Low-level simultaneous determination of As and Sb in standard reference materials using radiochemical neutron activation analysis with isotopic ^{77}As and ^{125}Sb tracers

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Summary. The aim of the present work was to develop an older method used in our laboratory based on selective solvent extraction of As and Sb as their iodides with toluene, and by the use of the radioisotopic tracers ^{77}As and ^{125}Sb, to improve the accuracy by better control of the radiochemical yields. ^{77}As was produced for each sample run by concurrent irradiation of a few mg of GeO_2 followed by a rapid separation of ^{77}As from ^{77}Ge. The radiochemically purified sample fraction containing $^{76+77}$As and $^{122+125}$Sb was counted on a Ge detector in good geometry. The γ-lines of the four nuclides do not mutually interfere so that a combined measurement of As and Sb may be made.

The method was applied to IAEA Milk Powder A-11, Animal Muscle H-4, Bowen's Kale and some other SRMs. The results obtained are discussed in the light of literature measurements. From present and previous results, together with data by Heydorn, the presently accepted value for As in Bowen's Kale of 140 ng · g^{-1} may be 20% too high.

Introduction

Notwithstanding considerable interest in the biomedical and environmental sciences in these two trace elements, the number of reference materials for which they are certified is meagre. This is particularly true of Sb, where according to Parr's [7] summary of the status of biological CRMs and SRMs (Certified or Standard Reference Materials), Bowen's Kale (with about 70 µg · kg^{-1}) represents the only material certified for antimony (if we exclude NBS Orchard Leaves, which is no longer commercially available, and with a content of 2.9 mg kg^{-1} unsuitable for low level work).

If we consider reference materials appropriate for nanogram level or ultra-trace analysis, the situation for As is also very poor. Both elements in fact occur in many real samples such as tissues, blood and milk at the 1 µg kg^{-1} level or below.

This situation evidently needs to be improved, nor is it clear why these two elements should present such difficulties, as radiochemical neutron activation analysis (RNAA) is capable of determining both with good accuracy and precision at the required levels. This was recently demonstrated for As in the follow-up study organized to improve the status of IAEA CRMs Milk Powder A-11 and Animal Muscle H-4 [4]. However, these materials are as yet uncertified.

The present work was designed to test a method and present results for simultaneous RNAA of As and Sb at low nanogram level in reference materials, using iodide extraction and the radioisotopic tracers ^{77}As and ^{125}Sb to measure the chemical yields of the procedure. The iodide extraction was based on previous work reported from our laboratory [1, 2]. Use of ^{77}As has also been reported in RNAA by Schelhorn and Geisler [8].

Experimental

Preparation of ^{77}As and ^{125}Sb

Both tracers were produced and purified in our laboratory using selective solvent extraction of their iodides.

77-Arsenic. The method has been described in detail elsewhere [3]. Briefly, it consists of irradiation of mg quantities of GeO_2, its rapid dissolution in KOH, acidification to 4 M H_2SO_4 and adjustment to 0.5 M KI, followed by toluene extraction of $^{77}AsI_3$ (^{77}Ge is not extracted at all below 5 M H_2SO_4 – 0.5 M KI). The organic phase is washed twice with the same medium, and ^{77}As is then stripped with 10% H_2SO_4, boiled with a few drops of H_2O_2 to remove iodine and diluted as required. This solution is carrier-free.

^{125}-Antimony. High-flux neutron irradiated Sn metal is well cooled, then dissolved in hot H_2SO_4. ^{125}Sb [from ^{124}Sn (n,γ) $^{125}\mathrm{Sn}\xrightarrow[9.7\ \mathrm{min}]{}{}^{125}\mathrm{Sb}$] is selectively extracted from 1.5 – 2 M H_2SO_4/0.1 M KI with toluene, the organic phase washed twice with the same medium, and then ^{125}Sb stripped into dilute mineral acid and iodide removed with H_2O_2 as above.

Irradiations

Samples, preweighed and doubly encapsulated in polythene, were irradiated in our TRIGA MK II reactor at a thermal flux of 2×10^{12} n · cm^{-2} s^{-1} for about 20 h together with standards in quartz tubes. Standards consisted of weighed aliquots of solutions of As and Sb, separately, of 10 µg · g^{-1}, prepared from their trioxides in 1% HNO_3 and 2 N HCl, respectively, by dilution of 1 mg · g^{-1} stock solutions.

