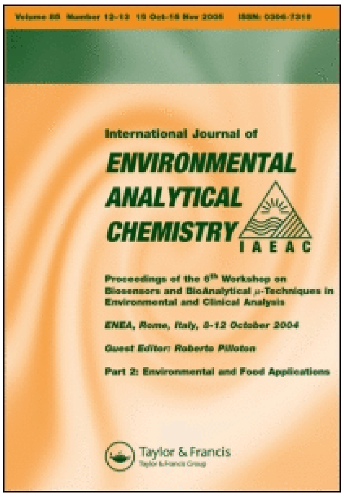

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DETERMINATION OF IODINE IN CEREAL GRAINS AND STANDARD REFERENCE MATERIALS BY NEUTRON ACTIVATION ANAYLSIS

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Trace amounts of iodine in thirty-eight cereal grain samples cultivated at different locations in Austria were determined for the first time in this study by radiochemical neutron activation analysis. For the dissolution of cereal grain samples and standard reference materials, two different procedures, alkaline and acidic dissolution, were applied in the presence of an iodine carrier. Rapid and simple dissolution procedure with acidic solution was demonstrated in this study. The analytical values in the cereal grain as well as in the standard reference materials obtained by the different dissolution procedures were in good agreement within one standard deviation. The iodine in cereal grains and the standard reference materials ranged from 0.002 to 0.03 μg g^{-1} and 0.0015 to 0.30 μg g^{-1}, respectively. The distribution of relative standard deviation (RSD) for iodine concentration below 0.01 μg g^{-1} were 21 % and 24 % of all data for the range 1–10 % RSD and 11–20 % RSD, respectively. The RSD for 0.1 μg g^{-1} of iodine concentrations were around 10 %.

Keywords: Iodine; cereal grain; standard reference materials; neutron activation analysis; radiochemistry

INTRODUCTION

Iodine is an essential nutrient whose metabolic function appears to be due entirely to its presence in the thyroid hormones. Adequate iodine levels in food and feed plants are required in animal nutrition and in human diets [1]. On the other hand, release of the long-lived radionuclide ^{129}I ($T_{1/2} = 1.6 \times 10^7$ y) from the plants of the nuclear fuel cycle results in a small fraction of environmental iodine ^{129}I. Iodine-129 is expected to behave in the environment in a similar way as stable iodine over a long time scale [2]. Therefore, in both contexts the estima-

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tion of iodine concentrations in an important foodstuff is quite important. Very few data on iodine contents in cereal grains have been reported up to now [3–5].

Because of low concentrations of iodine in some biological and geological materials, and the difficulty of precise determination of iodine, many investigations on the analysis for trace amounts of iodine have been performed. Neutron activation analysis has been frequently used being the most sensitive analytical technique for trace amounts of iodine [6- 9]. With very low levels, radiochemical separation techniques were additionally applied to the instrumental neutron activation analysis (INAA) [3,4,6,8]. Isotope dilution mass spectrometry has also been used for the measurement of trace amounts of iodine since the 1980th [8,10,11]. Due to recent developments of instruments and analytical techniques, the inductively coupled plasma mass spectrometry (ICP-MS) can be mentioned [12–14]. The advantage of ICP-MS analysis is a simultaneous determination of chlorine, bromine and iodine [12]. Detection limits of iodine of 0.7 ng (plant sample) [6] and 0.2 ng (rock sample) [8] by radiochemical neutron activation analysis (RNAA), and 0.5 ng ml^{-1} or 30 ng g^{-1} by ICP-MS for plant and rock samples were reported [12].

The procedures of sample dissolution for iodine depend on the matrix of sample. They can be roughly classified in two ways; in alkaline dissolution and acidic dissolution procedures. The most serious problems for iodine during the chemical separation are the volatility and equalizing the chemical forms of iodine in a sample matrix and a carrier solution if a carrier is used in the procedure. Some iodine species, such as hydrogen iodide, are gaseous at room temperature and therefore volatile[13]. The risk of loosing the volatile species can be reduced by adjusting the analyzing solution to an alkaline pH level and hence suppressing the volatility of hydrogen iodide [15–17]. Acidic mixtures for wet digestion of organic samples should convert the volatile iodine species to non-volatile species. Perchloric acid is often used for such an oxidation at elevated temperature. Although the dissolution procedures were adapted depending on the type of sample, Johansen and Steinnes have pointed out that the use of an alkaline rather than an acidic dissolution process may result in a smaller risk of incomplete equilibration between carrier and induced activity affecting the results by RNAA [3].

