Arch. Environ. Contam. Toxicol. 32, 431–436 (1997)

ARCHIVES OF
Environmental
Contamination
and Toxicology

Antimony in Drinking Water, Red Blood Cells, and Serum: Development of Analytical Methodology Using Transversely Heated Graphite Furnace Atomization-Atomic Absorption Spectrometry

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Received: 10 August 1996/Accepted: 20 November 1996

Abstract. An atomic absorption spectrometric (AAS) method has been developed for determining µg/L levels of Sb in samples of water and blood. The AAS method is based on the concept of stabilized temperature platform furnace atomization (STPF) realized through the use of a transversely heated graphite atomizer (THGA) furnace, longitudinal Zeeman-effect background correction, and matrix modification with palladium nitrate-magnesium nitrate-nitric acid. The method of standard additions is not mandatory. The detection limit (3 standard deviations of the blank) is 2.6 µg Sb/L for the water, red blood cells (RBCs), and serum samples. Data are presented on the degree of accuracy and precision. The THGA-AAS method is simple, fast, and contamination-free because the entire operation from sampling to AAS measurement is carried out in the same tube. The method has been applied to the determination of Sb in some leachate tap water samples derived from a static copper plumbing system containing Sn/Sb solders, and in small samples (0.5 ml) of RBCs and serum derived from rats given Sb-supplemented drinking water.

Antimony is found at trace levels in drinking water as the metalloid enters the aquatic environment from the natural weathering of rocks, from mining and manufacturing (textile, rubber, ceramic) effluents, and from municipal discharges (Norseth and Martinsen 1988). The concentration of Sb in Canadian drinking water supplies is generally less than 10 µg/L and probably close to 1 µg/L (Health and Welfare Canada 1980). However, due to the expected replacement of Sn/Pb solder with Sn/Sb solder in new and renovated household plumbing, it is likely that the leaching of Sb resulting from the galvanic corrosion of plumbing components may lead to an increase in the Sb concentration of drinking water. Under these conditions, drinking water may become one of the major routes of exposure to Sb. In view of this, there is concern regarding the potential harmful health effects of the chronic ingestion of low levels of Sb in drinking water, and the Health and Welfare Department is considering the establishment of a drinking water guideline for Sb. However, reliable monitoring and exposure data at low levels of Sb are lacking, probably because it is not easy to measure the metalloid at the µg/L levels present in drinking water and biological media (Norseth and Martinsen 1988; Subramanian 1986, 1988a). We have therefore initiated studies on the extent of the leaching of Sb from Sn/Sb-soldered household copper plumbing and on the effect of antimony salts in rats following a 90-day exposure via drinking water. These studies require the development of simple, sensitive, rapid analytical methods capable of determining low levels of Sb in drinking water and small samples of biological tissues such as blood.

Atomic absorption spectrometry (AAS), in conjunction with flame, hydride generation, or graphite furnace, is the most widely used technique for the determination of Sb in environmental and biological media at present (Norseth and Martinsen 1988; Subramanian 1988a, 1988b). Flame AAS sensitivity is poor for low level Sb determination and often requires preconcentration via hydride generation or solvent extraction. Graphite furnace AAS is 50 to 100 times more sensitive than flame AAS, requires only small sample sizes (5–50 µl), and offers the possibility of the direct analysis of the biological fluids through the incorporation of STPF features. These attributes are essential in this work, especially in view of the small samples of red blood cells available.

The present work explores the feasibility of developing a sensitive method for determining Sb in drinking water and blood (RBCs and serum) based on the STPF concept using a unique state-of-the-art THGA–AAS instrumentation.

Materials and Methods

A Perkin-Elmer Model 4100 ZL compact atomic absorption spectrometer featuring a uniquely designed transversely heated graphite atomizer (THGA), an inverse longitudinal Zeeman-effect background corrector, pyrolytically coated electrographitic THGA tubes containing integrated small mass L'vov platforms, an AS-70 autosampler, an

*Dedicated to John Connor, who passed away of a heart attack on October 1, 1996, at age 48. John, a loveable colleague and a conscientious and tireless worker, assisted with the experimental part of this study.

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Okidata Model 320 printer for plotting the time-resolved peak absorbance pulses, and a Perkin-Elmer System-2 EDL power supply with an Sb EDL lamp operated at 300 mA and at a resonance line of 217.6 nm (spectral band pass 0.7 nm) was used for the determination of Sb. The AAS system is totally automated with an IBM-compatible, MS window-based computer control of all components, namely, the spectrometer, furnace, Zeeman-effect background corrector, autosampler, and all data handling features. Argon served as the purge gas and its flow was interrupted during atomization.

