Determination of Iodine in Biological Materials using Instrumental Neutron Activation and Anti-coincidence Gamma-ray Spectrometry

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SUMMARY. An epithermal instrumental neutron activation analysis (EINAA) method in conjunction with anticoincidence gamma-ray spectrometry has been developed for the determination of ppb levels of iodine in biological materials, foods and diets in particular. Several reference materials have been analyzed to evaluate the precision and accuracy of measurements. The detection limit for iodine can be improved by a factor of 2 to 5 depending on the sample matrix, and other factors. The detection limit of 5 ppb can be achieved for low-salt foods.

1. INTRODUCTION

Iodine is an element of much interest in nutritional research. The daily dietary safe and adequate intake range of iodine for adults is reported to be 150-200 ug. Iodine deficiency is considered to be a serious problem in many countries. Excessive iodine intake can also contribute to certain thyroid disorders in susceptible individuals. In many countries regulations require the control of the level of daily iodine intake through diet. The accurate determination of iodine in materials such as diets and individual food items is of considerable interest. The analytical techniques most commonly employed for measuring iodine levels are colorimetry, ion selective electrode, isotope exchange, gas chromatography, and neutron activation analysis (NAA).

The NAA technique has excellent intrinsic sensitivity for the measurement of iodine. Iodine has been determined by instrumental NAA (INAA) in many biological materials. Compared to some other medium-lived nuclides such as ^{52}V, ^{27}Mg and ^{66}Cu, ^{128}I has a slightly longer half-life of 25.0 min, and thus the stable isotope ^{127}I needs a longer irradiation time to reach saturation activity. However, the irradiation time is limited because of interferences from the high activities of thermal neutron activation products of the major elements in the sample. Low levels of iodine cannot be easily measured by thermal INAA.

In order to circumvent this problem, epithermal INAA (EINAA) has been used by a few researchers with some success. The EINAA methods are based on the fact that the resonance integral cross section for iodine is much larger (147 b) than that for some of the interfering elements such as Na, Cl, Al, and Mn (0.31, 0.21, 0.17, 14 b, respectively). Background activities can be reduced to some extent by EINAA. The use of cadmium and/or boron shields to absorb thermal neutrons in EINAA allows for increased irradiation time. But the residual activity produced in the cadmium shield, for example, may cause a radiation safety and heating problem. These factors can limit the irradiation time, the removal of the sample from the shield within a reasonably short time, and the reuse of the shield for subsequent irradiations. Much of this problem can be eliminated by irradiating samples in a cadmium- or boron-lined pneumatic site. Although a cadmium-lined site is available at the Dalhousie University SLOWPOKE-2 Reactor

(DUSR) facility, not many reactors are fitted with this type of site. The EINAA detection limit for iodine can be as low as 200 ppb, depending on the neutron flux used. Detection limits can be further improved by increasing the sample mass, irradiating for a longer period, and by counting the samples in a more sensitive detector. However, the background in the region of the 443 keV photopeak of ^{128}I is often dominated by Compton scattering from the gamma-rays of ^{24}Na, ^{56}Mn, ^{82}Br, and ^{38}Cl, so the detection limits are often not that greatly improved.

Radiochemical NAA (RNAA) and preconcentration NAA (PNAA) methods have been used to eliminate interfering elements as well as to further suppress background and improve the sensitivity of measurement. Both PNAA and RNAA are destructive methods, involve complicated operations, and are time consuming compared to INAA. Moreover, in PNAA precautions must be taken to ensure minimal contamination from reagents and handling.

We have developed several NAA methods in our laboratory for the determination of iodine in a number of materials for various purposes. These methods include (1-4) epithermal instrumental NAA (EINAA) using cadmium and boron shields, preconcentration NAA (PNAA) using bismuth sulfide coprecipitation, PNAA using solvent extraction, and radiochemical NAA (RNAA) using palladium chloride in conjunction with conventional gamma-ray spectrometry.