In this study, the low concentrations of iodine in cereal grains cultivated in Austrian agricultural area and in the four standard reference materials for plants and rock were determined by RNAA and INAA. The samples were dissolved in an alkaline and acidic solution and iodine was separated from the solution as palladium iodine. For the acidic dissolution, the mixed solution of three different ratios of HNO_3, HCl, and $HClO_4$ was examined to find out the suitable solution to dissolve the sample. The decontamination factors, detection limits for each method, and the standard deviations were estimated, and the precision and the accuracy of presented methods were discussed.

The information on iodine contents in cereal grains is very limited, mainly due to the difficulty of determination of trace amount of iodine in plant samples. The concentrations of iodine in cereal grains cultivated in Austria were estimated for the first time in this study. The analytical data obtained in this study could be important for further study on human diet and ecosystem of iodine, e.g. transfer factor, which will be published elsewhere [18].

EXPERIMENTAL

Standard preparation

Superior grade reagent of KI was dissolved in distilled water containing a few drops of 6 % Na_2SO_3 and the solution was adjusted approximately to pH 10 by Li(OH). A solution (5 µg I) was transferred onto a filter paper and dried at room temperature. The filter paper was doubly sealed in a polyethylene bag for irradiation.

Austrian cereal grains and plant- and rock- Standard Reference Materials

The cereal grains samples analyzed in this study were collected in different agricultural regions in Austria. They are classified in winter wheat, spring wheat, wheat, and winter rye.

Standard reference materials, wheat flour (SRM 1567a), orchard leaves (SRM 1571), and apple leaves (SRM 1515) processed and distributed by the National Institute of Standards & Technology, and the rock-standard reference material (JF-1: mixture of orthoclases and albite) processed and distributed by the Geological Survey of Japan were analyzed.

Irradiation of samples and gamma-ray measurements

The cereal grain samples were pulverized and dried at 85 °C for a few days. The standard reference materials were also dried at the same conditions. About 1 g of plant sample and plant standard materials (except apple leaves) and about 0.5 g of rock sample were weighed and doubly sealed in a polyethylene bag for irradiation. About 0.1 g of apple leaves were used for the RNAA and INAA.

Duplicate plant and rock samples were irradiated in a vial with a standard sample of iodine for 5 min in the boron carbide (B_4C) irradiation facility (thermal neutron flux: 5×10^{12} n cm^{-2} s^{-2} epithermal/thermal neutron: ~30) of ASTRA reactor at the Austrian Research Center Seibersdorf. In this cylindrical irradiation facility, the sample is shielded against thermal neutrons by a B_4C layer surrounding the irradiation space. The polyethylene vial enclosing the samples and the standard was positioned between additional B_4C holders during irradiation. The irradiation was also performed at the TRIGA reactor (thermal neutron flux: 2.5×10^{12} n cm^{-2} s^{-2} epi-thermal/thermal neutron: ~12) at the Atomic Institute of Universities in Austria. The samples were irradiated for 20–25 min with this reactor.

Gamma ray of ^{128}I was measured by high-resolution gamma-spectroscopy on Ge(Li)-detectors at 442.9 keV for about 20 min.

Determination of chemical yield

Chemical yield was determined using ^{125}I measured with a low energy photon counter (Li-intrinsic-detector) at 0.0355 keV for about 5 min. The determined values were corrected with the chemical yield.

Procedure of chemical separation – alkaline dissolution

The chemical separation of iodine by alkaline dissolution was mainly performed according to the procedure reported by Takagi et al [6]. The irradiated sample was immediately transferred into a glass beaker and moistened with 1 ml of 0.2M NaOH. A carrier solution of iodine (10 mg I) and the radioactive tracer ^{125}I were added and heated gradually adding about 30 ml of sodium hypochlorite to dissolve the sample. After the sample dissolution, the solution was made acidic by HCl and boiled to remove chlorine. The solution was filtered by a glass filter to remove remnants and the remnants were washed with distilled water. A few drops of 6% Na_2SO_3were added in this filtrate to reduce iodate ions to iodide ions. After 1 mg of Br^- was added to the solution, $PdCl_2$ (15 mg as Pd) was administered and the iodine precipitated as PdI_2. The precipitation was collected on a glass filter and fixed with tapes, and then measured by γ-spectroscopy.

Procedure of chemical separation – acidic dissolution

The mixed solution of three different ratios of HNO_3, HCl, and $HClO_4$ (1:3:3, 1:1:1, and 1:0:1) was examined to find out the suitable solution to dissolve the sample. The same procedure for the chemical separation as described for the alkaline dissolution except the pH adjustment of solution was applied.