High-purity water, obtained by distilling doubly deionized water in a Corning AG-11 Distillation Unit, was used throughout this work. A certified Sb(III) standard of 1000 mg/L was purchased from British Drug Houses (BDH) (Toronto, Canada). Standards of lower Sb concentrations were prepared by serial dilution of the stock. A 1% solution of palladium nitrate was prepared by dissolving an appropriate amount of $Pd(NO_3)_2 \cdot 2H_2O$ (certified to contain 8.5% Pd; Johnson Matthey, NH, USA) in high-purity water, as described in a previous publication (Subramanian *et al*. 1993). A 5% solution of $Mg(NO_3)_2$ was prepared by dissolving an appropriate amount of $Mg(NO_3)_2 \cdot 6H_2O$ (BDH, Toronto, Canada) in high-purity water. All other reagents and solutions used were of the highest purity available.

The water samples were obtained from a leaching study conducted in a static setup consisting of copper plumbing with 95%-Sn/5%-Sb–solder, as described in a previous publication (Subramanian *et al*. 1991). Both fluoridated and nonfluoridated tap water samples were used in the leaching study at alkalinity values of 50, 100, 200, and 500 mg/L as $CaCO_3$, and at pH values of 4.5, 5.5, 6.5, and 8.0. The water samples were withdrawn for analysis at time intervals of 0, 1, 3, 7, 24, 168 (7 days), and 672 (28 days) hours.

The serum and RBC samples were obtained from rats. Groups (n = 5) of young female and male rats weighing 125 ± 10 g were given tap water supplemented with 0.5, 5, 50, and 500 mg/L Sb(III) in the form of potassium antimony tartrate for a period of 13 weeks. Control rats received tap water derived only from copper plumbing with Sn/Pb solder. Regular rat chow was provided *ad libitum*. At termination, the animals were sacrificed and the whole blood samples were withdrawn into heparinized trace-element–free Becton Dickinson tubes. The whole blood samples were centrifuged to obtain serum and RBCs.

The optimum amounts of palladium nitrate, magnesium nitrate, and nitric acid used in the procedures outlined below were obtained by doing the studies: at palladium(II) values of 0, 25, 50, 100, 200, 400, and 600 mg/L while maintaining the magnesium nitrate and nitric acid concentrations constant at 25 mg/L and 0.2%, respectively; at $Mg(NO_3)_2$ values of 0, 25, 50, 100, and 200 mg/L while keeping the Pd(II) and HNO_3 values at 100 mg/L and 0.2%, respectively; and at HNO_3 values of 0, 0.1, 0.2, 0.5, 1, 2, and 5% while keeping the Pd(II) and $Mg(NO_3)_2$ values at 100 mg/L and 25 mg/L, respectively. An antimony concentration of 100 µg/L was used in the optimization study.

In the case of water, a known aliquot of the sample (10 or 20 µl) was mixed with aliquots of palladium nitrate, magnesium nitrate, and nitric acid in the autosampler cup so that the matrix modifier composition in the final solution corresponded to 100 mg/L Pd(II), 25 mg/L $Mg(NO_3)_2$, and 0.2% HNO_3. In the case of RBCs, aliquots of the sample (200, 50, and 25 µL for Sb levels of $<$10, $<$150, and $>$150 mg/Kg, respectively, were lysed with a 10% aqueous solution of Triton X-100, and aliquots of the matrix modifier solutions [Pd(II), magnesium nitrate, HNO_3] were added and diluted appropriately (5-, 20-, and 500-fold for levels of $<$10, $<$150, and $>$150, respectively, with high-purity water so that the matrix modifier concentrations in the final solution corresponded to the same levels as in the case of water and the concentration of Sb in the sample was within the linear calibration range. The dilution factor used varied depending on the concentration of Sb in the sample. The serum samples were processed exactly the same way as the water samples.

The autosampler cups containing the reagent blanks (nitric acid plus palladium nitrate plus magnesium nitrate), calibration standards (5, 10, 25, 50, 75, and 100 µg/L Sb in the matrix modifier medium), and the matrix-modified sample solutions were arranged in the sample tray. Also, the calibration standard of 50 µg/L and a sample (water, RBC, or serum) supplemented with 50 µg/L were used as part of the quality assurance program. The autosampler was switched on and a 20-µl aliquot was automatically transferred onto the THGA tube. The Sb in the sample was atomized according to the instrumental arrangements shown in Table 1. The reagent blanks, samples, and standards were measured in duplicate. Three replicate injections were made for each aliquot, thus making a total of 6 measurements. The peak area absorbance values of these 6 measurements were averaged and corrected for the reagent blank. The Sb concentration in the sample was obtained from the linear calibration plots.