Anticoincidence counting as a background suppression technique can be used in conjunction with EINAA to further reduce the background. This approach can have the advantage of simplicity; it can be less time consuming and free from reagent blanks, and can lower the detection limit even further. For this reason, an EINAA method using anticoincidence counting has been developed in the present study for the determination of low levels of iodine.

2. EXPERIMENTAL

The anticoincidence spectrometer used in this work consists of a 25% relative efficiency HPGe detector surrounded by a 10" x 10" NaI(Tl) annulus and a 3" x 3" NaI(Tl) plug as well as timing electronics. This system has a peak-to-Compton ratio of about 650 to 1 for the 661.6-keV photopeak of ^{137}Cs. An improvement factor of 7 can be achieved compared to a single HPGe detector. Several factors that can influence efficiency of the methodology have been evaluated. The distance of the sample from the HPGe detector surface and the relative position of the NaI(Tl) annulus with respect to the HPGe detector have been investigated to obtain the best efficiency (5).

In the present study, an EINAA method in conjunction with anti-coincidence counting has been developed for the determination of ppb levels of iodine in individual food items. Typically 200-700 mg of a sample are irradiated for 10 or 20 min at the DUSR facility in an epithermal flux of 1×10^{11} n cm^{-2} s^{-1}, followed by 1 min decay and then counting for 30 min. The 442.9-keV gamma-ray of ^{128}I is used for measuring iodine content by anticoincidence counting. A sensitivity of 4536 counts per μg of iodine was obtained using 20 min irradiations. An internal quality assessment chart was constructed by irradiating iodine comparator standards with every batch of samples; all results were found to be within $\pm2\sigma$.

In order to evaluate the applicability of the EINAA method in conjunction with anticoincidence gamma-ray spectrometry to a wide variety of biological materials, several reference materials containing various levels of iodine and background interfering elements were chosen. Materials such as NIST Corn Bran, Corn Starch, Wheat Gluten, Soft Wheat Flour, Hard Wheat Flour, Durum Wheat Flour, Rice Flour, and Peach Leaves contained low levels of interfering elements such as Cl and Na, and gave low induced activities on neutron irradiation. They were irradiated for 20 min, allowed to decay for 1 min, and counted for 20 min. Reference materials such as NIST Whole Egg Powder, Non-Fat Milk Powder, Bovine Liver, Spinach, and Pine Needles, and IAEA Horse Kidney, Animal Muscle and Animal Blood contained high levels of Cl and Na. These samples were originally irradiated for 20 min and allowed to decay for 1 min before counting. These conditions gave high activities and dead-time of greater than 10% which could introduce errors unless appropriate corrections are made. The dead-

time was reduced to about 5% to 8% employing 10-min irradiations and 1-min decays which were then routinely used for measuring iodine in the above materials.

3. RESULTS AND DISCUSSION

The reference materials used in this work cover a wide range of iodine concentrations as shown in Table 1. Precision of the EINAA-anticoincidence method was checked by triplicate analysis. It was found that the RSD was about ±5% above 200 ppb, increasing to ±10% at 20 ppb and then to >±30% at about 5 ppb iodine level. The results are summarized in Table 1 along with the certified values and current literature data. The analytical uncertainty reported with each value is ±1σ.

Among the 17 reference materials analyzed here, only 6 have certified iodine values. The results obtained in this work for four of these materials are in good agreement with the certified values. Values for the other two, namely NIST Whole Egg Powder and Non-Fat Milk Powder, agree better with the literature values than with the certified values. The iodine levels of NIST Hard Wheat Flour, Durum Wheat Flour, Corn Bran, Wheat Gluten, Spinach, Whole Egg Powder, and Non-Fat Milk Powder were earlier measured by a PNAA method (2), and generally agree well with the values obtained in this work. Three of these materials were also analyzed by RNAA. The certified iodine content of NIST Pine Needles agrees with the values obtained here by EINAA but without Compton suppression. There are no data available for the other materials. A comparison of the measured *vs.* literature and/or certified values reveals that the EINAA method in conjunction with anticoincidence counting can produce reliable values.

