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DETERMINATION OF TRACE ELEMENTS IN BRAZILIAN RICE GRAINS AND IN BIOLOGICAL REFERENCE MATERIALS BY NEUTRON ACTIVATION ANALYSIS

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Instrumental neutron activation analysis was applied to the determination of the elements Na, K, Br, As, Rb, Zn, Co, Fe and Sc in Brazilian rice samples and in biological standards. Hg and Se concentrations were determined by using a simple radiochemical separation. The chemical procedure was carried out by means of distillation of Hg and Se in HBr medium and subsequent precipitation of selenium by sodium metabisulfite and mercury by thioacetamide. The accuracy of the instrumental and radiochemical methods was evaluated by means of analysis of the Reference Materials NBS-Bovine Liver, Bowen's Kale and NBS-Rice Flour.

Introduction

The study of trace element contents, such as Hg, Se, As, Zn, Cd, Fe, Al, Cr in food, environmental and biological samples has attracted worldwide interest. The determination of trace quantities of elements present in these types of matrices is of considerable importance because of their essential and toxicological action in the human body. This has strenghtened the need to use reliable analytical methods capable of analyzing food samples as well as other matrices.

In recent years many researchers have applied Neutron Activation Analysis (NAA) for the study of several biological samples.[1-3] According to PARR,[4] activation analysis is the most widely applicable analytical method for trace element research. This method is applied mainly for multielemental studies and for the analysis of trace elements that are present at extremely low concentrations. In this last case it is necessary to develop radiochemical procedures to remove the interfering radionuclides.[5-6] CUNNINGHAN[7] studied a method for the analysis of As, Cr, Mo, Sb, Se in foods. These elements were retained on hydrated manganese dioxide resin while interfering elements were removed. Activities from Br, K, Na and P interferences were reduced by up to six orders of magnitude and detection limits for food analysis were

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reduced by factors of 100–2000, compared with those normally found for instrumental neutron activation analysis. GRIMANIS[8] developed a radiochemical procedure for the simultaneous determination of Hg and Se in biological materials. The procedure is based upon the digestion of samples in H_2SO_4/HNO_3, followed by extraction of Hg and Se into toluene, first mercury from 7.5M H_2SO_4 – 0.01M HBr media and then selenium from 7M H_2SO_4 – 1M HBr media.

The aim of this work is to apply neutron activation analysis to the determination of toxic and other elements in Brazilian foodstuffs, mainly rice that is widely consumed in the country. In Brazil there are not many data available concerning food analysis and it is felt that NAA can give an important contribution in this matter. Data obtained will be compared to the maximum permissible levels of our legislation for foodstuffs.

This paper presents a simple radiochemical separation procedure for the simultaneous determination of Hg and Se in Brazilian rice grains and in the biological reference materials NBS-Bovine Liver (SRM 1577-a) and Bowen's Kale. Even at very low levels, mercury has hazardous effects on the biosphere. Selenium is considered both essential and toxic within a relatively narrow concentrations range, but when present in high levels in the diet it can be extremely toxic.[9] The experimental procedure used was based on the digestion of the food sample in a mixture of HNO_3, H_2SO_4 and H_2O_2 in a closed system. After distillation of Hg and Se in the bromide form, selenium was precipitated by sodium metabisulfite and Hg by thioacetamide.

Instrumental neutron activation analysis was also applied, to determine the concentrations of As, Br, Zn, Rb, Na, K, Fe, Co and Sc in several types of rice and in biological reference materials.

Experimental

Sample treatment

The following types of rice grains were analyzed: (a) Polished treated rice: (a.1.) long fine-needle grains – type 1 and 2, (a.2.) long yellow grains, (a.3.) Japanese grains (Catete); (b) Parboiled rice.

The rice samples were collected in supermarkets of the city of São Paulo.

One kilogram of each brand was first homogenized by mixing, then quartered. One quart of each (250 g) was then washed with one liter of deionized and distilled water. This procedure, except for the purity of water, is the same used in this country up to the moment of cooking of the rice. After washing, the humid rice was ground in a mechanical agate mill, in small portions. The ground rice was then submitted to lyophilization during 24 hours and submitted to another grinding step, in a manual agate mortar, up to a granulometry of 80 mesh.

