Toxic Heavy Metals and Other Trace Elements in Foodstuffs from 12 Different Countries

An IAEA Coordinated Research Program

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ABSTRACT

A research program related to the assessment of toxic heavy metals and essential trace elements in foodstuffs has been carried out in 12 countries under the auspices of the IAEA. The main purpose of this program was to obtain data on the elemental concentrations of potentially toxic elements in foodstuffs in various countries, and to compare them with the maximum permissible levels specified in

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Biological Trace Element Research Editor: G. N. Schrauzer

national legislation and international guidelines. High-priority elements for this study were As, Cd, Cr, Pb, Hg, and Se. Also of interest, but of lower priority, were Sb, Cu, and Zn. Emphasis was placed on the use of nuclear and nuclear-related analytical techniques, complemented by conventional methods, and on quality assurance.

Index Entries: Foodstuff analysis; nuclear analytical techniques; essential elements; toxic elements; analytical quality control; reference materials.

INTRODUCTION

Human growth and metabolism depend mainly on a well-balanced diet in terms of macronutrients (proteins, lipids, carbohydrates and so on). However, traces of some inorganic elements are also an important component of human nutrition because of their essential role in various metabolic processes *(1)*, or because their presence in excessive or deficient amounts may disturb normal biochemical functions of the body. Human exposure to these elements is mainly through the diet.

The IAEA recently organized a 5-yr research program to determine and assess the concentrations of toxic heavy metals and some other—mainly essential—trace elements in foodstuffs in 12 countries. The main purpose of this Coordinated Research Program (CRP) was to obtain analytical data on the elemental concentrations of potentially toxic elements in foodstuffs and to compare them with the maximum permissible levels specified in national legislation and international guidelines *(2)*. The matrices of interest were foodstuffs that comprise together more than 50% of the average daily intake. Drinking water was also considered to be highly relevant and was studied by some participants. An important supplementary purpose of the program was to help establish analytical expertise for work of this kind in individual countries, allowing such laboratories to offer analytical quality-control services and to provide validation support for their own national food monitoring programs. A detailed research protocol was prepared by the IAEA *(3)*. It contains guidelines on the types and amounts of food to be collected to obtain a representative analytical sample, how to prepare it for analysis, and procedures for analytical quality control and data evaluation. Emphasis was placed on the use of nuclear and nuclear-related analytical techniques, complemented by conventional methods in cases where these were considered more appropriate. Quality assurance was emphasized, and the IAEA organized external analytical quality-control exercises to ensure that the analytical data produced by the laboratories was reliable.

EXPERIMENTAL

Sampling and Sample Preparation

Food items that were important components of the diet of the selected populations groups were sampled and analyzed. Some partici-

pants collected the samples at local markets, whereas others received samples from local nutritional institutes that identified representative diet samples from selected population groups according to statistical information available to them. The amount of food collected was normally a few kilograms, from which subsamples for analysis were taken. Only edible parts of the foods were used for analysis. The samples were cleaned and prepared as they normally would be in the home. Foods that are eaten raw were just cleaned and washed. All food items were of the same degree of freshness as for normal consumption. Homogenization or mixing was carried out using a suitable food blender and, in some cases, also by the brittle fracture technique *(4)*. Moisture was determined from a small aliquot taken from the mixed homogenous sample. The samples were in most cases dried by freeze-drying. Prior to analysis, the samples were stored in clean polyethylene bottles with screw caps.

Elements of Interest

According to the protocol issued for this CRP, each participant had to determine as many of the following elements as possible, depending on the availability of analytical methods of proven reliability: As, Cd, Hg, Pb, and Se. A second group of elements to be determined, depending on national perceptions of their importance, were: Br, Cr, Cu, Fe, I, Mn, Sb, and Zn.

