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Direct Determination of Potentially Toxic Elements in Rice by SS-GF AAS: Development of Methods and Applications

Daniel Menezes Silvestre and Cassiana Seimi Nomura*

Instituto de Química, Universidade de São Paulo, CEP 05508-000, São Paulo, SP, Brazil

ABSTRACT: The development of methods for direct determinations of Al, Cd, and Pb in rice by SS-GF AAS is presented. Heating program optimization associated with the use of an adequate chemical modifier containing Pd + Mg allowed direct analysis against aqueous calibrations. The obtained LOD values were 114.0, 3.0, and 16.0 $\mu\text{g kg}^{-1}$ for Al, Cd, and Pb, respectively. Important parameters associated with a solid sampling analysis were investigated, such as minimum and maximum sample mass size and analyte segregation. Seventeen rice samples available in São Paulo City were analyzed, and all of them presented analyte mass fractions less than the maximum allowed by legislation. The influences of rice washing and the cooking procedure were also investigated. The washing procedure diminished the Al and Pb total mass fractions, indicating an exogenous grain contamination. The cooking procedure diminished the Cd total mass fraction. Rice cooking using an aluminum container did not cause a significant increase in the Al mass fraction in the rice, indicating no translocation of this element from container to food. In general, coarse rice presented higher levels of Al when compared to polished or parabolized rice.

KEYWORDS: solid sampling, atomic absorption, graphite furnace, microanalysis, rice

INTRODUCTION

Rice is a staple food for more than 40% of the world's population.¹ Considering that the main cause of contamination by potentially toxic elements occurs by food ingestion, the World Health Organization (WHO) regulates the levels of certain contaminants.² In the case of Al, the Provisional Tolerable Weekly Intake is 7.0 mg kg^{-1} body weight as established by the European Food Safety Authority.³ The European Community (EC) established 0.2 mg kg^{-1} as the maximum level of Cd and Pb allowed in rice and cereals.⁴ In Brazil, the maximum values for these elements in cereals and grain are not described. For seafood, the maximum levels of Cd and Pb are 1.0 and 2.0 mg kg^{-1} , respectively.⁵

Elemental determination in food samples is not an easy task, especially when analytes are present in low concentrations, such as occurs with potentially toxic elements. Most analytical techniques require sample decomposition procedures prior to analysis, increasing the risks of contamination, analyte loss, reagent consumption, and residue generation. One interesting alternative is the possibility of practicing a direct solid sampling analysis that eliminates the time-consuming sample decomposition process. Improved detectability due to not diluting the sample is an important advantage associated with solid sampling techniques, making it useful in trace and ultratrace analysis.⁶ Instrumental neutron activation analysis (INAA), X-ray fluorescence (XRF), laser-induced-breakdown spectrometry (LIBS), electrothermal vaporization inductively coupled optical emission spectrometry or mass spectrometry (ETV-ICP OES/MS), laser ablation inductively coupled optical emission spectrometry or mass spectrometry (LA-ICP OES/MS), and solid sampling graphite furnace atomic absorption spectrometry (SS-GF AAS) are some of the techniques applicable to direct solid sample analysis.⁷

SS-GF AAS deserves special attention due to its high sensitivity and selectivity, beyond all of the other characteristics

associated with generic solid sampling techniques. However, it also suffers from several drawbacks that have to be overcome. The low precision of the results due to the low sample mass size required for analysis, matrix interference, and calibration is one of the difficulties associated with solid sampling analysis.^{8,9} Considering all characteristics, it has been explored in direct food analysis.^{10–14}

To establish highly efficient analytical procedures, the aim of this work was methods development for direct determinations of Al, Cd, and Pb in rice samples by SS-GF AAS. Using the developed methods, commercially available rice samples in the city of São Paulo then were analyzed. The influence of washing the rice samples and the cooking procedure were also investigated.

