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DETERMINATION OF As, Cd, Cr, Cu, Hg, Sb AND Se CONCENTRATIONS BY RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS IN DIFFERENT BRAZILIAN REGIONAL DIETS

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The present paper describes radiochemical separation procedures developed for the determination of seven elements: As, Cd, Cr, Cu, Hg, Sb and Se in different Brazilian regional diets. In the case of the elements As, Hg, Sb and Se, the procedure was based on retention in inorganic exchanger TDO (tin dioxide) and determination of Hg by extraction with $Ni(DDC)_2$. For determination of Cd, Cr, Cu and Se the procedure chosen was based on retention in inorganic exchanger HMD (hydrated manganese dioxide) and extraction of Cu and Cd as diethyldithiocarbamate compounds. The accuracy and precision of the methods studied were tested by means of analyses of different reference materials. Due to the lack of data on trace element levels in Brazilian foodstuffs and diets, these methods were applied to determination of these elements in different Brazilian regional diets. These diets were supplied by the Food and Experimental Nutrition Department of the Faculty of Pharmaceutical Science, University of São Paulo. The daily dietary intake values for these diets are presented for As, Cd, Cr, Cu, Hg, Sb and Se.

Certainly food is the main transporting medium carrying trace elements into the human body. Other than food, modern agricultural practices including fertilizers, insecticides, processing and packaging are co-responsible for the continuous changing of the food character itself. This is the way toxic elements are most usually introduced into food items.[1] Monitoring toxic element levels became then a rule because of the adverse impact of the toxic metals. Since the diet is the main source of nutrients, it is important to study the elemental concentration of the diet.[2] 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.

During the past years some Brazilian food items such as bread and milk,[3] rice,[4] and drinking water,[5] have been analyzed for their elemental contents by nuclear methods.

In the last three years, our efforts were concentrated on the development of radiochemical separations in order to determine the elements As, Cr, Hg, Sb and Se.[6]

These elements are commonly found in biological materials, at the ppm or subppm level. At these levels, problems occur in accurately determining the concentrations of

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these elements due to several reasons: losses during sample treatment, contamination, reagent blank and interferences.

Faster and more reliable radiochemical methods other than distillation and precipitation[4] were achieved for the determination of As, Cd, Cr, Cu, Hg, Sb and Se. These elements were separated by means of retention on inorganic exchangers and solvent extraction. These techniques have also been employed by other authors for biological material analyses, showing good results.[7–13]

The developed procedures were applied to the analysis of several biological reference materials and in four human diet samples: diet of University Students, diet of Manaus region (North of the country), and two diets of Santa Catarina region (South of the country).

Experimental

Diet preparation

Student's diet: About 50 meals (lunch and dinner) served at the central restaurant in the campus of the University of São Paulo, used by students and staff, were collected by duplicate analysis. Foodstuff contents in these meals follow Brazilian basic diets for medium to high income groups and are composed of rice, beans, meat or derivates, greens and vegetables, fruits, sweets, bread and milk.[14]

The meals collected were then transported to the Nutrition Laboratory of the FCF-USP. The foods were separately weighed, placed in stainless steel trays and dried in a ventilated oven at 60 °C during 12 hours or until totally dried.

The foods were pulverized and homogenized in a knife mill and kept at 4 °C before analysis.

Manaus and Santa Catarina diets: These diets were prepared from foods consumed and produced in these respective regions by dietary recall data. The Manaus and Santa Catarina 1 diets are related to low-income groups, while Santa Catarina 2 is related to an average of groups of several incomes.

The foods were obtained in the local supermarkets and fairs and prepared according to habits of each region. Thereafter, the preparation procedure of the diets was as previously described.

Determination of water contents: After drying at 60 °C during preparation steps, diets were dried before analysis in a conventional oven at 85 °C, for 2 hours, in order to determine their water contents. The results obtained were: 8.0% for the student's diet, 4.9% for the Manaus diet, 4.8% for the Santa Catarina 1 diet and 4.7% for the Santa Catarina 2 diet.

Irradiation and dissolution of the reference materials and samples

About 200 mg of reference materials and samples were weighed in clean quartz ampoules. A multielemental standard containing elements As, Hg, Sb and Se and another with Cd, Cr, Cu and Se were prepared by mixing appropriate aliquots of solutions of these elements made from spectroscopically pure reagents. Aliquots of the multielemental solutions were pipetted into quartz ampoules.

Samples together with standards were irradiated in the IEA-R1 Research Reactor for 8 hours under a thermal neutron flux of 10^{13} n · cm^{-2} · s^{-1}. After irradiation, samples and standards were processed in the same way.