Measurements

Final fractions of 10 ml in 50 ml polythene bottles were counted directly on the surface of an intrinsic Ge detector of 17% efficiency and 1.8 keV resolution (at 1,332 keV). Total peak areas were calculated by the Canberra-80 analyser system.

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Table 1. RNAA of As and Sb in SRMs using ^{77}As and ^{125}Sb tracers; results in µg · kg^{-1}, dry weight

Material	Arsenic			Antimony		
	This work	Certified	Literature	This work	Certified	Literature
Bowen's Kale	114 ± 3 (6)	140 [5]	118 [1], 117 [2], 118 [6]	56 ± 6.7 (6)	70 [5]	
IAEA milk powder A-11	4.70 ± 0.15 (4) 4.8 ± 0.20 (6)[a]		4.86 ± 0.20 [2]	1.2 ± 0.26 (7)		
IAEA animal muscle H-4	5.76 ± 0.26 (8)		5.95 ± 0.35 [2]	1.8 ± 0.12 (6)[b]		
NBS new bovine liver SRM 1577a	48.5 ± 2.6 (10)	47 ± 6		3.81 ± 0.46 (11)	(3)[c]	

Results given with standard deviations and number of aliquots in parentheses

[a] Without ^{77}As tracer; yield assumed 99%

[b] Rejecting two outliers (2.9, 1.4)

[c] Information value

Table 2. Instrumental NAA of Sb in two reference materials; results in µg · kg^{-1}, dry weight

Material	Aliquot	Cooling period	Antimony content				Certified
			Energy of γ-ray used (keV)			Mean	
			564	602	1,691		
NBS orchard leaves SRM 1571	1		2,880	2,810	2,820	2,810 ± 110 (4)	2,900 ± 100
	2		2,900	2,950	2,850	(at 1,691 keV)	
	3				2,900	2,830 ± 100 (9)	
	4			2,690	2,650	(all results)	
Bowen's Kale	1	7 days	55.1		57.8		
	2	8 days	63.2		58.5		
	3	9 days	67.0		58.9	57 ± 4 (6)	70 [5]
	4	10 days	80.8		61.7	(at 1,691 keV)	
	5				54.9		
	6				49.1		

Some non-destructive measurements of ^{122}Sb and ^{124}Sb were made; the energies used are described below under Results.

Radiochemical procedure

The irradiated sample was transferred into a 100 ml long-necked quartz Kjeldahl flask containing 7 ml of conc. (18 M) H_2SO_4, about 0.5 mg each of As^{3+} and Sb^{3+} carriers, and weighed amounts of ^{77}As and ^{125}Sb tracers. The quantity of tracer added was such as to give suitable count rates in the major peaks used for yield evaluation (239 keV for ^{77}As, 428 keV for ^{125}Sb) under the actual measurement conditions, considering the length of the count required for ^{76}As and ^{122}Sb.

The sample was wet-ashed with successive additions of HNO_3 until a pale yellow liquid was obtained which did not darken on heating. 30% H_2O_2 was added dropwise to complete wet-ashing (some arsenic compounds are very resistant) and drive off traces of HNO_3. Water was added cautiously and boiled to destroy traces of H_2O_2. The solution was transferred into a 50 ml separatory funnel, 2 ml 0.5 M KI added and the volume adjusted to the 20 ml mark, i.e. to 6 M H_2SO_4 – 0.05 M KI. As and Sb were extracted into 10 ml toluene by shaking for 1 min. The drained organic phase was washed twice with the same aqueous phase, draining well each time. As and Sb were then stripped by two 5 ml portions of 10% H_2SO_4, running it into a 50 ml polythene counting bottle.

As and Sb are easily separated if desired; this separation is required if the resolution of the detector is poor (^{76}As – 559.1 keV, ^{122}Sb – 564.1 keV) and/or the ratio of ^{76}As: ^{122}Sb is unfavourably high, since ^{76}As has a minor peak at 562.8 keV with an abundance relative to the 559 keV peak of 3.6%. In this case before stripping, the organic phase was transferred into a second separatory funnel containing 5 ml of 3 M H_2SO_4 – 0.05 M KI and arsenic washed out; the stripping and transfer of ^{76}As was completed with a second 5 ml portion of 3 M H_2SO_4 – 0.05 M KI. Antimony was then stripped with 2 × 5 ml portions of 10% H_2SO_4. Alternatively, antimony may be stripped first with 6 M HCl – 0.5 M KI (2 × 5 ml) and arsenic then stripped with 10% H_2SO_4 (2 × 5 ml).