MATERIALS AND METHODS

Instrumentation. All measurements were carried out with a model ZEE nit 60 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) equipped with a transverse heated graphite tube atomizer, an inverse and transverse two-field and three-field mode Zeeman effect background corrector, and a hollow cathode lamp of aluminum, cadmium, and lead. Pyrolytically coated transverse heated graphite tubes and pyrolytically coated boat-type solid sampling platforms (Analytik Jena) were used throughout. A solid sampling accessory (SSA-6 Z; Analytik Jena AG, Germany) with preadjusted micro-tweezers was used to transfer the boat-type platform from the microbalance (Auto Balance AD-4; Perkin-Elmer, Norwalk, CT) to the graphite tube. A stainless steel microspatula was used to transfer the samples to the pyrolytic boat-type platform. All measurements were based on integrated absorbance values. Argon 99.998% (v/v) (Air Liquide Brasil, São Paulo, Brazil) was used as the purge gas. The instrumental parameters, experimental conditions, and heating

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program used for Al, Cd, and Pb determinations by GF AAS and SS-GF AAS are presented in Table 1.

Table 1. Instrumental Parameter and Heating Program Used in the Total Al, Cd, and Pb Mass Fraction Determination in Rice Samples by SS-GF AAS

element	wavelength (nm)	bandpass (nm)	lamp current (mA)		
Al	309.3	0.8	6.0		
Cd	228.8	0.8	4.0		
Pb	283.3	0.8	4.0		

step	temp (°C)	ramp (°C s ⁻¹)	hold (s)	argon flow (L min ⁻¹)
drying	130	10	20	1
pyrolysis	1000, ^a 700, ^b 850 ^c	100	20, ^a 40 ^{b,c}	1
atomization	2500, ^a 2300, ^b 2100 ^c	2500	6	0
cleaning	2550	1200	3	1

^aAl. ^bCd. ^cPb.

A freeze-dryer (Thermo Electron Corp.) was used to dry the samples, and a cryogenic mill with a self-contained liquid nitrogen bath (MA 775 model, Marconi, Brazil) was used to grind the samples. Acid decomposition of samples was performed using a high-pressure microwave oven (Microwave 3000; Anton Paar, Graz, Austria). Glass beakers and an aluminum container (Brics, S.V.M. Indústria e Comércio Ltda, São Paulo, Brazil) were used to cook the rice samples.

Reagents and Samples. All solutions were prepared using high-purity deionized water obtained from a Milli-Q water purification system (Millipore, Bedford, MA). Analytical reference solutions of Al(III), Cd(II), and Pb(II) were prepared by successive dilutions of stock solutions containing 1000 mg L⁻¹ AlCl₃, CdCl₂, or Pb(NO₃)₂, respectively (Sigma-Aldrich, Germany). Stock solutions containing 10 g L⁻¹ Pd(NO₃)₂, Mg(NO₃)₂, or Na₂WO₄·2H₂O (Suprapur, Merck) were used as chemical modifiers. Triton X-100 (Suprapur, Merck) was used together with the coinjected Pd+Mg chemical modifier. Nitric acid and H₂O₂ (Suprapur, Merck) were used for acid decomposition of rice samples.

Certified reference materials (CRMs) of unpolished rice flour from the National Institute for Environmental Studies (NIES 10a), peach leaves from the National Institute of Standards and Technology (NIST 1547), and wheat flour from the National Bureau of Standards (NBS 1567a) were used to check the accuracy of total analyte mass fraction determinations.

Seventeen rice samples of diverse varieties were obtained in markets in the city of São Paulo, Brazil.

All solutions and samples were stored in decontaminated polypropylene bottles (Nalge Co., Rochester, NY).