The standard reference materials Bovine Liver (SRM 1577-a), Rice Flour (SRM 1568) and Bowen's Kale were prepared following the procedure for drying recommended by NBS[10,11] and BOWEN,[12] respectively.

Preparation of standards

Multielemental standard solutions of Zn, Rb, As, Fe, Co, Sc, K, Br and Na were prepared by mixing aliquots from dilute solutions of these elements. Fifty to hundred microlitres of multielemental standard solutions were pipetted onto a Whatman 42 filter paper and dried under an infra-red lamp.

Standards of Hg and Se were also prepared for the determination of these elements by using radiochemical separation. The mercury standard solution was pipetted into quartz ampoules to avoid losses during irradiation and selenium standard solution was pipetted onto Whatman filter paper.

Counting equipment

The gamma-ray measurements of the irradiated samples and standards were carried out by using, two counting systems: (1) Ge(Li) detector, Ortec model 8001-1022 V (resolution of 2.6 keV at the 1332 keV gamma-ray peak of ^{60}Co) coupled to a 4096 channel ORTEC 6240B multianalyzer and to a minicomputer (Digital PDP 11/04); (2) Ge(Li) detector, Ortec, model 8001-1521 V (resolution of 2.8 keV for the 1332 keV of ^{60}Co) coupled to a 4096 channel Hewlett Packard Multianalyzer and to a HP 2100 A minicomputer.

The analysis of gamma-ray spectra were made by using the program FALA[13] in BASIC language and the program GELIGAM, in ORACL language, from ORTEC.

Instrumental neutron activation analysis (INAA)

Irradiation of rice samples and biological reference materials. About 150–250 mg of freeze dried rice or biological reference materials were weighed and irradiated in clean polyethylene vials for 8 hours at a thermal neutron flux of 10^{13} $n \cdot cm^{-2} \cdot s^{-1}$. Rice samples and biological reference materials were irradiated together with synthetic multielemental standards.

The concentrations of Na, Br, K, Zn, As, Rb, Co, Fe and Sc were determined in four types of rice grains and in the biological standards Rice Flour and Bowen's Kale The elements were determined employing different cooling times. Table 1 gives some nuclear data of the isotopes used in this analysis. Preference was given in some cases to interference-free gamma-ray peaks, even though they were not the most intense peak for a given radioisotope.

Table 1
Nuclear data for the elements determined by INAA

Target isotope	Radioactive isotope	Half-life	Gamma-ray used for calculation, keV	Cooling times
^{23}Na	^{24}Na	15 h	1368	2–3 d
^{41}K	^{42}K	12.52 h	1524	2–3 d
^{81}Br	^{82}Br	35.87 h	776	2–3 d
^{75}As	^{76}As	26.3 h	657	2–3 d
^{85}Rb	^{86}Rb	18.6 d	1076	2 w – 1 m
^{64}Zn	^{65}Zn	245 d	1115	2 w – 1 m
^{58}Fe	^{59}Fe	45.1 d	1099	2 w – 1 m
^{59}Co	^{60}Co	5.24 y	1172	2 w – 1 m
^{45}Sc	^{46}Sc	83.9 d	889	2 w – 1 m

Radiochemical separation procedure

Irradiation of samples. About 200–300 mg of lyophilized rice samples or biological Reference Materials (Bowen's Kale or Bovine Liver) were sealed in clean quartz ampoules for irradiations of 8 hours at a thermal neutron flux of 10^{13} $n \cdot cm^{-2} \cdot s^{-1}$ in the IEA-R1 research reactor.

Analytical procedure. After a cooling time of two or three days, the irradiated quartz ampoules containing food samples were washed with HNO_3 solution and deionized water and cooled in liquid nitrogen, broken and transferred to a distillation apparatus containing 100 μg of Hg and 10 mg of Se carriers. The sample and broken pieces of quartz were processed together.

The dissolution was performed with a $HNO_3/H_2SO_4/H_2O_2$ 120 vol. mixture (5 ml/3 ml/15 ml). After cooling to room temperature, 48% HBr (5 ml) was added to the flask (two more additons of 48% HBr were made), and the temperature was raised to over 250 °C.

The distillate was collected in two collector flasks containing 20% hydroxylamine and urea solutions. The solution was transferred into a beaker and after addition of 1 g of sodium metabisulfite it was heated to boiling. After 15 hours the selenium precipitate was filtered onto a Gelman filter paper and dried with alcohol.