Preparation of the $Ni(DDC)_2$, $Zn(DDC)_2$ and $Bi(DDC)_3$ solutions: Nickel, bismuth and zinc diethyldithiocarbamates (DDC) were prepared by mixing aqueous solutions of Na(DDC) with their respective nitrate salts.[15]

Counting systems

Gamma ray measurement of irradiated samples and standards was carried out by using either of three counting systems.

(1) Gamma-X detector coupled to a multichannel EG&G Ortec model 7450 (resolution of 1.14 keV for the 121.97 keV γ-ray peak of ^{57}Co and 2.5 keV for the 1332.49 keV γ-ray peak of ^{60}Co) and IBM/PC microcomputer, Monydata model NYDA 200 plus.

(2) GEM 20190 POP TOP detector coupled to an ORTEC ACE 4K card plus IBM/PC microcomputer (resolution of 1.14 keV for the 121.97 keV γ-ray peak of ^{57}Co and 1.94 keV for the 1332.49 keV γ-ray of ^{60}Co).

(3) GEM 20190 POP TOP detector coupled to an ORTEC ACE 8K card plus IBM/PS2 microcomputer (resolution of 0.92 keV for the 121.97 keV γ-ray peak of ^{57}Co and 1.77 keV for the 1332.49 keV γ-ray peak of ^{60}Co).

Spectrum analysis was performed by means of the Vispect2 software, developed by Dr. D. PICCOT, Saclay, France.

Separation procedures

Procedure I

Determination of As, Hg, Sb and Se by using inorganic exchanger TDO and Hg by extraction with $Ni(DDC)_2$: Irradiated samples and standards were transferred to teflon bombs and 100 µg carriers of each element were added. After addition of 4 ml of concentrated HNO_3, teflon bombs were taken to a conventional oven at 130 °C, for 15 to 20 hours, depending on the reference material.

Dissolved samples were cooled and 10 drops of H_2O_2 and distilled water were added to make the solution 1M HNO_3. The solution was passed through a TDO column, at a flow rate of about 1 ml/min. The column was washed twice with 15 ml of 1M HNO_3, allowed to dry, and the TDO transferred to a plastic counting vial for the measurement of ^{76}As, ^{75}Se and $^{122-124}Sb$ on a γ-ray spectrometer.

The effluent of the column was adjusted to pH 1 with NH_4OH and Hg was extracted with 20 ml 0.005M $Ni(DDC)_2$ in chloroform. The total extraction of Hg was obtained with a shaking time of 15 minutes. The aqueous phase was discarded and the organic phase was measured for $^{197-203}Hg$.

Yields obtained for elements As, Se, Sb, and Hg, in the complete radiochemical procedure, as calculated from the tracer experiments, were $95.5 \pm 0.6\%$, $81.7 \pm 0.8\%$, $95 \pm 3\%$ and $97.3 \pm 0.7\%$, respectively.

Procedure II

Determination of Cd, Cr, Cu and Se by using inorganic exchanger HMD and solvent extraction using diethylditiocarbamate compounds: After irradiation, samples and standards were transferred to Parr acid digestion bombs 20 μg of Cr, 50 μg of Se, 500 μg of Cu and 500 μg of Cd carriers and 4 ml of concentrated nitric acid were added.

The dissolved samples after 2 minutes at 360 watts in a microwave oven, were transferred to teflon vessels with a small amount of water. Two milliliters of concentrated perchloric acid and 5 drops of concentrated HF were added and the solution was slowly evaporated to a final volume of about 0.5 ml. This solution was diluted with 15 ml 1M HNO_3 and passed through a preconditioned HMD column at a flow rate of 0.5 ml/min by varying the packing density of the HMD. Selenium and chromium were retained in the HMD bed. Sodium-24, the major interference in both biological and environmental matrices, passed through in the eluate. Columns were washed twice with 15 ml of 1M HNO_3 each time, dismantled, and the HMD transferred to polyethylene counting vials and the 320 keV γ-ray peak of ^{51}Cr and 264 keV peak of ^{75}Se were measured. The eluted fraction was saved for the subsequent Cu and Cd separation.

This procedure was adapted from the procedure developed by GREENBERG.[7]

The pH of the eluted fractions was adjusted to 1.5 with NH_4OH, and 100 mg of Zn holdback carrier was added. Solutions were placed in separatory funnels and 25 ml of 0.003M $(Bi(DDC)_3$ in chloroform was added in order to extract copper. Solutions were shaken for 30 minutes and the organic fractions containing Cu were placed in glass bottles for counting. The aqueous fraction was washed with 5 ml of chloroform and the wash was combined with the organic fraction.