Sample Preparation. Approximately 45 mg of each rice sample was divided into three portions (A, B, and C) of 15 mg each. Each portion was submitted to a different procedure. Portion A was ground in a cryogenic mill using the following grinding program: 5 min of freezing followed by 3 cycles of 2 min of grinding, with 1 min of freezing between each grinding cycle. Portion B was washed three times with 10.0 mL of deionized water, freeze-dried for 72 h, and ground in a cryogenic mill. Portion C was washed following the procedure adopted with portion B, cooked in a glass container (decontaminated beaker) with 50 mL of deionized water until complete vaporization of the water occurred (30–40 min), then freeze-dried for 72 h and ground in a cryogenic mill. One polished rice sample was also submitted to the same procedure adopted for portion C using an aluminum container instead of a glass container to cook the rice sample. The cooking procedures were performed on a heating plate (Fisatom Equipamentos Científicos Ltda., São Paulo, Brazil).

Evaluation of Method Accuracy. The accuracy of the developed method was checked by three different procedures: direct analysis of CRM, spiking, and analysis after sample acid decomposition.

A spiking procedure was performed to check the accuracies of the Pb results, because rice CRMs for these elements were not available.

For Al measurement, sample was acid digested and analyzed by GF AAS, without any addition because the Al concentration was detectable. To 3.5 mg samples of ground polished rice were added 5.0 mL of solution containing 0.14 mg L⁻¹ of Pb. The sample was freeze-dried for 72 h and cryogenically ground. The spiked sample was analyzed by GF AAS after acid decomposition to check the exact concentrations of these elements. For this purpose, around 200 mg of spiked rice was mixed with a diluted oxidant solution (2 mL of HNO₃ + 1 mL of H₂O₂ + 3 mL of H₂O), and the following heating program was performed (temperature (°C), ramp (min), hold (min)): (140, 5, 1), (180, 4, 5), and (200, 4, 10).

Method Development for Total Al, Cd, and Pb Mass Fraction Determinations in Rice by SS-GF AAS. Pyrolysis and atomization temperatures were optimized for all elements using 10 µL of standard aqueous solutions containing 25.0 µg L⁻¹ Al, 1.0 µg L⁻¹ Cd, or 40.0 µg L⁻¹ Pb prepared in 0.1% HNO₃ v v⁻¹. The thermal behavior of the analytes was also evaluated in the presence of rice matrix. For this, masses between 250 and 600 µg (depending on the analyte concentration) of rice (CRM NIES 10a for Cd; a polished rice sample for Al and spiked rice for Pb) were directly inserted into the graphite furnace. All studies were performed in both the presence and the absence of chemical modifiers. For this, 10 µL of the following chemical modifiers was added into the standard aqueous solution and rice samples: 0.5 mg L⁻¹ Pd(NO₃)₂ + 0.3 mg L⁻¹ Mg(NO₃)₂ + 0.1% w v⁻¹ Triton X-100 for Cd and Pb and 0.5 mg L⁻¹ Pd(NO₃)₂ + 0.3 mg L⁻¹ Mg(NO₃)₂ for Al. For Al determination, 300 µg of W permanent chemical modifier permanently deposited onto the boat type platform was used together with coinjection of the Pd+Mg chemical modifier. Tungsten thermal deposition was performed according to the literature.⁸

Calibration curves were obtained in two different ways: aqueous calibration and solid calibration. The first was based on the use of 10 µL of different reference solutions (10.0–40.0 µg L⁻¹ for Al, 0.2–1.5 µg L⁻¹ for Cd, and 4.0–100.0 µg L⁻¹ for Pb) prepared in 0.1% v v⁻¹ HNO₃. The second was based on directly weighing increasing masses (200–600 µg) of rice samples onto the boat-type platform.

Investigation of Sample Mass Size and Analyte Segregation on Al and Cd Determinations. To investigate the influence of sample mass size on the precision and accuracy of the results, the homogeneity of a rice CRM (NIES 10a) for Al and Cd determinations was determined. For this, sample masses between 80 and 1300 µg were analyzed.

Putative Al and Cd segregation in Arborio rice was checked by analyzing different particle sizes of this sample. For this purpose, an Arborio rice sample was cryogenically ground, sieved, and separated into four fractions: <150 µm, 50–100 µm, 400–500 µm, and >500 µm.