Analytical Techniques

Purely instrumental analytical methods could not be used for most of the elements and samples of interest because the concentration levels were too low. Most of the analytical methods used by the different laboratories were therefore based on the destruction of the sample followed by a preconcentration, a preseparation, or a postirradiation radiochemical separation procedure. Using these approaches, most of the participants were able to determine the actual concentrations of the elements of interest in all the selected food items and diets. The analytical techniques used were neutron activation analysis (NAA), either instrumental (INAA) or radiochemical (RNAA), anodic stripping voltammetry (ASV), inductively coupled plasma emission spectrometry (ICP-ES), atomic absorption spectrometry (AAS), direct current plasma emission spectrometry (DCP-ES), inductively coupled plasma mass spectrometry (ICP-MS), and proton-induced X-ray emission (PIXE). One of the participants studied arsenic speciation in environmental waters and described suitable techniques to be used for the characterization of dissolved arsenic species in such samples.

Analytical Quality Assurance

In a CRP such as this, where several analytical techniques were to be used in different laboratories with diverse infrastructures and levels of experience, efforts had to be made to assure similar quality of the ana-

lytical data. Participants were requested to validate their analytical methodology **before** the analysis of actual samples and to comply with prescribed analytical quality-control procedures. Several mechanisms were implemented to assure accurate and precise results. The determination of the limit of quantitation for each element and sample type, the routine use of certified reference materials during the analytical phase of each individual project, and the analysis of "blind" quality-control samples (actually certified reference materials provided by the IAEA) were ways of assessing the quality of the analytical data.

RESULTS

Only an overview of the large amount of data supplied by the participants is presented here. A technical document containing full reports of all the participants is in preparation and will be issued shortly by the IAEA. Table 1, showing data for Japanese foodstuffs, illustrates the wide range of elements and samples studied.

Rice was one of the major staple foodstuffs within this CRP, since it is an important component of the diet in many of the participating countries. Participants analyzed various types of rice (e.g., raw, boiled, or after different industrial processes). Table 2 shows the results obtained for the analysis of rice by one participating country.

Among the target elements for the CRP, Se was of particular interest to several of the participants on account of its essentiality to humans as well as its potential toxicity. Tables 1 and 3 give values for the Se contents of foodstuffs in two of the countries involved in this program. Particular care is needed with the analysis of foodstuffs that have been homogenized by the brittle fracture technique in Teflon™ containers, since this can lead to fluorine contamination. When analyzed by INAA via the $^{77}Se^{m}$ activation product, a careful correction has to be applied for interference from ^{20}F, which has a similar half-life.

The quality of the data reported was monitored throughout the CRP. Table 4 illustrates the kinds of data collected. It shows the results reported by a participant for the analysis of one set of "blind" quality-control samples supplied by the IAEA.

Results from one participant permitted an assessment of the relative merits of NAA and ICP-MS for the determination of toxic and other trace elements in foodstuffs and diets. NAA gave precisions of 10% or better for the determination of As, Br, Ca, Cl, Cr, Co, Cu, Fe, Hg, K, Mn, Mo, Na, Rb, Se, and Zn in IAEA H-9 (a mixed human diet reference material). In most cases, the analysis could be done by INAA. However, some elements present at low concentrations (e.g., As, Hg) and those subject to interferences (e.g., Cu, Mo) required the use of RNAA, which can be very time-consuming. In contrast, the analysis of solutions by ICP-MS is extremely rapid. A typical semiquantitative, multielemental analysis (70 elements, 20% precision) can be undertaken in 5 min and quantitative analysis (5% precision, 10 elements) within 15 min (these times do not

Table 1
Representative Values of the Elemental Concentrations in Selected Foods for Each Food Category†