Results and Discussion

Schlemmer and Welz (1986) and Welz *et al*. (1988a, 1988b), using the Massman-type gradient furnace, found that the palladium nitrate-magnesium nitrate modifier could stabilize Sb (100 µg/L) up to a pyrolysis temperature of 1300°C whereas, in the presence of HNO_3 and Ni as modifiers, the stabilization temperatures were 900 and 1100°C, respectively. Thus, pretreatment of the sample and standard solutions with the Pd-Mg modifier allows the use of higher pyrolysis temperatures than with the previously recommended Ni or nitric acid modifiers. Although it is not usually necessary that the highest possible pyrolysis temperatures be applied for the analysis of water samples, a better thermal stability of the analyte element offers more flexibility in selecting a suitable temperature program, especially in the analysis of biological samples such as RBCs and serum.

Preliminary attempts to adapt the Pd-Mg modifier at the concentrations recommended by Welz *et al*. (1988a) to the THGA furnace used here resulted in broad, noisy peaks which did not return to the baseline even within an integration time of 5 s. Therefore, we decided to investigate the effect of Pd(II), Mg(II), and nitric acid on the peak profile. The optimum palladium(II), magnesium nitrate, and nitric acid concentrations at which symmetric peaks with rapid return to the baseline occurred were found to be 100 mg/L, 25 mg/L, and 0.2%, respectively.

The optimized dry-char-atomize parameters for Sb in the water and biological samples at the above composite matrix-modifier concentrations were arrived at by a systematic evaluation of the temperature program of the THGA furnace. At drying temperatures $>$200°C and at ramp-hold times of 10–20 s, there was loss of Sb due to sample spattering. In order to facilitate rapid determination, the drying temperature and times were fixed at 120°C with a 10-s ramp and a 20-s hold. The optimum pyrolysis temperature at which the peak area signal remained constant was found to be $\leq$1300°C, which was larger than that obtainable with Ni(II) or HNO_3, and which was the same as found for the Massman furnace (Schlemmer and Welz 1986). The use of an ashing temperature of 1000°C, however, ensured complete ashing of organic matter and the absence of any carbonaceous residue within the graphite tube. Although the optimum atomization temperature was found to be at 1900°C, the peak profiles were found to be symmetric at atomization temperature ranges of 1950–2050°C. It is important to optimize the atomization temperature with respect to an atomization pulse which is fairly symmetric with minimum tailing and which returns to the baseline within 2–4 s after its appearance (Schlemmer and Welz 1986). Based on these criteria, the optimum atomization temperature for Sb was found to be at 2050°C which was therefore chosen in this work.

Table 1. Optimized instrumental arrangements for determination of antimony[a]

Setting	Antimony
EDL lamp current, mA	300.0
Wavelength, nm	217.6
Slit, nm	0.7
Integration time, s	3.0
Drying temperature, °C	120
Drying time (ramp/hold), s	10/20
Ashing temperature, °C	1000
Ashing time (ramp/hold), s	10/20
Atomization temperature, °C	2050
Atomization time (ramp/hold), s	0/3
Cleaning temperature, °C	2200
Cleaning time (ramp/hold), s	1/2

[a] Perkin-Elmer Model 4000 ZL transversely heated graphite furnace atomic absorption spectrometer (THGA-AAS) equipped with an inverse, longitudinal Zeeman-effect background corrector, THGA tube, AS-70 autosampler set up to deliver 20 µL, and total automation with computer control. The argon purge gas flow was 300 mL/min during the drying and ashing cycles, and was interrupted (0 mL/min) during atomization

Optimization studies with samples of tap water, red blood cells, and serum supplemented with Sb showed the same results indicating that the matrix did not have any influence on the optimum furnace temperature parameters.

Analytical parameters

The sensitivity, defined as concentration at 0.0044–absorbance-units, was 3.5 µg/L. In terms of characteristic mass (pg/0.0044 A.s), the sensitivity value was 46.8 ± 0.1, based on 10 consecutive measurements of a 20-µg/L Sb solution in the composite modifier. The characteristic value remained more or less the same when similar measurements were made with tap water, RBC, and serum samples—clearly indicating that the instrument was operating under true STPF conditions. The detection limit, calculated as 3 standard deviation of the reagent blank, was 2.6 µg/L. The calibration was linear at least up to 100 µg Sb/L.

