

MULTIELEMENTAL ANALYSIS OF BRAZILIAN MILK POWDER AND BREAD SAMPLES BY NEUTRON ACTIVATION*

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The concentrations of Na, Cl, Mn, Br, Fe, Zn, Rb, Sb, Sc, Cr, Al and Mg were determined in some types of bread and in some brands of milk powder consumed in the city of São Paulo (SP - Brasil), by instrumental neutron activation analysis. Radiochemical separations were carried out by means of retention of ^{24}Na on hydrated antimony pentoxide (HAP) from a 8N HCl solution, after digestion of the organic matter. It was possible in this way to determine the radioisotopes ^{64}Cu , $^{69\text{m}}\text{Zn}$ and ^{140}La in the effluent solution. The detection limits of the trace elements analyzed in bread and milk powder samples were determined using the Currie and Girardi criterions.

Introduction

The importance of trace elements to human and animal health has stimulated the analysis of their concentrations in a wide variety of biological materials. Several mechanisms of trace element actions in living species still are not very clear and many studies have been carried out to examine the participation of those elements in essential life processes.¹⁻³ For these investigations it is very important to know the concentrations of elements presents in human diet, since foodstuffs are important intakes of the trace elements in human organisms.

According to UNDERWOOD,¹ there are only three elements that are considered toxic, viz. mercury, cadmium and lead. However, the elements cannot be classified according to their toxicity, since any element will be toxic if it is inhaled or ingested in high quantities for a long period of time.

During the last years, public attention has been particularly concerned with contamination of the biosphere by pollutants, since the development of industrial and

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agricultural activities of man have introduced changes in food composition. Therefore, it is important to verify if the foodstuffs that are part of the human diet have the adequate amounts of essential trace elements, and if the concentrations of elements with toxic effects are below safety limits, so that they do not imply risks to human health.

The recognition of the importance of trace elements to human health has enhanced the need for application of sensitive, precise and accurate analytical methods to the determination of these elements in biological samples. A number of papers have been published on the analysis of food samples, employing several analytical methods.⁴⁻⁶ Among these methods neutron activation analysis is one of the most efficient for simultaneous determination of a number of elements in the ppm to ppb levels.⁷⁻¹⁰

This work is part of an IAEA research contract, which is part of a Coordinated Research Program on application of nuclear techniques to toxic elements analysis in foodstuffs. Milk powder and bread samples were analyzed employing thermal neutron activation analysis by non-destructive and destructive methods, since they are considered as two of the most important foodstuffs consumed by the local population.

Most biological samples contain large amounts of K, P and Na, the radioactivity of the radioisotopes ^{42}K , ^{32}P and mainly ^{24}Na strongly interfering with the determination of many elements.

Radiochemical procedures¹¹⁻¹³ are used to separate the elements of interest from interfering activities. In this work the interference of ^{24}Na was eliminated using the hydrated antimony pentoxide inorganic exchanger. It was possible, in this way, to determine some radioisotopes such as ^{64}Cu , $^{69\text{m}}\text{Zn}$ and ^{140}La that could not be determined using the purely instrumental method.

Special attention was payed to the calculation of detection limits of the elements analyzed, since the way of determining these limits is not uniform throughout the literature. The detection limits were calculated by using the CURRIE¹⁴ and GIRARDI¹⁵ criterions and the results obtained in both cases were compared.

Experimental

Sample collection and preparation

Two different types of bread, "bread roll" (type I) and "sandwich bread" (type II) and three brands of milk powder that are most widely consumed by local population were obtained from bakeries and supermarkets of the city of São Paulo.

The bread slices and rolls samples were dried at 50 °C for about 30 hours, and were afterwards crushed in an agate mortar in order to obtain an adequate granulometry for

the analysis. Milk powder samples from each can were analyzed without any further treatment.