RESULTS AND DISCUSSION

Method Development for Total Al, Cd, and Pb Mass Fraction Determinations in Rice by SS-GF AAS. Pyrolysis temperature is the most critical parameter in SS-GF AAS. As the sample is introduced into a graphite furnace without any pretreatment, an effective pyrolysis step is essential. Adequate graphite furnace heating program optimization associated with the use of a chemical modifier allows comparative analysis against aqueous calibration. Pyrolysis and atomization temperatures for Al, Cd, and Pb in aqueous solution and in rice samples in the presence and absence of chemical modifiers were evaluated. The use of Triton X-100 together with an aqueous Pd+Mg chemical modifier was necessary to improve the interaction between the solid sample and the chemical modifier solution. In the case of Al, Triton X-100 was omitted because it caused a high blank value.

The best pyrolysis temperature for Al was achieved at 1200 °C for the aqueous solution as well as for the solid rice sample, with and without the chemical modifier. However, the use of Pd+Mg was adopted because it allowed the use of aqueous

calibration for direct analysis of solid rice samples. The use of 300 μg of W as a chemical modifier also improved the sensitivity and standard deviation probably because the formation of aluminum carbide is avoided, making the forming of oxide specie the path for Al atomization.¹⁵ For all of these reasons, the use of Pd+Mg associated with the W permanent chemical modifier was adopted in direct determinations of Al.

For Cd, the maximum pyrolysis temperature achievable in the absence of a chemical modifier was 400 °C for an aqueous solution and 500 °C for a solid rice sample. In the presence of the Pd+Mg chemical modifier, the best pyrolysis temperature achieved was 700 and 800 °C for the aqueous solution and a solid rice sample, respectively. The use of 700 °C as the pyrolysis temperature associated with the use of a chemical modifier was the condition adopted for Cd determination, because it allowed the use of aqueous calibration.

The action of the Pd+Mg chemical modifier was also effective on Pb determinations. While the best pyrolysis temperatures obtained in the absence of a chemical modifier were 750 and 700 °C in aqueous solution and in a solid rice sample, respectively, in the presence of Pd+Mg, 950 and 850 °C were the best conditions obtained for aqueous solution and rice, respectively. The use of aqueous calibration was possible only when the Pd+Mg chemical modifier was used. In this case, the best pyrolysis temperature was 850 °C. The atomization temperatures were also optimized for all analytes. The best conditions found are summarized in Table 1.

Calibration and Analytical Features. The equations for the analytical calibration curves obtained for Al, Cd, and Pb using aqueous solutions and solid rice samples (CRM NIES 10a and spiked rice) are shown in Table 2. A comparison of the

Table 2. Analytical Calibration Curves Made with Aqueous Solution and Solid Rice Standard for Total Al, Cd, and Pb Mass Fraction Determination

	aqueous calibration		solid calibration	
	equation	r^2	equation	r^2
Al	$y = 0.00028x + 0.01265$	0.9958	$y = 0.00025x + 0.00458$	0.9860
Cd	$y = 0.00246x - 0.00042$	0.9909	$y = 0.00241x - 0.00002$	0.9765
Pb	$y = 0.00020x + 0.00106$	0.9990	$y = 0.00019x + 0.00040$	0.9932

slopes observed for equations obtained from aqueous solution with those in the presence of rice samples can be used to estimate the effect caused by the matrix. In the absence of a matrix effect, the ratio between the slopes obtained from aqueous solutions and sample should be approximately 1, and this condition ensures the adequacy of using an aqueous reference solution for method calibration. The regression coefficients (r) and slopes obtained from the aqueous solutions were very close to those obtained from the rice samples. The ratio between the slopes obtained from aqueous and rice samples for Al ($0.00028/0.00025 = 1.12$), Cd ($0.00246/0.00241 = 1.02$), and Pb ($0.00020/0.00019 = 1.05$) showed no significant matrix effect. In all cases, the calibration curve's regression coefficients and slopes are in good agreement (according to t -Student at a 95% confidence level).