In the filtrate, immersed in ice bath, the mercury was precipitated after addition of NH_4OH (40 ml) and thioacetamide (150 mg). After 15 hours the precipitate was filtered through Whatman filter paper and dried with alcohol.

The selenium and mercury precipitates were counted for 5 to 15 hours.

Results and discussion

Instrumental neutron activation (INAA)

The concentrations of nine trace elements were determined in seven different brands of four types of rice grains that are normally consumed by the local population, by INAA. These elements were also measured in the certified biological reference materials Rice flour and Bowen's Kale, in order to check the accuracy of this method.

In Tables 2 and 3, respectively, the non-destructive analysis results of rice grains and reference materials are shown. The precision of the method was in the range of 2–15% for all elements, except for Co and Sc, present at ng/g levels.

The comparison of the data obtained with the certified values showed good accuracy for the elements K, As, Br, Rb, Zn and Fe (relative error about 10%) in both reference materials. The experimental conditions used were not very favourable for determination of small quantities of elements Co and Sc, due to their poor counting statistics.

In general the determination of As in biological samples is made by destructive method, due to its low content and the interfering elements present, such as Na, K and Br. When the concentrations of these interfering elements are low, such as occurs in rice samples, the determination of As by INAA is possible. The gamma ray peak which provides the best sensitivity is 559 keV for ^{76}As. A major interference for ^{76}As is from the 554 keV peak from the decay of ^{82}Br, which can affect the measurements of As. Due to this fact, it was used the 657 peak of ^{76}As for analysis by INAA, which showed no interference.

The results obtained in the analysis of rice grains, presented in Table 2, show that the various types are very similar with respect to the content of the trace elements analyzed. It was also observed that the concentration of elements present in rice samples does not exceed the maximum permissible limits specified by Brazilian legislation (Decree Number 55/871 of 26/03/65).

Destructive analysis

The chemical separation procedure was first tested with non-irradiated food samples and radioactive tracers of mercury and selenium to check the recovery of ^{197}Hg (65 h) and ^{75}Se (121 d).

The trace experiments showed relatively high and constant recovery: (99.3 ± 4.0)% for ^{75}Se and (97.2 ± 4.0)% for ^{197}Hg.

The whole separation procedure in executed in three days. In the organic matter digestion it occurs liberation of the nitroso oxides that interfere in the formation of

Table 2
Elemental concentrations in Brazilian rice grains by INAA

Element	Means ± S. D. (n)*		
	Polished grains		
	Long Fine 1		Long Fine 2
	Cergal	Campeão	Camil
As	0.272± 0.022 (11)	0.279±0.027 (5)	0.271± 0.035 (6)
Br	0.46 ± 0.04 (8)	2.11 ±0.18 (4)	0.36 ± 0.02 (6)
Na	15.0 ± 1.4 (12)	8.9 ±0.7 (4)	13.5 ± 0.6 (5)
K	328 ±16 (8)	419 ±6 (4)	418 ±10 (4)
Rb	2.32 ± 0.27 (11)	3.28 ±0.21 (6)	3.67 ± 0.39 (7)
Zn	14.0 ± 1.6 (10)	15.01 ±0.63 (6)	15.2 ± 0.5 (6)
Fe	–	–	5.76 ± 0.13 (2)
Co ng/g	–	–	–
Sc ng/g	–	–	–

*Means and standard deviation of (n) individual determinations.
– : Not detected.

selenium element.[14] Urea was added to the 20% hydroxylamine solution to avoid this interference since the nitroso oxide and urea do not coexist in solution.

Table 4 shows the results of analysis of Se and Hg in four types of rice.