Standard

BOWEN's Kale¹⁶ was chosen as reference material to analyze most of the elements. However, in some cases stock solutions of elements such as Na, Cl and Mn were prepared by dissolution of the elements or their salts in suitable reagents. From these solutions aliquots were taken in order to prepare standards of these elements for irradiation.

Counting equipment

Samples and standards were counted using a 4096 channel ORTEC model 6240 B multianalyzer coupled to an ORTEC Ge(Li) detector, with a FWHM of 2.6 keV for the 1332 keV peak of ⁶⁰Co. The gamma-ray spectrometer is connected on line with a PDP-11/04 computer to process the gamma-ray spectra using the GELIGAM program developed by ORTEC in ORACL language.

Instrumental Neutron Activation Analysis

Irradiations of bread and milk powder samples and standards. Samples weighing about 100 mg and BOWEN's Kale standard (50 mg) were weighed and sealed in high purity polyethylene vials (Free University, Amsterdam), and irradiated for 15 minutes (bread samples) and for 3 minutes (milk powder) at a thermal neutron flux of about $10^{11} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ in the IEA-R1 swimming pool type research reactor. After a cooling period from about 2 minutes to 2 hours, the short-lived radioisotopes were measured (⁵⁶Mn, ³⁸Cl, ²⁸Al, ²⁷Mg, ²⁴Na). The longer lived species were determined after irradiations for 8 hours at a flux of $10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and after cooling periods from 3 to 15 days.

Results of non-destructive analysis. The concentrations of 10 trace elements were measured in bread samples. The elements Mn, Na, Cl were determined employing short irradiation times whereas long irradiations times were used for the determinations of Br, Zn, Rb, Cr, Fe, Sb and Sc. In the milk powder samples the following elements were determined: Al, Cl, Mn, Mg, in the short irradiations and Na, K, Br, Rb, Sb, Ca, Cr and Zn in the long irradiations. In Tables 1 and 2, respectively, of non-destructive analysis results of bread and milk powder samples are shown.

In these tables are also shown the values of the mean and standard deviations of 2 or 3 individual determinations.

Table 1
Results of non-destructive analysis of

Type	Brand	Slice	Elemental concentrations (dry weight)			
			%		mg/kg	
			Na	Cl	Mn	Br
I (Bread Koll)	A	1	0.77±0.02	1.04±0.06	10.2 ±0.8	10.9±0.3
		2	0.78±0.02	1.14±0.01	12.8 ±0.8	9.5±0.5
		3	0.76±0.02	1.16±0.09	12.9 ±0.8	10.4±0.4
	B	1	0.86±0.04	1.35±0.03	6.98±0.08	7.8±0.3
		2	0.86±0.01	1.38±0.06	7.04±0.08	11.4±0.4
		3	0.90±0.02	1.43±0.02	6.83±0.07	8.7±0.4
II (Sandwich Bread)	C	1	0.96±0.01	1.49±0.07	7.4 ±0.3	12.5±0.7
		2	0.75±0.03	1.27±0.03	6.4 ±0.2	10.5±0.4
		3	0.73±0.02	1.17±0.04	8.8 ±0.6	10.7±0.1

^aMean and standard deviation of 2 or 3 individual determinations.^bValue of a single determination.^cSample probably contaminated during sieving.

ND - Not detected.

Table 2
Results of non-destructive analysis of the

Brands	Can	Elemental concentrations				
		%				mg/kg
		K	Cl	Na	Ca	Mg
A	1	1.15±0.02	0.76±0.05	0.323±0.004	1.0 ±0.1	1040±25
	2	1.13±0.02	0.67±0.04	0.302±0.006	0.9 ±0.1	1035±59
B	1	1.18±0.03	0.65±0.01	0.311±0.002	0.80±0.22	1029±40
	2	1.16±0.01	0.68±0.03	0.307±0.002	0.67±0.08	897±72
C	1	1.26±0.01	0.79±0.04	0.388±0.003	0.88±0.06	840±54
	2	1.25±0.04	0.86±0.04	0.377±0.005	0.77±0.04	1179±78