The good agreement between the calibration curves from the two procedures can be credited to the similar atomization mechanism of the analytes in aqueous solution and in the sample, because Pd+Mg chemical modifier acts to minimize the

interference caused by matrix.¹⁶ The peak shapes of the analytes in aqueous solution are similar to those obtained in the matrix. This fact can be attributed to heating program optimization and the use of an appropriate chemical modifier.

The accuracy of the developed method was checked by analyzing CRMs for Al, Cd, and Pb determinations (Table 3).

Table 3. Total Al, Cd, and Pb Mass Fraction in Various Certified Reference Materials and Results for Total Al and Pb Mass Fraction Obtained by SS-GF AAS ($n = 7$) and GF AAS ($n = 5$) after Acid Digestion in Microwave, Including Addition and Recovery Test

CRM		certified value ($\mu\text{g g}^{-1}$)	found value ($\mu\text{g g}^{-1}$)	
Al	NBS 1567a	5.7 ± 1.3	5.6 ± 0.6	
Cd	NIES 10a	0.023 ± 0.003	0.023 ± 0.002	
Pb	NIST SRM1547	0.87 ± 0.03	0.90 ± 0.10	
	SS-GF AAS ($\mu\text{g g}^{-1}$)	GF AAS ($\mu\text{g g}^{-1}$)	added ($\mu\text{g g}^{-1}$)	recovery (%)
Al	8.3 ± 1.1	7.6 ± 0.8	0	109
Pb	0.25 ± 0.02	0.21 ± 0.03	0.20	119

An addition and recovery test and comparison of the results from analysis by GF AAS after acid decomposition of polished rice samples were also performed to check the accuracies of the Al and Pb results (Table 3). The found values are in good agreement (according to t -Student at a 95% confidence level) with the certified values and also with the results obtained by analysis by GF AAS after sample acid decomposition. The addition and recovery test showed recovery close to 100%.

The limits of detection were calculated on the basis of the zero mass response, which is the ratio between 3 times the standard deviation of 10 readings of the chemical modifier solution and the slope of the calibration curve adjusted to a sample mass of 1 mg.¹⁷ The limits of detection obtained for Al, Cd, and Pb were, respectively, 114.0, 3.0, and 16.0 $\mu\text{g kg}^{-1}$. The characteristic masses based on integrated absorbances were 27.0 pg for Al, 2.0 pg for Cd, and 22.0 pg for Pb.

Investigation of Sample Mass Size and Analyte Segregation on Al and Cd Determinations. Considering that one of the main difficulties associated with solid sampling analysis is its low precision due to the lack of homogeneity in the low sample mass sizes applied in these methods, the influence of this parameter on the analytical results was checked. It is known that most commercially available CRMs are certified for high sample mass sizes (100–500 mg). Because of to this, the applicability of these materials to microanalysis involving low sample mass sizes (<10 mg) is unclear. The influence of sample mass size on the results of Al (Figure 1a) and Cd (Figure 1b) determinations in a rice CRM (NIES 10a) was evaluated. Only these two analytes were investigated because they were naturally found in most of the analyzed rice samples. For both analytes, low precision results were observed when a sample mass size less than 0.3 mg was used. Silva and co-workers¹⁰ also observed deteriorated precision for Fe measurement in rice samples. As the strategy, the authors proposed the use of less sensitive analytical line to allow the analysis of higher sample mass size. According to Belarra and co-workers,¹¹ it is possible to state that when the direct determination of metals in organic solid samples by GF AAS is carried out, the nonhomogeneity of subsamples used is the principal cause of the poor precision of the technique.