The peak efficiency reduction factor (PERF) of the 442.9-keV peak of ^{128}I is 0.92 ± 0.04 using the anticoincidence counting mode. This means that background suppression should provide a lower detection limit. In order to illustrate this point, three NIST reference materials were selected. One of them (Non-Fat Milk Powder) had a high iodine level and a high background, the second SRM (Bovine Liver) had a low iodine content but a high background, and the third SRM (Rice Flour) had both low iodine level and low background. These three materials were analyzed for iodine using both conventional and anticoincidence counting modes. Various limits of detection, as defined by Currie (6), were calculated. The values of L_C, L_D, and L_Q for iodine in the three SRMs are given in Table 2. It is evident that the detection limits for iodine in all cases have been lowered by anticoincidence counting. Although Non-Fat Milk Powder had high background activities due to ^{38}Cl, ^{56}Mn and ^{24}Na, its iodine content of about 3100 ppb (Table 1) was greater than L_Q by both conventional and anticoincidence spectrometry. The iodine content of about 180 ppb in Bovine Liver (Table 1) was greater than the L_Q of 170 ppb by anticoincidence counting. The 442.9-keV peak of ^{128}I in Rice Flour was undetectable using the conventional system but became detectable in the anticoincidence system as the L_C was lowered (Table 1).

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Table 1. Concentration of iodine measured in reference materials by EINAA and anticoincidence gamma-ray spectrometry.

Reference materials	This work, ppb	Certified, (info.), ppb	Literature values, ppb
Hard Wheat Flour (NIST RM 8437)	3.0 ± 1.5	----	4.2 ± 0.3
Durum Wheat Flour (NIST RM 8436)	5.7 ± 1.7	6 ± 4	5.9 ± 2.1
Corn Starch (NIST RM 8432)	6.0 ± 1.4	----	
Rice Flour (NIST SRM 1568a)	15 ± 4 (9)		
Animal Muscle (IAEA RM H-4)	15.4 ± 9	14.3 ± 1.7	17 ± 2
Soft Wheat Flour (NIST RM 8438)	18 ± 2	----	
Corn Bran (NIST RM 8433)	28 ± 3	26 ± 6	26.5 ± 2 26 ± 1.4
Wheat Gluten (NIST RM 8418)	61 ± 7	60 ± 13	62 ± 4 59 ± 3
Animal Blood (IAEA RM A-13)	82 ± 9	----	
Horse Kidney (IAEA RM H-8)	142 ± 7.4	----	
Pine Needles (NIST SRM 1575)	168 ± 13	----	140 ± 20 145
Bovine Liver (NIST SRM 1577b)	180 ± 8		187 ± 12
Peach Leaves (NIST SRM 1547)	300 ± 14	(300)	
Spinach (NIST SRM 1570)	775 ± 21	----	1160 ± 40
Spinach (NIST SRM 1570a)	1265 ± 75	----	
Whole Egg Powder (NIST RM 8415)	1820 ± 40	1970 ± 460	1875 ± 94 2040 ± 20
Non-Fat Milk Powder (NIST SRM 1549)	3110 ± 30	3380 ± 20	3150 ± 75

Table 2. Comparison of detection limits (ppb) for iodine in three SRMs using Conventional and Anticoincidence counting systems.

Detection limits	Counting mode	Non-Fat Milk Powder (NIST SRM 1549)	Bovine Liver (NIST SRM 1577b)	Rice Flour (NIST SRM 1568a)
L_C	conv.	1.1×10^2	6.8×10^1	3.5×10^1
	anti.	6.7×10^1	3.0×10^1	1.0×10^1
L_D	conv.	2.1×10^2	1.4×10^2	7.2×10^1
	anti.	1.3×10^2	6.2×10^1	2.1×10^1
L_Q	conv.	6.7×10^2	4.4×10^2	2.4×10^2
	anti.	4.3×10^2	1.7×10^2	8.2×10^1