Cadmium was extracted from the original aqueous solution remaining in the separatory funnel into 25 ml of 0.005M of $Zn(DDC)_2$ in chloroform. A shaking time of 30 minutes was used. The resulting extract was also placed in glass vials for counting and the aqueous fraction was washed and combined with the organic fraction.

The organic fractions containing ^{64}Cu were counted immediately after separation. The organic fractions containing the Cd were allowed to stand for 24h to establish the equilibrium between ^{115}Cd–^{115m}In. Gamma rays from the decay of both of these isotopes were used for Cd analysis.

Chemical yields obtained in this procedure by means of tracer experiments were: $99 \pm 1\%$, $98 \pm 2\%$, $95 \pm 4\%$, and $97 \pm 4\%$, for Se, Cu, Cd and Cr, respectively.

Results and discussion

Table 1 presents the results obtained for the analysis of As, Hg, Sb and Se in several reference materials, as well as the literature values,[16] obtained by Procedure I. Table 2 shows the results obtained for the determination of Cu, Cd, Cr and Se in several reference materials by Procedure II.

The results obtained using radiochemical separation schemes presented in this work (Tables 1 and 2) are, in general, in good agreement with literature and reference concentration values.

The method using TDO in HNO_3 medium for As, Sb and Se retention and $Ni(DDC)_2$ for Hg extraction (Table 1) was applied to six reference material analysis. Relative standard deviations ranging from about 4 to 20% were obtained for Bowen's Kale, Copepod, Bovine Liver and Fish Flesh reference materials, which is acceptable at these concentration levels. In the case of Sb in H-9 and Bowens' Kale and Se in Rice Flour, the relative standard deviations were above 20%.

Five reference materials were analyzed using HMD in HNO_3 medium for Cr and Se retention and Cu and Cd extraction as diethyldithyocarbamate compounds (Table 2). Relative standard deviation ranged from 3,3% for Se in Bovine Liver to 17% for Cd in Total Diet. The relative errors were from 0% for Cd in Mussel Tissue to 20% in Citrus Leaves, which is acceptable at these concentration levels.

The results for Cr were not satisfactory with standard deviation and relative errors above 20%. A possible conclusion may be that the problem for Cr determination is related to the dissolution steps. This part of the procedure needs to be improved.

The dissolution procedures employing conventional ovens are less rapid than those using microwave ovens.

Table 1
Results of the determination of As, Hg, Sb and Se in biological materials using TDO inorganic exchanger (PROCEDURE 1)

Reference material		This work, μg/g dry weight	RSD, %	Relative error, %	Literature values[16]
Bowen's Kale	As:	0.135 ± 0.019	14.1	3.1	0.131 ± 0.045
	Hg:	0.192 ± 0.014	7.3	12.3	0.171 ± 0.027
	Sb:	0.078 ± 0.017	21.8	13.9	0.0685 ± 0.0140
	Se:	0.127 ± 0.005	3.9	5.2	0.134 ± 0.020
Copepod	As:	7.3 ± 0.7	9.6	8.9	6.7 ±0.6
IAEA-MA-A-1	Hg:	–	–	–	0.28 ± 0.01
	Sb:	–	–	–	0.07 ± 0.03
	Se:	2.4 ± 0.2	8.3	20.0	3.0 ± 0.2
Bovine Liver	As:	0.056 ± 0.004	7.1	19.1	0.047 ± 0.006
NBS-SRM-1577a	Hg:	nd	–	–	0.004 ± 0.002
	Sb:	nd	–	–	0.003
	Se:	0.61 ± 0.05	8.2	14.1	0.71 ± 0.07
Fish–flesh	As:	2.61 ± 0.12	4.6	0.4	2.6 ± 0.1
IAEA-MA-A-2	Hg:	0.51 ± 0.05	9.8	8.5	0.47 ± 0.02
	Sb:	0.014 ± 0.002	14.3		0.005 ± 0.001
	Se:	1.18 ± 0.09	7.6	30.6	1.7 ± 0.3
Mixed human diet	As:	0.072 ± 0.008	11.1	18.2	0.088 ± 0.033
IAEA-H-9	Hg:	–	–	–	0.0048 ± 0.0014
	Sb:	0.016 ± 0.004	25.0	33.3	0.012 ± 0.008
	Se:	0.094 ± 0.019	20.2	14.5	0.11 ± 0.01
Rice flour	As:	0.372 ± 0.020	0.0	9.3	0.41 ± 0.05
NBS-SRM-1568	Hg:	0.0067 ± 0.0003	4.5	11.7	0.0060 ± 0.0007
	Sb:	0.016 ± 0.002	12.5	26.0	0.0127 ± 0.0007
	Se:	0.32 ± 0.09	28.1	20.0	0.40 ± 0.10

– not determined.
nd – not detected.

