior to milling or storing, rice may be parboiled, which involves soaking the paddy rice in warm water, followed by steaming and drying (14). It has been pointed out that parboiling rice prior to cooking preserves some of the nutrient content, chiefly due to the retention of minerals and water-soluble vitamins. The higher retention of micronutrients (Ca, Cu, Fe, Zn, etc.) in parboiled rice has been assigned to their solubilization and migration from the aleurone and germ into the starchy endosperm (13,14). Paddy rice is parboiled and dehusked to obtain parboiled brown rice; once it is submitted to milling and polishing, parboiled milled rice is obtained.

From the rice samples studied here we found that the mean level of Sr in parboiled brown rice ($0.73\ \mu\text{g g}^{-1}$) is higher than in parboiled milled rice ($0.287\ \mu\text{g g}^{-1}$) which is in good agreement with the idea that most of the Sr in rice is situated in the outer layers. The Sr is solubilized and introduced into the endosperm, so the milling and polishing process used to obtain parboiled milled rice causes a significant reduction in Sr concentration.

Yet, the implication of the benefits (from a nutritional or contamination point of view) of parboiled rice is still arguable, mostly due to the lack of uniform commercial processes applied in different countries. It is believed that the retention pattern of some minerals (Ca, Na, Cu, Fe, Mo, etc.) is the result of the interaction of factors such as mineral location in the grain and their solubility during soaking, different ratios of migration as well as variations in the hydrothermal process, and milling resistance of the parboiled grain (14). Hence, further studies should be carried out for a more complete understanding of mineral retention.

CONCLUSION

Since rice is the predominant staple food for more than half of the world's population, its nutritional vs. toxic composition is of special interest.

This is the first study reporting the concentration of Sr in different types of rice cultivated in Uruguay. The methodology employed for the determination of Sr was validated against a certified reference material. The good recoveries obtained make us conclude that the method used was appropriate.

Removal of the outer layers of the rice grain results in a large reduction of Sr concentration. The average concentration of Sr in paddy rice was $1.16\ \mu\text{g g}^{-1}$ (which is a non-processed form of rice), while in milled rice it was $0.281\ \mu\text{g g}^{-1}$. This behavior suggests that the greater amount of Sr is situated in the non-edible parts of the grain (i.e., husk) and confirms that the highest levels of Sr found in this work were in the rice's husk ($3.44\ \mu\text{g g}^{-1}$).

Although further studies should be carried out, the results here presented suggest that there is no Sr contamination from the atmosphere in rice produced in Uruguay and its consumption, therefore, presents no health threat. Unfortunately, no government or other official regulation was found to support our claim concerning limits for Sr levels in rice. However, the United States Government (15) has set a limit of $4000\ \mu\text{g L}^{-1}$ of Sr in drinking water, and the Sr concentrations in all of the samples analyzed in this survey are far below this regulation (considering consumption, preferences, etc.). Therefore, we can assume that no Sr contamination has occurred in Uruguay. Since Uruguay is one of the world's top ten rice exporters, it is crucial to be able to demonstrate that its rice is of high quality with regard to Sr content.

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