Food category**	Food consumption (g)	As	Ca	Cd	Cu	Fe	Hg	K	Mg	Mn	P	Pb	Se	Zn
Cereals (dry)														
Rice	208.8	0.08	100	0.1	2.2	3.9	0.005	810	370	10	1000	0.05	0.02	18
Wheat and others	93.3	0.01	130	0.01	1.5	10	0.005	1300	290	4.2	950	0.05	0.1	4.3
Potatoes	61.3	0.01	150	0.01	1.3	5.1	0.003	4000	200	2.7	400	0.05	0.03	3
Pulses and their products	64.4	0.02	100	0.03	4	40	0.02	5000	800	9	3000	0.01	0.03	30
Vegetables														
Green and yellow vegs.	71.1	0.01	1300	0.05	1	15	0.01	4000	500	5	590	0.1	0.02	8
Other vegetables	183.5	0.001	500	0.01	0.4	4	0.003	3000	130	1.5	500	0.06	0.03	2.5
Fruits	137.9	0.005	100	0.005	0.6	3.5	<0.01	1900	130	1.3	180	0.05	0.001	0.6
Seafood														
Seaweed (dry)	5.5	35	5000	0.25	15	250	<0.01	10000	2500	20	750	1	0.1	40
Fish and shellfish	92.7	2	200	0.01	0.7	10	0.15	3900	360	0.2	2500	0.2	0.6	5
Meat and poultry	69.1	0.05	60	0.01	1	20	0.005	2500	150	0.4	1400	0.1	0.3	20
Eggs	40.1	0.05	600	0.01	0.9	30	<0.01	1300	100	0.3	2000	0.1	0.5	20
Milk and milk products	121.5	0.003	1100	0.001	0.1	1.0	0.001	1500	100	0.05	1000	0.05	0.02	3

†Data from Japan; food consumption in g/day; concentration values in mg/kg. Values are expressed on a wet wt basis excluding rice, wheat, and seaweeds (wet-to-dry ratio of seaweed is about 5:1).

**Major (representative) foods for each food category are: potatoes, potato and sweet potato; pulses and their products, soybeans and tofu; green and yellow vegetables, spinach and carrot; other vegetables, cabbage and chinese cabbage; fruits, orange and apple; seaweed, wakame-algae and hijiki-algae; fish, tuna, bonito, and salmon; meat and poultry; pork, beef, and chicken; milk and milk products, market milk.

Table 2
Elemental Concentrations[a] in Rice Grains by INAA[b]

ELEMENT	POLISHED GRAINS						PARBOILED GRAINS
	LONG FINE 1 CERGAL	LONGFINE 1 CAMPEAO	LONGFINE 2 CAMIL	LONGFINE 2 CEREJEIRA	YELLOW LONG LUMA	JAPANESE/CATETE YAMAGUI	LONG FINE MINGOTE
As	0.272 ± 0.022(11)	0.279 ± 0.027(5)	0.271 ± 0.035(6)	0.093 ± 0.014(2)	---	0.362 ± 0.025(4)	0.310 ± 0.021(4)
Br	0.46 ± 0.04(8)	2.11 ± 0.18(4)	0.36 ± 0.02(6)	0.43 ± 0.04(6)	0.36 ± 0.06(3)	0.93 ± 0.06(4)	0.33 ± 0.02(4)
Na	15.0 ± 1.4(12)	8.9 ± 0.7(4)	13.5 ± 0.6(5)	12.3 ± 1.6(5)	6.6 ± 1.0(4)	17.2 ± 1.0(4)	16.2 ± 0.7(4)
K	328 ± 16(8)	419 ± 6(4)	418 ± 10(4)	654 ± 41(6)	651 ± 29(3)	385 ± 10(2)	1079 ± 58(6)
Rb	2.32 ± 0.27(11)	3.28 ± 0.21(6)	3.67 ± 0.39(7)	3.81 ± 0.22(7)	5.17 ± 0.62(6)	3.67 ± 0.19(6)	11.0 ± 0.7(8)
Zn	14.0 ± 1.6(10)	15.01 ± 0.63(6)	15.2 ± 0.5(6)	16.4 ± 0.4(6)	17.9 ± 2.0(5)	15.9 ± 0.6(6)	7.61 ± 0.66(4)
Fe	---	---	5.76 ± 0.13(2)	7.58 ± 0.83(2)	20.5 ± 0.8(2)	88.0 ± 5.5(4)	12.6 ± 1.2(3)
Co ng/g	---	---	---	25.4 ± 5.7(2)	25 ± 7(2)	19.6 ± 0.3(2)	27.9 ± 4.3(2)
Sc ng/g	---	---	---	2.16 ± 0.08(4)	---	---	1.11 ± 0.08(2)

[a]Means and standard deviation of *(n)* individual determinations.
[b]Data from Brazil. Concentrations in mg/kg dry wt unless otherwise indicated.
---Not detected.