Results and discussion

The γ-spectra obtained by the proposed technique were radiochemically pure and free from any radionuclides other than $^{76+77}$As and $^{122+125}$Sb. (If traces of ^{82}Br are observed, this is a sign of insufficiently vigorous wet-ashing.)

^{77}As, with its main peak at 239 keV, is almost ideal as far as γ-energies are concerned, since all of its peaks lie below the ^{76}As and ^{122}Sb peaks at 559 and 564 keV, respectively, and thus do not contribute to the background continuum under these peaks. ^{125}Sb, with only a minority of peaks above 600 keV, is also a relatively favourable tracer for ^{122}Sb, and its long half life (2.77 years) is more convenient than that of ^{77}As (38.8 h). The radiochemical yields of ^{76}As and ^{122}Sb, as determined by their isotopic tracers ^{77}As and ^{125}Sb, were high and consistent, being 98.5 ± 1.6% and 94.9 ± 2.0%, respectively, from over twenty runs.

Of the four reference materials studied, only NBS New Bovine Liver SRM 1577a required a separation of ^{76}As from ^{122}Sb due to the unfavourable As:Sb ratio (see above). (In samples with sufficient ^{122}Sb activity, the ^{76}As:^{122}Sb ratio can be improved by waiting, as in three days it decreases by a factor of three.)

The results obtained in four important reference materials are shown in Table 1. Results for As are in excellent agreement with recent data for IAEA A-11 and H-4 collected in a follow-up study [4], and with the certified value of NBS New Bovine Liver SRM 1577a. For Bowen's Kale, the present values are in good agreement with those we have reported previously of 118 ± 4 (6) [1] and 117 ± 2 (6) [2] by similar iodide extraction method but without ^{77}As as yield monitor. Heydorn, who exercised much care over the accuracy of arsenic results in efforts to persuade the NBS to reduce the initially certified value of As in Orchard Leaves from 14 to 10 $\text{mg} \cdot \text{kg}^{-1}$, the present value, reported [6] results of 118 ± 4 for Bowen's Kale. (Results obtained in our Laboratory for Orchard Leaves, in 1972 before its first certification at 14 $\text{mg} \cdot \text{kg}^{-1}$, were 9.9 ± 0.4 [1], and 9.85 ± 0.5 [2] in 1974 afterwards.) Therefore, we believe we have good grounds for considering the presently accepted value [5] of 140 $\mu\text{g} \cdot \text{kg}^{-1}$ for As in Bowen's Kale to be too high. (Note that this concentration was given [5] the status of an "indicated value", not a recommended value.)

Considering the values reported here for Sb in Table 1, the literature offers little help in assessing them. In order to obtain additional confirmation of these values, some nondestructive or instrumental neutron activation analyses (INAA) were performed on Bowen's Kale and NBS Orchard Leaves. Though the latter has a certified value of 2,900 ± 100 $\mu\text{g kg}^{-1}$ for antimony which is too high to be suitable as a reference material for trace level work, it could be used to confirm that there were no gross errors, for example in the standard used, and thus help establish the reliability of the INAA values obtained for Bowen's Kale. (INAA could not be applied to the other three reference materials due to their low Sb contents.) The most reliable mode of INAA is based on the 1691 keV peak of ^{124}Sb, whereas the peaks of ^{122}Sb at 564 and ^{124}Sb at 602 keV are subject to interferences from ^{134}Cs. This is demonstrated in Table 2, where as decay of ^{122}Sb occurs, the apparent Sb content based on the 564 keV peak increases. (Measurements at shorter cooling periods are not feasible due to excessive shorter lived activities, notably ^{82}Br.) However, the 1691 keV peak gives consistent values (though long counting periods are required) and the data obtained in this way confirm the RNAA values for Sb in Bowen's Kale. The value given [5] by the IUPAC Commission of 70 ± 10 (accepted range 62–95) is an "indicated value" rather than a "recommended value".

In spite of the fact that the lack of SRMs for As and Sb (as well as for several other important trace elements such as I, Ni, Sn and V) has been commented on for a number of years now, and is evidently a stumbling block to quality control in trace element research, little progress seems to have been achieved. The present results are a modest effort to improve the situation. There is currently a great need for reference materials not merely certified for total element content but giving the speciation of the element, e.g. for arsenic, a trimethylated arsenic fish or shellfish standard is urgently required.

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