RESULTS AND DISCUSSION

Decontamination factor and detection limit

The decontamination factors for ^{82}Br, ^{56}Mn, and ^{38}Cl, which determined with γ-ray intensity in the non-destructive sample divided by γ-ray intensity in the final fraction of standard wheat sample determined in the TRIGA reactor, were ^{82}Br: 1×10^2, ^{56}Mn: 3×10^2, and ^{38}Cl: 2×10^2 with the alkaline decomposition, and ^{82}Br: 1×10^1, ^{56}Mn 8×10^1, and ^{38}Cl: 2×10^1 with the acidic dissolution. The decontamination factors obtained in this study were the same for ^{82}Br, and one order (^{56}Mn) and two orders (^{38}Cl) lower than those for rice samples with alkaline dissolution reported by Takagi et al.[6] This might be caused by the different matrix of rice grain and wheat flour.

The detection limits based on three standard deviations of background in the present study were about 0.4, 0.4, and 10 ng, and 0.7, 0.8, and 60 ng for the alkaline and acidic dissolution, and non-destructive analysis with the ASTRA and TRIGA reactor, respectively. With the ASTRA reactor, lower detection limit than with the TRIGA reactor was obtained. This is due to the higher neutron flux and the effective B_4C shielding of ASTRA-irradiation facility. The ratio of epi-thermal / thermal neutron flux in the irradiation position is higher and thus the production of disturbing radionuclides, e.g. ^{56}Mn, was lower compared with ^{128}I.

Acidic solution for sample dissolution

Three different ratios of acids in the solution were examined for the sample dissolution. Significantly high yield of PdI_2 was obtained only from the solution of HNO_3, HCl, and $HClO_4$ (1:3:3) and very little PdI_2 yield was obtained from the other two solutions. Larsen and Ludwigsen reported on risk of iodine volatilization during sample dissolution by HNO_3.[16] They dissolved biological samples with a mixture of $HClO_4$ and HNO_3 in closed high-pressure steel bombs at 170 °C to prevent the loss of iodine during the procedure. In this study, we decomposed the samples in a glass beaker at more than 200 °C, since a rapid chemical separation was required. With the solution described above, the rapid and simple procedure for sample decomposition was available. The results obtained using a mixture of HNO_3, HCl, $HClO_4$ (1:3:3) was shown in the Table I.

TABLE I Analytical results of iodine determination

Sample	*Type*	*Dissolution*[a]	*n*[b]	*Mean* ($\mu g\ g^{-1}$)	*SD*[c] ($\mu g\ g^{-1}$)
SRM 1567a	Wheat flour	Al[d]	10	0.0017	0.0006
		Ac[e]	3	0.0009	0.0002
		T[f]	12	0.0015	0.0006
		(Ref.[g] 19)		[0.0009][h]	
SRM 1571	Orchard leaves	Al	2	0.17/0.23	
		Ac	7	0.18	0.02
		T	9	0.18	0.03
		(Ref. 20)		[0.17]	
SRM 1515	Apple leaves	Ac	9	0.32	0.03
		Nd[i]	4	0.29	0.02
		T	13	0.30	0.03
		(Ref. 21)		[0.30]	
JF-1	Volcanic rock[j]	Ac	3	0.0118	0.0004
		(Ref. 8)		[0.009]	[0.004]
Austrian cereal grain WW- 1	Winter wheat	Al	3	0.0049	0.0002
		Ac	5	0.0059	0.0006
		T	8	0.0055	0.0007
2		Ac	3	0.0046	0.0011
3		Ac	3	0.0035	0.0001
4		Al	4	0.0031	0.0010
5		Al	6	0.0029	0.0015
6		Al	3	0.006	0.003
7		Al	2	0.006/0.004	
8		Al	1	0.004	
9		Al	3	0.009	0.005
10		Ac	3	0.0025	0.0011
11		Al	3	0.0092	0.0011
12		Ac	3	0.0036	0.0011
13		Ac	2	0.009/0.008	

Sample		*Type*	*Dissolution*[a]	*n*[b]	*Mean* (μg g^{-1})	*SD*[c] (μg g^{-1})
	14		Al	3	0.0026	0.0013
	15		Al	3	0.025	0.004
	16		Al	3	0.005	0.003
	17		Al	3	0.0040	0.0007
	18		Al	2	0.003/0.004	
	19		Al	2	0.026/0.033	
	20		Al	3	0.005	0.002
SW-	1	Spring wheat	Al	3	0.0052	0.0006
	2		Al	3	0.0078	0.0012
	3		Al	3	0.0048	0.0007
W-	1	Wheat	Al	3	0.0046	0.0011
WR-	1	Winter rye	Al	3	0.0040	0.0004
	2		Al	3	0.0032	0.0006
	3		Al	3	0.0034	0.0008
	4		Al	3	0.0062	0.0005
	5		Al	2	0.004/0.005	
	6		Al	6	0.0070	0.0015
	7		Ac/Al	2	0.004/0.005	
	8		Al	2	0.004/0.005	
	9		Al	3	0.0022	0.0006
	10		Al	2	0.015/0.007	
	11		Al	3	0.008	0.004
	12		Al	3	0.0025	0.0006
	13		Ac	3	0.0040	0.0002
	14		Al	2	0.002/0.003	