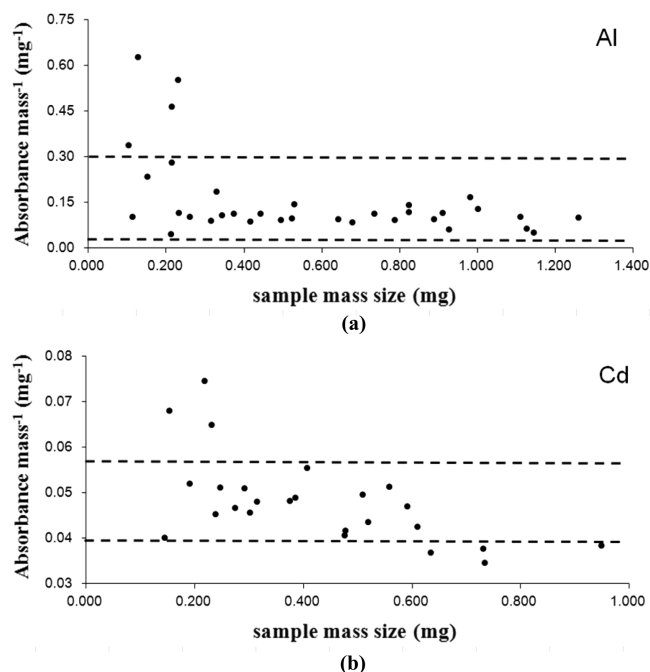


Figure 1. Precision of the results for (a) Al and (b) Cd determinations according to sample mass size analyzed. Horizontal lines show the standard deviation of measurements.

For Cd (Figure 1a), large amounts of sample (>0.6 mg) resulted in underestimating the analytical signal. This fact can be attributed to matrix interference caused by analyte occlusion due to the large amounts of matrix. Similar results were shown by Belarra et al.¹² while determining Cu in vitamins by SS-GF AAS. A different behavior was observed in the case of Al measurement. The analytical signal was constant in this case, even using a sample mass size as high as 1.3 mg. It is believed that matrix interference is much less pronounced in this case because a higher pyrolysis temperature (>1000 °C) was used, increasing the efficiency of matrix volatilization. These results showed that, although NIES 10a is recommended for a sample mass size of 400 mg, analysis of as little as 0.3 mg allowed us to achieve an accurate result.

Sample homogeneity is improved by sample grinding.^{12,18–20} The narrower is the particle size distribution, the better is the sample homogeneity and the more precise are the results. The grinding process may avoid inhomogeneity caused by analyte segregation. Thus, knowing the analyte content in a variety of particle sizes is important for preventing sampling errors, especially because, during RM storage, different sized particles tend to become separated.²¹ Analyte segregation was checked by determining the total Al and Cd mass fractions in fractions containing different particle sizes obtained by sieving cryogenically ground rice (Table 4). The results presented in Table 4 show all fractions presented statistically equivalent (p -value > 0.05) total Al and Cd mass fractions, indicating a homogeneous distribution of these analytes among the different particle sizes. The results (Table 4) also showed the coefficient of variation increasing with particle size, indicating better homogeneity and consequently better precision in the results for smaller particles (<100 μm). The coefficient of variation for cryogenically ground Arborio rice (nonsieved sample) was similar to that observed for particles between 50 and 100 μm or less than 50 μm . This result is due to the fact that only 50% of this sample is

Table 4. Evaluation of the Homogeneity and Analyte (Al and Cd) Segregation in Cryogenically Ground Arborio Rice

mass fraction \pm standard uncertainty $\mu\text{g g}^{-1}$ (CV, %) $n = 7$		
	Al	Cd
nonsieved	0.80 ± 0.39 (48%)	0.010 ± 0.01 (13%)
>500 μm	0.88 ± 0.36 (41%)	0.009 ± 0.004 (50%)
$500\text{--}400$ μm	0.81 ± 0.56 (69%)	0.009 ± 0.005 (52%)
$100\text{--}50$ μm	0.81 ± 0.30 (37%)	0.011 ± 0.001 (12%)
<50 μm	0.89 ± 0.23 (26%)	0.010 ± 0.001 (12%)

constituted of particles less than 100 μm . Only 10% of the particles present had a size greater than 400 μm .