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		3	0.76±0.02	1.16±0.09	12.9 ±0.8	10.4±0.4
	B	1	0.86±0.04	1.35±0.03	6.98±0.08	7.8±0.3
		2	0.86±0.01	1.38±0.06	7.04±0.08	11.4±0.4
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II (Sandwich Bread)	C	1	0.96±0.01	1.49±0.07	7.4 ±0.3	12.5±0.7
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Table 2
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		%				mg/kg
		K	Cl	Na	Ca	Mg
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	2	1.13±0.02	0.67±0.04	0.302±0.006	0.9 ±0.1	1035±59
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C	1	1.26±0.01	0.79±0.04	0.388±0.003	0.88±0.06	840±54
	2	1.25±0.04	0.86±0.04	0.377±0.005	0.77±0.04	1179±78

^aMean and standard deviation of 2 or 3 individual determinations.^bValue of a single determination.

bread (mean \pm standard deviation)^a

Elemental concentrations (dry weight)					
		mg/kg			$\mu\text{g/kg}$
Fe	Zn	Rb	Cr	Sb	Sc
75 \pm 3	14.9 \pm 0.6	3.4 \pm 0.4	0.30 \pm 0.01	0.90 \pm 0.01 ^c	2.36 \pm 0.56
72 \pm 2	20 \pm 3	2.2 \pm 0.1	0.18 \pm 0.03	0.24 ^b	ND
54 \pm 1	15 \pm 3	4.1 \pm 0.4	0.18 \pm 0.02	0.21 \pm 0.04	2.60 ^b
41 \pm 4	11 \pm 1	2.2 \pm 0.1	0.24 \pm 0.01	0.22 \pm 0.02	2.02 \pm 0.31
60 \pm 8	10.6 \pm 0.4	2.4 \pm 0.2	0.19 \pm 0.03	0.24 ^b	1.70 ^b
44 ^b	11 \pm 1	2.1 \pm 0.1	0.26 \pm 0.04	0.21 ^b	2.37 \pm 0.30
60 \pm 7	9.7 \pm 1.1	2.4 \pm 0.3	0.21 \pm 0.01	0.29 \pm 0.04	2.63 ^b
45 ^b	9.7 \pm 1.3	2.7 \pm 0.3	0.24 ^b	0.28 ^b	2.47 ^b
37 \pm 2	10 ^b	2.2 \pm 0.2	0.13 \pm 0.01	0.32 \pm 0.03	1.65 ^b

milk powder (mean \pm standard deviation)^a

Elemental concentrations						
			mg/kg			
Al	Mn	Br	Cr	Zn	Rb	Sb
10.4 \pm 0.2	0.52 \pm 0.04	14.7 \pm 0.4	0.21 \pm 0.03	24 \pm 3	25 \pm 2	1.07 \pm 0.06
11.2 \pm 0.2	0.57 \pm 0.06	15.6 \pm 0.2	0.24 \pm 0.01	22 \pm 3	25 \pm 1	0.78 \pm 0.03
10.9 \pm 1.0	0.53 \pm 0.09	34.2 \pm 0.3	0.18 \pm 0.01	22 \pm 1	38 \pm 2	0.64 \pm 0.06
11.2 \pm 1.0	0.72 \pm 0.06	31.9 \pm 1.0	0.23 \pm 0.04	23 \pm 1	48 \pm 1	0.72 \pm 0.08
13.3 \pm 1.2	0.55 \pm 0.04	18.6 \pm 0.3	0.21 \pm 0.03	25 \pm 1	36 \pm 1	0.60 \pm 0.05
13.5 \pm 1.0	0.58 \pm 0.02	17.6 \pm 0.7	0.22 \pm 0.03	24 \pm 1	36 \pm 2	0.57 ^b

Activation analysis with radiochemical separation

Dissolution of bread and milk powder samples. After irradiation for 8 hours (neutron flux of $10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) and cooling time of about 60 hours, the bread samples (100 mg) and BOWEN's Kale standard (50 mg) were transferred from the high purity plastic irradiation vials to beakers containing 2 ml of carrier solutions of the elements La, Sb, Zn and Sc. Dissolution was performed with concentrated HNO_3 and 70% HClO_4 . The mixture was heated in a sandbath to complete digestion of the organic matter. The solution was evaporated to dryness and the residue taken up in 8N HCl with gentle heating.