Table 3
Analysis of biological reference materials by INAA. Concentration in μg/g (dry weight)

Element	Means ± S. D. (n)*			
	Rice Flour (SRM 1568)		Bowen's Kale	
	Certified value	This work	Certified value	This work
K%	0.112±0.02	0.115±0.009 (3)	2.425 ± 0.131	2.490± 0.184 (3)
As	0.41 ±0.05	0.405±0.020 (6)	0.126 ± 0.041	–
Br	1	1.08 ±0.06 (3)	24.6 ± 2.3	26.3 ± 0.3 (3)
Na	–		2392 ±326	2479 ±249 (3)
Rb	7	7.5 ±0.5 (7)	52.9 ± 4.4	53.9 ± 4.5 (11)
Zn	19.4 ±1.0	20.9 ±1.6 (6)	32.7 ± 2.3	35.8 ± 3.2 (11)
Fe	8.7 ±0.6	10.1 ±1.3 (2)	118 ± 17	123 ± 10 (5)
Co	0.02 ±0.01	0.033±0.006 (3)	0.0624 ± 0.011	0.094± 0.021 (3)
Sc	–	–	0.00816± 0.00140	0.014± 0.001 (3)

*Means and standard deviation of (n) individual determinations.
–: Not detected.

Concentrations in μg/g dry weight, unless indicated

Means ± S. D. (n)*			
Polished grains			Parboiled grains
Long Fine 2 Cerejeira	Yellow Long Luma	Japanese/ Catete Yanagui	Long Fine Mingote
0.093± 0.014 (2)	–	0.362± 0.025 (4)	0.310± 0.021 (4)
0.43 ± 0.04 (6)	0.36± 0.06 (3)	0.93 ± 0.06 (4)	0.33 ± 0.02 (4)
12.3 ± 1.6 (5)	6.6 ± 1.0 (4)	17.2 ± 1.0 (4)	16.2 ± 0.7 (4)
654 ±41 (6)	651 ±29 (3)	385 ±10 (2)	1079 ±58 (6)
3.81 ± 0.22 (7)	5.17± 0.62 (6)	3.67 ± 0.19 (6)	11.0 ± 0.7 (8)
16.4 ± 0.4 (6)	17.9 ± 2.0 (5)	15.9 ± 0.6 (6)	7.61 ± 0.66 (4)
7.58 ± 0.83 (2)	20.5 ± 0.8 (2)	88.0 ± 5.5 (4)	12.6 ± 1.2 (3)
25.4 ± 5.7 (2)	25 ± 7 (2)	19.6 ± 0.3 (2)	27.9 ± 4.3 (2)
2.16 ± 0.08 (4)	–	–	1.11 ± 0.08 (2)

Detection limit values obtained were 1.2 ng/g for mercury and 24 ng/g for selenium. These limits were calculated according to CURRIE's criterium[15] in the experimental conditions of the present work.

For the determination of the accuracy of this method, Reference Materials NBS Bovine Liver and Bowen's Kale were analyzed. The results are shown in Table 5, as

Table 4
Determination of Hg and Se in polished rice samples using a radiochemical separation procedure

Concentration, ng/g dry weight*			
Type	Brand	Hg	Se
Long Fine 1	Cergal	7.65	< 24
	Campeão	11.54; 19.39	36.80; 44.38
Long Fine 2	Camil	10.80; 15.23	< 24
	Cerejeira	14.70; 18.89	34.70; 18.67
Yellow Long	Luma	< 1.2	< 24
Japanese/Catete	Yanagui	2.19; 3.01	< 24
Parboiled-Long Fine	Mingote	5.20; 2.67	< 24

*Values of individual determination.

Table 5
Determination of Hg and Se in the biological standards NBS Bovine Liver (SRM 1577a) and Bowen's Kale. Concentration in μg/g dry weight

Element	Means ± S. D. (n)*			
	Bovine Liver		Bowen's Kale	
	Certified value	This work	Certified value	This work
Hg	0.004±0.002	0.0054±0.0014 (4)	0.168±0.025	0.169±0.019 (4)
Se	0.71 ±0.07	0.638 ±0.075 (7)	0.133±0.021	0.123±0.020 (4)

*Means and deviation standard of (n) individual determinations.

well as the certified values for each sample. As can be seen from the data presented, the values obtained are in good agreement with the certified values.

Conclusion

This work has provided information on the levels of As, Hg, Se, Br, Na, Zn, K, Rb, Co, Fe and Sc present in various types of Brazilian rice grains. This kind of food was analyzed since it is one of most widely consumed by the local population. The levels of toxic elements Hg, As and Se were below the values established by national legislation.

The radiochemical separation procedure developed resulted simple and sensitive for determination of Hg and Se in biological materials. The method was applied to the analysis of the reference materials Bovine Liver and Bowen's Kale in order to check the accuracy and reproducibility.

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