Analysis of Rice Samples. Using the developed method of analysis, Al, Cd, and Pb mass fractions were measured in samples of diverse varieties of rice acquired in São Paulo markets (Figure 2). In general, coarse rice presented higher Al, Cd, and Pb levels than were observed for polished or parboiled rice. The obtained results for these three analytes are less than those allowed by legislation^{4,5} and are in accordance with results obtained by Qian et al.,²² who found 0.05 $\mu\text{g g}^{-1}$ of Cd and 0.06 $\mu\text{g g}^{-1}$ of Pb. The results obtained for Al (Figure 2a)

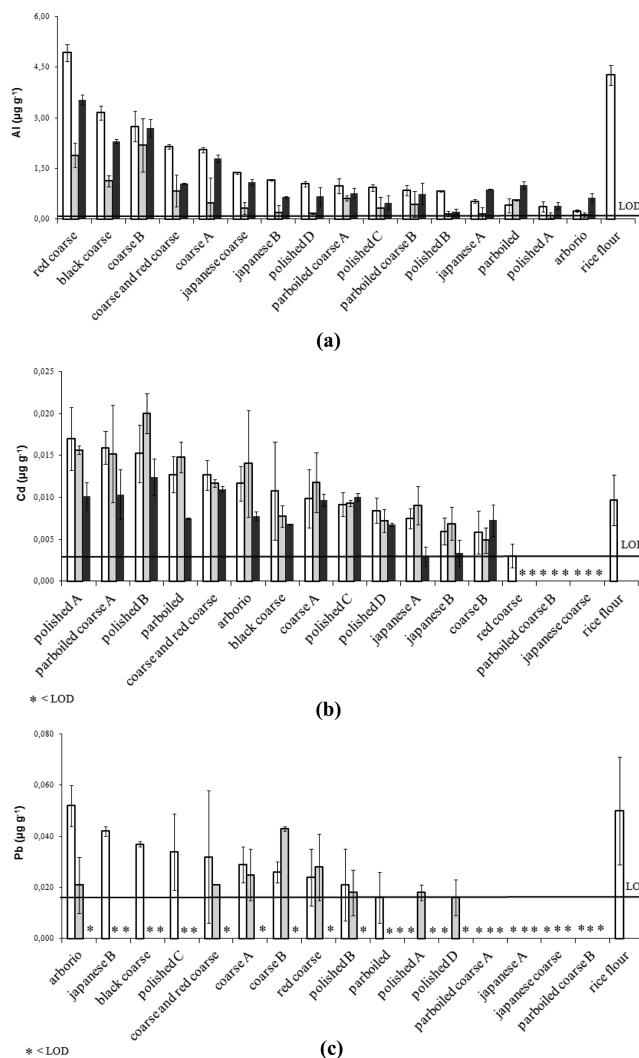


Figure 2. Total (a) Al, (b) Pb, and (c) Cd mass fraction determinations in (□) raw, (gray) washed, and (■) washed and cooked rice ($n = 3$).

were approximately 3 times lower than those obtained by Wang et al.²³ or Brakatos et al.²⁴

For most of the samples, a washing procedure caused diminutions in Al (Figure 2a) and Pb levels (Figure 2b), indicating exogenous contamination of the rice grains. Cadmium levels decreased with cooking procedure, probably due to analyte volatilization (Figure 2c). On the other hand, Al levels were increased by the cooking procedure. A rice sample was also cooked using an aluminum container instead of a glass beaker, but no further increase in Al level was observed even when it was cooked in an aluminum container polished with steel-wool. These results indicate there was no translocation of Al from the container to the food.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +55 (11) 3091-1467. E-mail: csnomura@iq.usp.br.

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Notes

The authors declare no competing financial interest.

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