A mixture of concentrated HNO_3 and 120 vol. H_2O_2 was used to dissolve the milk powder samples (100 mg) and biological standard (50 mg). After the evaporations of the acids the residue was taken up in 8N HCl with gentle heating.

A clear solution was obtained for all the samples subjected to the above described dissolutions.

Retention of ^{24}Na on hydrated antimony pentoxide (HAP). In the present work a small column of HAP was used for the retention of ^{24}Na . The preparation of the HAP column was carried out according to VASCONCELLOS.¹⁷

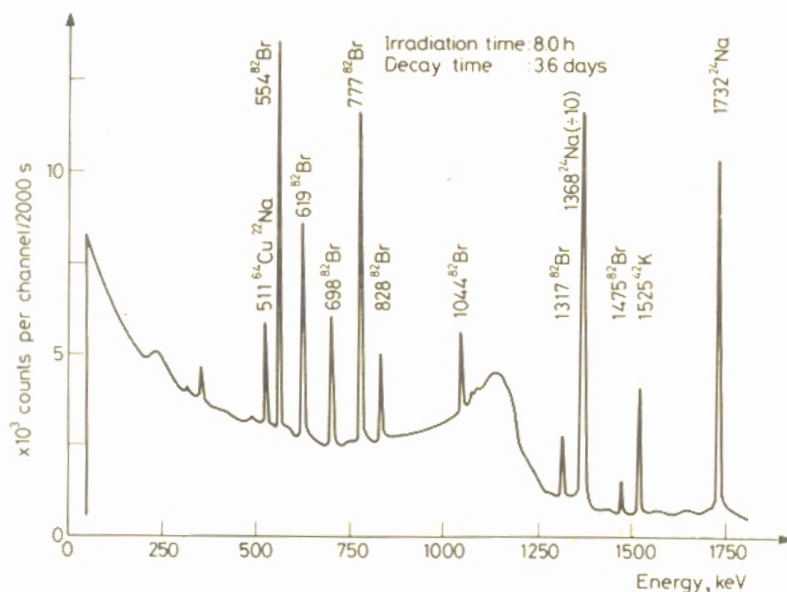


Fig. 1. Non-destructive analysis. Gamma-ray spectrum of the milk powder

The chloride solution of the sample was passed through a pre-equilibrated HAP column at a flow rate of 0.5 ml/min. The column was washed with 5 ml of 8N HCl. The effluent was counted in penicillin-type flasks in the same day of the chemical separations.

The column material was transferred to penicillin-type flasks, with the aid of deionized water. After 3 to 5 days from the chemical process, the HAP column was counted. After 13 days of cooling time, a second measurement of HAP columns and effluent solutions was performed, for the determination of longer lived species.

The same treatment as described above was carried out for the BOWEN's Kale standard.

Results of destructive analysis (RNAA). In the destructive analysis, it was possible to determine ^{64}Cu , $^{69\text{m}}\text{Zn}$, ^{122}Sb and ^{140}La in the effluent solution. The high activity of ^{24}Na produced by thermal activation interferes in the determination of these radioisotopes in the purely instrumental analysis as can be observed in Figure 1. There is also a strong interference of β -emitters, such as ^{32}P and ^{35}S present in the food samples analyzed, in the low energy region of the spectra (Figs 1 and 2).

About 99.9% of ^{24}Na was retained in the HAP column in the experimental conditions utilized. The 1524 keV peak of ^{42}K was detected both in the effluent and in the HAP column. The areas of the peaks were summed for the calculation of potassium concentration in the samples.