Table 3
Selenium Concentrations in Australian Foodstuffs (mg/kg wet wt basis)

Food Item	Range	Mean
White bread	0.04-0.15	0.08
Wholemeal bread	0.08-0.13	0.10
Infant cereal	0.06-0.12	0.09
Corn flakes	0.07-0.09	0.08
Wheat biscuits	0.09-0.35	0.15
White rice	0.01-0.05	0.03
Bran	0.09-0.24	0.16
Minced steak	0.06-0.19	0.12
Lamb	<0.02-0.13	0.13
Pork	0.09-0.23	0.15
Chicken	0.14-0.23	0.18
Canned meat	0.09-0.14	0.12
Fish	0.22-0.34	0.29
Salmon	0.22-0.38	0.27
Sardines	0.25-0.78	0.57
Eggs	0.15-0.23	0.19
Liver	0.20-0.54	0.30
Full cream milk	<0.01-0.03	0.02
Skim milk	<0.01-0.03	0.02
Lactogen	<0.01-0.01	0.01
Butter	<0.02	
Potatoes	<0.02	
Onions	<0.02	
Carrots	<0.01	
Green beans	<0.02	
Celery	<0.02	
Pumpkin	<0.02-0.02	0.01
Baked Beans	<0.02-0.04	0.02
Fruit	<0.02	
Infant dinner	<0.02	
Peanuts	0.06-0.21	0.14
Peanut butter	0.05-0.11	0.08

Table 4
IAEA External Analytical Quality-Control Program†

Element	Sample STD-1 Rice flour NIST-SRM-1568		Sample STD-2 Copepoda IAEA-MA-A-1/TM		Sample STD-3 Fish flesh IAEA-MA-A-2/TM	
	Reported	Expected	Reported	Expected	Reported	Expected
As	0.43	0.41	7.0	6.7	2.8	2.6
Br	0.98	---	950	---	21.9	---
Cu	1.96	2.2	7.5	7.6	3.6	4.0
Co*	22	20	126	120	82	80
Cr	---	---	1.0	1.1	1.5	1.3
Fe	9.0	8.7	61.3	60.0	52.2	54
Hg*	8.0	6.0	310	280	550	470
Mn	18.9	20.1	3.0	2.9	0.92	0.81
Rb	7.8	7.0	3.5	---	8.2	---
Sb*	---	---	80	70	---	5
Se	0.48	0.4	2.8	3.0	1.9	1.7
Zn	22	19.4	166	158	34	33

*values in μg/kg
†Concentrations expressed in mg/kg unless otherwise specified.

include the time needed for dissolving solid samples). Spectral interferences occurring in the argon plasma owing to the presence of chlorides and sulfates in the samples can reduce the effectiveness of the technique for As, V, Cr, Se, Ti, Zn, and Ca. Analysis of H-9 by ICP-MS produced significantly more data than NAA in much less time, but sample dissolution made this technique more labor-intensive than INAA. Although NAA cannot match the superior sensitivity obtained by ICP-MS for a

wider range of elements, its usefulness has been verified for a wide range of food samples. Although NAA is a time-consuming technique for many applications, it does not suffer from blank problems after irradiation of the sample, and it becomes the preferred technique where low limits of detection are required for trace concentrations in solid samples.

CONCLUSIONS

A large variety of foodstuffs were selected, collected, and analyzed in different countries using analytical techniques, such as INAA, RNAA, ASV, ICP-ES, ICP-MS, AAS, DCP-ES, and PIXE. All the concentration levels of toxic elements in foodstuffs and diets were within the limits specified in national and international guidelines. Nuclear analytical techniques proved to be sensitive, accurate, and precise for the analysis of this type of matrix. Improvement in detection limits (compared with INAA) was achieved by using destructive methods to eliminate potential interferences. New analytical methodologies, in particular, radiochemical separation procedures, were developed, and the feasibility of using other new analytical techniques (e.g., ICP-MS) was studied. Through this CRP, the participating laboratories were able to validate and improve the quality of their analytical data through extensive analytical quality-control procedures and exercises.

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