Table 3 gives the within-run and day-to-day precision for the determination of Sb in some water, RBC, and serum samples. These values are judged to be sufficient for the leaching studies and also for screening the Sb-exposed rats in the present work. No standard reference materials certified for Sb in water, RBC, or serum are available at present. Therefore, accuracy of the proposed method was assessed indirectly by doing recovery studies. As shown in Table 2, the recovery was quantitative in the three types of samples tested, attesting to the accuracy of the present method.

Interferences

It is well documented in the literature that spectral interferences are encountered in the determination of Sb in the presence of iron (Fernandez and Giddings, 1982; Letourneau *et al.* 1987) and phosphate (Martinsen *et al*. 1988) when continuum source background correction is used. These spectral interferences are, however, completely eliminated using Zeeman-effect background correction (Schlemmer and Welz 1986; Slavin 1994) as in the present case.

The nonatomic absorption signals were brought well within the correction capabilities of the Zeeman-effect background corrector using the palladium-magnesium-nitric acid matrix modification and the optimized furnace temperature program. Thus, the background absorbance value (peak area) at the pyrolysis-atomization temperatures of 1000–2050°C was only

Table 2. Recovery of antimony added to some water, red blood cell and serum samples[a]

	% Recovery of antimony at spike levels (µg/L) of		
Samples	10	25	50
Water			
AUD-06	95.0 ± 1.7	99.2 ± 5.8	94.9 ± 3.9
ION-91	102.3 ± 4.8	102.7 ± 4.4	103.0 ± 2.1
ION-92	108.7 ± 5.1	106.1 ± 6.3	107.6 ± 3.4
ION-94	101.4 ± 6.5	104.8 ± 8.3	103.1 ± 3.7
ION-95	112.0 ± 9.6	106.0 ± 5.7	103.8 ± 2.2
ION-96	107.0 ± 6.2	105.6 ± 5.6	94.2 ± 6.4
Red Blood Cell			
111	94.3 ± 3.6	96.8 ± 2.4	100.2 ± 3.9
123	96.8 ± 2.4	93.3 ± 1.7	103.6 ± 1.5
211	103.6 ± 4.0	101.4 ± 2.8	104.5 ± 4.9
213	96.8 ± 3.7	105.2 ± 4.1	93.6 ± 1.2
217	104.4 ± 3.2	97.6 ± 2.8	101.6 ± 2.6
Serum			
147	99.9 ± 4.8	102.3 ± 3.8	97.5 ± 3.2
151	98.4 ± 3.3	97.8 ± 2.0	105.0 ± 3.6
212	96.0 ± 1.1	103.2 ± 2.7	104.4 ± 2.5
217	100.4 ± 5.0	101.6 ± 4.1	101.2 ± 2.0
236	104.8 ± 6.2	102.8 ± 2.5	103.6 ± 5.3

[a] Average recovery (±standard deviation at 95% confidence level) of Sb from samples with endogenous Sb levels at or below the detection limit

Table 3. Precision at some Sb concentrations in water, red blood cell and serum samples

		Precision	
Sample	Antimony Level	Within-run % CV[a]	Day-to-day % CV[b]
Water[c]	µg/L		
ION-96	10	6.2	6.5
ION-91	25	4.4	4.1
ION-94	50	3.7	4.3
Red Blood Cell	µg/Kg		
134	0.20	5.0	5.9
235	0.47	6.4	6.6
151	10.2	1.9	2.2
Serum	µg/L		
262	71.6	10.1	9.8
164	140.6	3.9	4.4
166	237.0	3.1	3.3

[a] Based on 6 repetitive measurements
[b] Based on 40 measurements over a 10-day period
[c] The water samples were supplemented with Sb as the Sb concentration of these samples were below the instrumental detection limit

0.082 even in the case of RBCs and was well within the Zeeman background correction capabilities. Also, chemical interferences were absent as was evident from the identical slope values (0.001) of the linear calibration plots obtained for Sb-supplemented matrix-modified solutions of high-purity water, tap water, RBC, and serum. Further evidence for the absence of chemical interference was obtained by doing recovery studies using a series of quality control water samples (Canada Centre for Inland Waters, Ontario, Canada), RBC samples, and serum samples supplemented with different levels of Sb. The results in Table 2 show nearly quantitative recovery of Sb corroborating the absence of chemical interference and confirming the validity of using matrix-modified aqueous linear calibration graphs.