The results obtained by Procedure II for determination of Cd, Cr, Cu and Se in Brazilian diets (Table 3) had standard deviations ranging from 2 to 21%, the highest errors being found for Cd determination. For Cr, these deviations were lower than 12%.

The results obtained for Se concentration agreed with those obtained by Procedure I.

Comparing the results obtained for Cr and Se in Brazilian diets with diets from different countries[17] (Table 4), it can be seen that the results for Cr were higher than those obtained in other countries. It could be that the diets were contaminated during the preparation steps.

Table 2
Results for Cd, Cr, Cu and Se determination in reference materials by using inorganic exchanger HMD (PROCEDURE II)

Reference material		This work, μg/g dry weight		RSD, %	Relative error, %	Literature values[16]
Mussel Tissue	Cu:	9.0 ± 0.5	(4)	5.6	6.3	9.6 ± 0.2
(IAEA-MA-M-2)	Cd:	0.34 ± 0.02	(4)	7.2	0	0.34 ± 0.02
	Se:	1.64 ± 0.08	(4)	4.8	1.2	1.66 ± 0.04
	Cr:	1.2 ± 0.2	(4)	16.7	50.0	0.80 ± 0.08
Bovine Liver	Cu:	157 ± 5	(5)	3.5	0.6	158 ± 7
(NBS-SRM-1577a)	Cd:	0.45 ± 0.02	(5)	5.5	2.3	0.44 ± 0.06
	Se:	0.80 ± 0.03	(5)	3.3	12.7	0.71 ± 0.07
	Cr:	–	–	–	–	
Fish-flesh	Cu:	3.7 ± 0.2	(6)	5.6	7.5	4.0 ± 0.1
(IAEA-MA-A-2)	Cd:	0.067 ± 0.004	(4)	5.3	1.5	0.066 ± 0.004
	Se:	1.4 ± 0.2	(6)	10.6	17.6	1.7 ± 0.3
	Cr:	1.8 ± 0.3	(5)	16.7	38.5	1.3 ± 0.1
Citrus Leaves	Cu:	16.3 ± 2.3	(6)	14.1	1.2	16.5 ± 1.0
(NBS-SRM-1572)	Cd:	0.036 ± 0.002	(5)	5.6	20.0	0.03 ± 0.01
	Se:	0.036 ± 0.006	(4)	16.7	–	0.025
	Cr:	1.0 ± 0.2	(5)	20.0	25.0	0.8 ± 0.2
Total Diet	Cu:	2.7 ± 0.2	(4)	7.4	3.8	2.6 ± 0.3
(NBS-SRM-1548)	Cd:	0.029 ± 0.008	(4)	17.2	3.6	0.028 ± 0.004
	Se:	0.26 ± 0.03	(4)	11.5	6.1	0.245 ± 0.005
	Cr:	0.5 ± 0.2	(4)	40.0	–	–

Number of determinations are in parentheses.

For the other elements, literature values of concentration in diets were not found for comparison. However, Se content in Student diet, showed a very low concentration level, as observed in other studies of Brazilian diets.[18,19]

Table 5 shows the results obtained for daily dietary intake in different Brazilian Regional diets. Since the Brazilian population is composed from many ethnic groups, food habits differ according to the various parts of the country and this can explain the different values obtained for the elements in these diets from different regions of the country.

In Table 6, daily amounts of the elements analyzed in this work As, Cd, Cu, Hg and Se are compared with data of daily intake in various countries and either the ADI or the RDA. It can be concluded from Table 6 that toxic elements analyzed (Cd and Hg) are

Table 3
Results of the determination of trace elements in diets by different radiochemical procedures