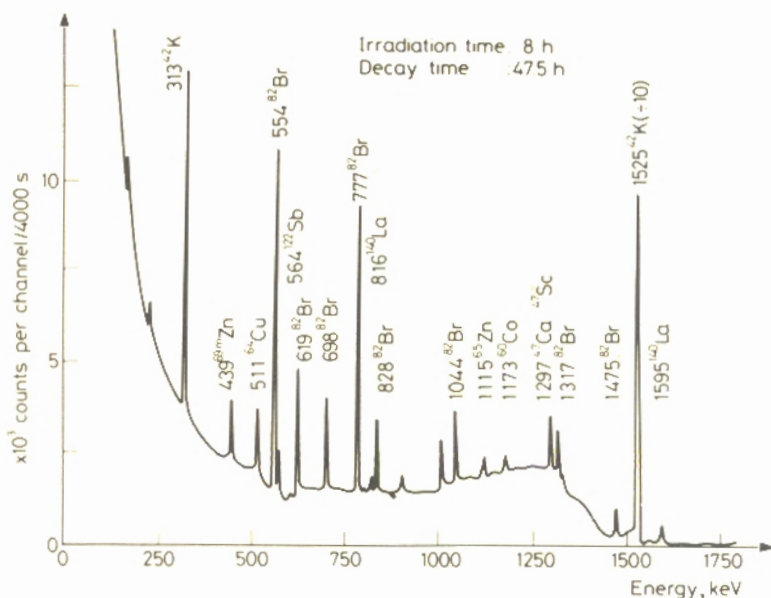


Fig. 2. Destructive analysis. Gamma-ray spectrum of the effluent solution of milk powder

Table 3
Results of the destructive analysis of bread (mean \pm standard deviation)^a

Type	Brand	Slice	Elemental concentrations (dry weight)									
			%			mg/kg				$\mu\text{g/kg}$		
			Na	K	Fe	Zn	Cu	Sb	La	Sc		
I (Bread roll)	A	1	0.78 \pm 0.04	0.34 \pm 0.05	66 \pm 4	20 \pm 2	7.9 \pm 1.1 ^c	1.20 ^c	19.6 ^b	4.2 \pm 0.9		
		2	0.79 \pm 0.01	0.33 \pm 0.01	72 \pm 2	18 \pm 1	3.0 \pm 0.2	ND	15.9 ^b	2.9 \pm 0.1		
		3	0.81 \pm 0.01	0.26 \pm 0.03	61 \pm 3	20 \pm 1	3.9 \pm 0.4	ND	8.1 ^b	2.4 \pm 0.1		
	B	1	0.84 \pm 0.02	0.250 \pm 0.004	43 \pm 6	12.6 \pm 0.3	2.5 \pm 0.1	0.3 \pm 0.1	12 \pm 2	2.3 \pm 0.5		
		2	0.88 \pm 0.02	0.209 \pm 0.006	63 \pm 7	13.0 \pm 0.4	2.9 ^b	0.22 ^b	27 \pm 8	ND		
		3	0.86 \pm 0.04	0.200 \pm 0.004	45 ^b	10.7 \pm 0.9	2.8 \pm 0.3	0.15 \pm 0.01	14 \pm 3	2.6 \pm 0.4		
	C (Sandwich bread)	1	0.95 \pm 0.06	0.30 \pm 0.02	62 \pm 9	12.1 \pm 0.9	2.1 \pm 0.1	0.18 ^b	13.2 ^b	2.2 \pm 0.1		
		2	0.72 \pm 0.02	0.30 \pm 0.06	52 \pm 1	10.6 \pm 0.5	2.3 \pm 0.2	0.25 ^b	12.5 ^b	2.1 \pm 0.1		
		3	0.75 \pm 0.04	0.31 \pm 0.02	36 ^b	10.8 \pm 0.3	2.5 \pm 0.3	0.42 ^b	ND	1.7 ^b		

^aMean and standard deviation of 2 individual determinations.

^bValue of a single determination.