a. Type of dissolution.
b. Number of analysis.
c. Standard deviation.
d. Sample dissolution in alkali.
e. Sample dissolution in acid.
f. All data from alkaline and acidic dissolution.
g. See the references.
h. [ ] Non-certified value.
i. Non-destructive analysis.
j. Mixture of orthoclases and albite.

Chemical yield

The chemical yields were typically 80–90% and no significant differences between values obtained by alkaline and acidic dissolution procedures were found. Sample matrix had no significant influence on chemical yields, though the chemical yields for the rock sample were about 100 %.

Accuracy of analysis for Standard Reference Materials

The analytical results of the standard reference materials are shown in Table I. Three different plant reference materials; wheat flour, orchard leaves, and apple leaves, and one volcanic rock standard reference material were analyzed. The values of wheat flour, orchard leaves, apple leaves, and volcanic rock were 0.0016, 0.18, 0.30, and 0.0118 μg g^{-1}, and their literature (non-certified) values were 0.0009, 0.17, 0.30, and 0.009 μg g^{-1}, respectively. The relative standard deviations (RSD) of this study were 38, 17, 10, 3.4 %, for the wheat flour, orchard leaves, apple leaves, and volcanic rocks, respectively. The RSD for wheat flour was quite large.

The values obtained by the two different dissolution procedures applied to wheat flour and orchard leaves were in good agreement within one standard deviation, although there is 50 % difference in results of the wheat flour (SRM 1567a). The relatively large difference between the values obtained by the alkaline and acidic dissolution for the wheat flour may be mainly due to the very low content of iodine which is close to detection limit. The non-destructive analysis was performed for the apple leaves and the results were in good agreement with the RNAA.

Schnetger and Muramatsu determined the iodine concentration in the orchard leaves by ICP-MS and reported 0.17 and 0.26 μg g^{-1} (duplicate analysis) [12]. The result obtained by RNAA by Takagi et al. was 0.192±0.010 μg I g^{-1}. Shinonaga et al. reported 0.009 μg g^{-1} of iodine in the JF-1 sample analyzed by RNAA applying an alkaline conversion for sample dissolution [8]. A high precision (RSD 3.4%) was obtained for JF-1 in the present study.

Concentration of iodine in Austrian cereal grains and precision of analysis

The analytical results of cereal grains are shown in Table I. The concentrations of iodine in cereal grains rang from 0.002 to 0.03 μg g^{-1} and the arithmetic mean was 0.0061 μg g^{-1} No characteristic ranges of iodine contents were found for winter wheat, spring wheat, and rye. The concentration of iodine in most of the samples was in the range of several ng g^{-1} and several ten ng g^{-1} of iodine was found only in WW-15, –19, and WR-9.

The RSD of WW-5 was large irrespective of the large number of replicates. The distribution of RSD for iodine concentration below 10 ng g^{-1} were 21, 24, 21, 10, and 24 % of all data for the range of 1–10, 11–20, 21–30, 31–40, and > 40 % of RSD, respectively.

Johansen and Steinnes, and Takagi et al. have obtained the analytical results of 0.0027 (RSD 12 %, n=7) and 0.0037 (RSD 16 %, n=5) for iodine in wheat flour (IAEA, RM-V-5).

CONCLUSION

The concentrations of iodine in cereal grains cultivated in Austria were estimated for the first time in this study. The analytical methods were confirmed by three different procedures (alkaline and acidic dissolution and non-destructive analysis) using standard reference materials by mean of neutron activation analysis. Rapid and simple acidic-dissolution procedure has been demonstrated in this study. The concentration of iodine in the wheat grain ranged from 0.002 to 0.03 $\mu g\ g^{-1}$ and the arithmetic mean was 0.0061 $\mu g\ g^{-1}$. Most of cereal grains analyzed in this study were at several ng g^{-1} level of iodine. The comparison among the results obtained by the tree analytical procedures and the agreements of analytical results of them confirm the determined results at low level of iodine in cereal grain, which have been scarcely reported before.

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