Diet	Procedure I			Procedure II		
	This work,* μg/g dry weight		RSD, %	This work,** μg/g dry weight		RSD, %
Students	As:	42.4 ± 0.9	2.1	Cd:	< 30	–
	Hg:	19 ± 3	15.8	Cr:	498 ± 60	12.2
	Sb:	10.6 ± 0.2	1.9	Cu:	3300 ± 200	6.1
	Se:	72 ± 5	6.9	Se:	70 ± 10	14.3
Manaus	As:	37.2 ± 0.5	1.3	Cd:	< 73	–
	Hg:	87 ± 9	10.3	Cr:	970 ± 50	5.2
	Sb:	7.4 ± 0.1	1.4	Cu:	2420 ± 20	0.8
	Se:	210 ± 16	7.6	Se:	208 ± 18	8.7
Santa Catarina 1	As:	138 ± 5	3.6	Cd:	21 ± 4	19.0
	Hg:	19 ± 3	15.8	Cr:	350 ± 40	11.4
	Sb:	9.0 ± 0.5	5.6	Cu:	1870 ± 50	2.7
	Se:	141 ± 19	13.5	Se:	147 ± 11	7.5
Santa Catarina 2	As:	259 ± 17	6.6	Cd:	24 ± 5	20.8
	Hg:	22 ± 3	13.6	Cr:	680 ± 10	1.5
	Sb:	10.7 ± 0.9	8.4	Cu:	2100 ± 100	4.8
	Se:	241 ± 12	5.0	Se:	246 ± 10	4.1

*Average of 2 determinations.
**Average of 4 determinations.

Table 4
Comparison of Cr and Se concentrations in freeze-dried diets consumed in Brazil and other countries[17]

Element	Cr, μg/g	Se, μg/g
Brazil*	0.35–0.97	0.07–0.25
USA	0.07 ± 0.01	0.26 ± 0.01
Norway	0.13 ± 0.09	0.13 ± 0.07
Germany	0.044	0.042
Turkey	0.13 ± 0.05	0.11 ± 0.04

*Range of results of diets analyzed in this work.

below the ADI values. Hg in the Manaus diet is on the limit. This diet involves considerable quantities of fish due to the food habits of this region.

We can also see that the calculated values for Cu are on the lower side of the RDA for Santa Catarina 1 and Manaus diets. For the other diets the results are at marginal

Table 5
Data of daily dietary intake for Brazilian Regional Diets

Element	Concentration units	Students	S. Catarina 1	S. Catarina 2	Manaus
As	μg/day	18.7–19.5	49.2–52.9	139.6–159.3	16.5– 17.0
Hg	μg/day	7.2– 9.9	7.2– 8.1	11.0– 14.4	35.1– 43.2
Sb	μg/day	4.7– 4.9	3.1– 3.5	5.7– 6.7	3.3– 3.4
Se	μg/day	30.2–34.7	45.1–59.2	132.1–146.0	87.3–101.7
Cd	μg/day	< 13.5	6.3– 9.3	11.0– 16.7	< 31.5
Cr	mg/day	194–248	115–144	387–398	414–459
Cu	mg/day	1.4–1.6	0.67–0.71	1.2–1.3	1.08–1.10

Table 6
Mean daily intake of some toxic and essential elements in various countries[20]

	The Netherlands	UK[1]	USA[2]	Belgium[3]	Present work,* range	ADI, μg/d	RDA, mg/d
As, μg	38	129	65	45	19–160	120	–
Cd, μg	21	20	33	18	< 31.5	60–70	–
Cu, μg	1.5	1.5	ND	1.4	0.7–1.6	–	1.5–3.5
Hg, μg	0.7	ND	5	13.5	7–43	43	–
Se, μg	72	60	138	ND	30–146	–	0.05–0.14

*Range of the results of diets analyzed in this work.
[1]HAZELL, 1985 (adults).
[2]GARTRELL et al., 1985 (market basket for 16 to 19 year-old males).
[3]BUCHET et al. (duplicate diets, adults).
ADI – acceptable daily intake.
RDA – recommended dietary allowance.
ND – not determined.

values. The recommendations for Se are met in all diets, with the exception of the Student diet.

Comparing our results to values from other countries, it may be seen that they are in accordance with them.

Conclusion

The radiochemical separation methods described in this paper present a good alternative to the isolation and subsequent determination of As, Cd, Cr, Cu, Hg, Sb and Se in different matrices.

The two sample dissolution approaches used in this work also present their applicability to different types of samples. The dissolution process using a microwave oven is the fastest of the two.

In relation to the results obtained for daily dietary intake for different Brazilian Regional diets it can be said that at the moment there is no danger of exceeding the acceptable daily intake levels of cadmium and mercury, or the recommended values for As, Cu and Se. Even the maximum value for As in Santa Catarina 2 diet was not alarming though the food habits of this region include a large consumption of the meat, fish and poultry group where the amount of arsenic is higher.[21]

The Cr content of the diets was very high and we concluded that the contamination of diets must have occurred during the drying in stainless steel trays or when the foods were transformed into powder by means of a knife mill and homogenized.

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