^cSample probably contamination during sieving.

ND - Element not detected.

Table 4
Results of the destructive analysis of milk powder (mean \pm standard deviation)^a

Brands	Can	Elemental concentrations									
		%				mg/kg				$\mu\text{g/kg}$	
		K	Na	Ca	Zn	Cu	Rb	Sb	La		
A	1	1.20 \pm 0.02	0.329 \pm 0.004	1.32 \pm 0.04	35 \pm 2	1.27 \pm 0.01	25 \pm 1	0.91 ^b	26 ^b		
	2	1.14 \pm 0.02	0.317 \pm 0.004	1.28 \pm 0.04	29 \pm 1	1.29 \pm 0.05	27 \pm 2	0.78 \pm 0.02	24 ^b		
B	1	1.21 \pm 0.03	0.310 \pm 0.026	0.88 \pm 0.25	22 \pm 2	1.1 \pm 0.1	41 \pm 3	0.73 \pm 0.08	ND		
	2	1.17 \pm 0.02	0.332 \pm 0.004	1.0 \pm 0.1	24 \pm 1	1.7 \pm 0.2	49 \pm 3	0.51 \pm 0.04	ND		
C	1	1.25 \pm 0.10	0.386 \pm 0.006	0.81 ^b	34 \pm 1	0.80 \pm 0.002	34 \pm 4	0.59 ^b	23 ^b		
	2	1.22 \pm 0.11	0.384 \pm 0.028	0.82 \pm 0.04	33 \pm 1	0.89 \pm 0.06	37 \pm 2	0.52 \pm 0.05	ND		

^aMean and standard deviation of 2 individual determinations,

^bValue of a single determination,

ND - Element not detected.

In Tables 3 and 4 the results of RNAA are presented. The concentrations of the elements Na, K, Fe, Zn, Cu, Sb, La and Sc were determined in the bread samples, and Na, Ca, K, Zn, Cu, Sb, Rb and La were determined in the milk powder.

Discussion and conclusions

Since in the present work it was possible to determine some elements using non-destructive and destructive analysis, a comparison has been carried out between results by both techniques using Student's *t* test.¹⁸ In Table 5 this comparison is presented. In general, there was good agreement between the means obtained by the two techniques employed. The only differences occurred for the elements zinc and calcium due probably to bad counting statistics for Ge(Li) counting in the destructive analysis.

The radiochemical separation used in this work allowed the determination of elements such as Cu, La and K, which could not be determined by the instrumental approach, due to the high activity of ²⁴Na.

The relative standard deviations obtained for most elements in the bread and milk powder (Tables 1–4) samples were about 10%, which is generally considered as a good

Table 5
Student's *t*-test applied to the comparison of INAA and RNAA

Element	Bread			Milk powder		
	A	B	C	A	B	C
Na	+	+	+	+	+	+
Fe	+	+	+	a	a	a
Zn	+	+	—	—	+	—
Sb	+	+	+	+	+	+
K	a	a	a	+	+	+
Sc	+	+	+	a	a	a
Rb	a	a	a	+	+	+
Ca	a	a	a	—	+	+

^aAnalysis not made.

+ Means not significantly different.

— Means significantly different.

result in trace analysis. For the elements Cr, Fe, and mainly Sc, the reproducibility was not so good due to their low activities for Ge(Li) counting. There was a small advantage of purely instrumental analysis in relation to destructive analysis concerning the reproducibility. This occurred probably because at the same time that some inter-

fering activities were eliminated in the chemical procedure, the total peak areas decreased due to a change in the counting geometry, since it was necessary to count liquid effluents that have a volume higher than those of powdered samples.

On the whole, the analytical method employed has proved to be efficient for determining the concentrations of Na, Cl, Mn, Mg, Br, Fe, Sb, Zn, Ca, Rb, Cr, La and Sc, in food samples, at concentrations ranging from percents to parts per billion (ppb). However, it has been observed that some important elements for the study of compositions of foodstuffs could not be analyzed: some toxic elements, such as Hg, Se, As because the analytical procedure employed has not been adequate for determining these toxic elements present at very low concentrations in the samples analyzed, and others such as Pb that do not have favourable nuclear characteristics for thermal neutron activation analysis.