Welz *et al*. (1988a) had raised the possibility of sulfate interference in water analysis although they did not show any data. To test this, we conducted recovery studies by supplementing the above quality control water samples with 50 µg/L Sb and sulfate levels of 0, 20, 50, 100, 250, and 500 mg/L. The recoveries were close to 100% in all cases showing the absence of any sulfate interference. It is unusual to find sulfate above 200 mg/L in water samples.

The absence of any interference and the ability to use aqueous calibration shows that the THGA furnace with Zeeman-effect background correction approaches the STPF concept more closely than the Massman furnace because the latter necessitated the use of standard addition calibration plots, as we found in our previous studies on Pb in bone (Subramanian *et al*. 1993) and As in blood (Subramanian 1988c) and urine (Subramanian 1988d). Thus, the lack of a uniform-temperature environment within the Massman furnace did not permit a truly STPF condition. The THGA furnace, used in the present work, with its uniform-temperature environment overcame this problem.

Application to Samples

The method was applied to water samples subject to leaching in a static setup of copper plumbing with Sb/Sn solder as a function of time. The concentrations of Sb in all the samples tested were below the instrumental detection limit of 2.6 µg/L, indicating no significant leaching of Sb from the Sn/Sb solder into the water samples. Thus, the replacement of the Sn/Pb solder with the Sn/Sb solder in household copper plumbing could be a safer alternative.

Figure 1 shows the Sb levels in RBCs from rats exposed to potassium antimony tartrate in drinking water at levels of 0.5, 5, 50, and 500 mg/L. As can be seen, the level of Sb in RBCs was dose-dependent and reached up to about 200 mg/Kg in both male and female rats exposed to 500 mg/L Sb in drinking water. On the other hand, serum values were less than 0.2 mg/Kg in both the control and exposed groups. Thus, one can conclude that Sb is concentrated in RBCs as in the case of As. This observation is in agreement with the studies of Felicetti *et al*. (1974) in hamsters and Edel *et al.* (1983) in rats. Dieter *et al.* (1991) also found accumulation of Sb in the whole blood of rats injected intraperitoneally with potassium antimony tartrate for 90 days. Although we did not identify the specific RBC fraction in which Sb accumulated, Edel *et al*. (1983) have shown that in 2 h following the intraperitoneal injection of ^{124}Sb(III), the radioactivity coeluted with the hemoglobin fraction. Our studies suggest that, in addition to the traditional systemic toxicity parameters for the assessment of adverse effects (*e.g.*, growth curve, organ weights, hematology, serum chemistry, and histopathology of major organs), special emphasis should be placed on the function and morphology of RBCs. Also, *in vitro* study of the effect of Sb on RBC biochemical and hemoglobin functions should be carried out. Of particular interest will be the effect of Sb on the RBCs of patients with hemoglobinopathies and/or glucose-6-phosphate dehydrogenase deficiency.

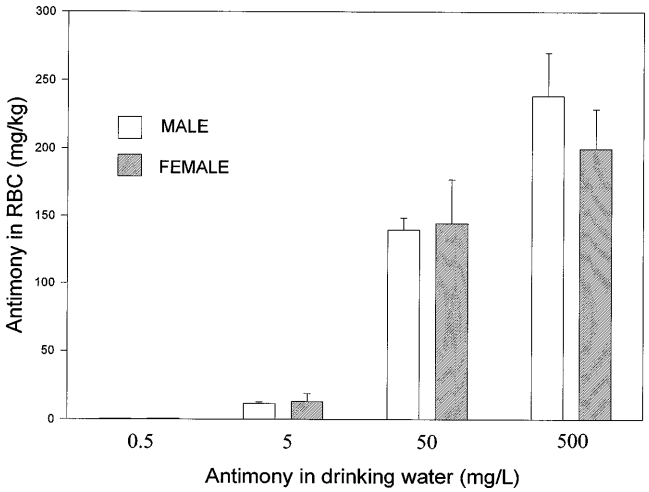

Fig. 1. Antimony levels in red blood cells from rats exposed for 90 days in drinking water supplemented with potassium antimony tartrate at levels of 0.5, 5, 50, and 500 mg/L as Sb(III). The Sb(III) levels correspond to Mean ±SD of 5 animals.

Conclusions

The THGA-AAS method proposed here was developed for the determination of Sb in leachate water samples exposed to copper plumbing joined with Sn/Sb solders, and in the RBCs and serum of rats subchronically exposed to this metalloid in the form of potassium antimony tartrate-dosed drinking water. The estimation of the antimony level in drinking water and in biological materials under nonexposed conditions would require the use of more sensitive methods such as ICP–MS or preconcentration via hydride generation prior to THGA-AAS determination.

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