Detection limits

For a correct appraisal of any analytical method, where trace elements are quantified in biological matrices, it is important to know the smallest concentration at which these elements can be determined. These values are generally expressed in terms of detection limits.

Table 6
Limits of detection (mg/kg) in bread and milk powder samples. Non-destructive analysis

Element	Bread		Milk powder	
	D _e	L _D	D _e	L _D
Cr	0.056	0.18	0.056	0.53
Sb	0.0051	0.028	0.0051	0.048
Br	0.051	1.1	0.020	0.77
Mn	0.018	0.47	0.0073	0.18
Sc	0.00035	0.0016	0.00035	a
Rb	0.17	0.49	0.16	0.23
Fe	7.4	34.3	7.4	a
Zn	0.12	2.8	0.12	1.8
Al	0.064	a	0.064	4.1

^aValue not calculated.

D_e - Detection limits by GIRARDI's method.

L_D - Detection limits by CURRIE's method.

Cooling time: 4.5 minutes (Al); 40 minutes - 3 hours (Mn); 4-6 days (Br); 10-13 days (Cr, Sb, Rb, Fe, Sc and Zn).

Counting time: 200 seconds (Al); 2000 seconds (Mn, Br); 10000 seconds (Cr, Sb, Sc, Rb, Fe and Zn).

Basically, the detection limit is a number, expressed in units of concentration (or mass) that describes the lowest concentration level (or mass) of the element of interest that can be determined to be statistically different from an analytical blank.

Although this definition seems simple, significant differences have been found in expressing these values, due to different forms of calculating the analytical blank, as well as to different approaches to calculate the blank standard deviation. A number of reports have been published to analyze the existing models to determine the detection limits.¹⁹⁻²² In radiochemical work, the criteria of GIRARDI¹⁵ and mainly of CURRIE¹⁴ are mostly utilized for the determination of detection limits of the elements analyzed by neutron activation analysis.

In Tables 6 and 7 are shown the values calculated for the detection limits of analyzed trace elements in bread and milk powder by non-destructive and destructive analysis respectively, in the experimental conditions of the present work.

The Tables show that the detection limits calculated by GIRARDI's method were always lower than those obtained by CURRIE's method. This can be explained by the fact that in GIRARDI's method the limits are calculated from standards of pure elements, while in CURRIE's method real samples are considered, where the interferences of other elements are taken into account.

For the elements whose limits were calculated for both non-destructive and destructive methods (Sb, Sc, Fe and Zn in bread and Sb, Rb and Zn in milk powder), it was verified that there were no significant differences between the values found.

Table 7
Limits of detection (mg/kg) in bread and milk powder samples. Destructive analysis

Element	Bread		Milk powder	
	D _e	L _D	D _e	L _D
Cu	0.0043	0.018	0.0040	0.048
Sb	0.0097	0.027	0.0097	0.032
Sc	0.00075	0.0017	0.00075	a
Fe	7.2	12.1	7.2	a
Zn	1.1	2.1	1.1	2.4
La	0.00064	0.0021	0.00064	0.024
Rb	0.16	a	0.16	0.33

^aValue not calculated.

D_e - Detection limits of GIRARDI's method.

L_D - Detection limits of CURRIE's method.

Cooling time: 41 hours (La); 45 hours (Cu); 13 days (Sb, Sc, Zn, Rb, Fe).

Counting time: 4000 seconds (Cu, La); 10000 seconds (Sb, Sc, Rb, Fe, Zn).

This fact indicates that the sensitivity of the analysis was not increased significantly when the radiochemical separation based on the retention of Na on HAP column was employed. For a significant increase in the sensitivity, it would be necessary to apply a more elaborate separation method.

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