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Determination of Sb in Sediment and Road Soil

Using the Agilent 240 Zeeman graphite furnace atomic absorption spectrometer

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Introduction

Antimony (Sb) is widely used as a flame-retardant in the textiles and plastics industries. It is also used as a paint pigment, and ceramic opacifier or catalyst. Its wide use means that it can find its way into the environment as a pollutant. Its main anthropogenic sources include smelting activities, emissions from vehicle brake pads, waste disposal or incineration, and shooting activities.

Recognized as potentially harmful at very low concentrations and listed by the US Environmental Protection Agency as a 'priority pollutant', antimony sources and pathways to the environment are the subject of investigation by researchers and regulators.

Soils or sediments are likely to hold Sb. They are complex matrices to analyze, requiring the development of a reliable analytical method for the determination of antimony at low levels. Graphite furnace atomic absorption spectrometry offers suitable sensitivity at a lower cost than ICP-MS for this analysis.

This study describes the method and performance of the Agilent 240Z graphite furnace atomic absorption spectrometer when measuring Sb at very low concentrations in environmental samples. Results were compared to those obtained using an ICP-MS instrument.

Experimental

Instrumentation

Furnace measurements were performed using an Agilent 240Z AA spectrometer with transverse Zeeman background correction. The instrument features the highly sensitive and accurate Agilent GTA 120 Graphite Tube Atomizer (GTA) and an Agilent PSD 120 Programmable Sample Dispenser (PSD) autosampler, as shown in Figure 1. The PSD automatically delivers measured volumes of the sample to the furnace. The Agilent PSD 120 provides the capacity for up to 135 solutions and performs automatic standard preparation, modifier addition, and overrange dilution.
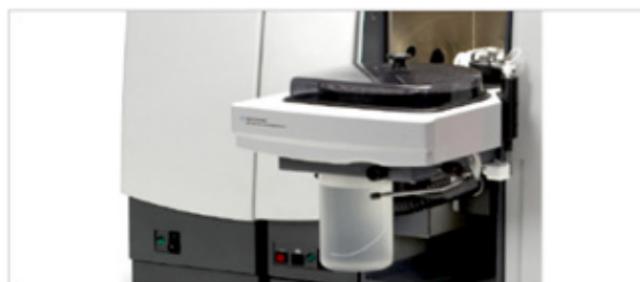
Figure 1. Agilent PSD-120 programmable sample dispenser.

The 240Z AA comprises patented longitudinal graphite tube heating and a Constant Temperature Zone (CTZ) design. In addition to prolonging the graphite tube lifetime, these features provide consistent, uniform heating, which is essential for the accurate low-level determination of complex samples.

Atomization for antimony was from a pyrolytic platform Omega tube. The inert gas used was 99.99 % pure argon.

Table 1 lists the instrument settings and Table 2 lists the furnace settings used in the analysis.

Table 1. Instrument Settings.

Instrument Parameter	Setting
Wavelength	217.6 nm
Slit	0.2 nm
Lamp current	10 mA
Background correction	Zeeman
Replicates	3
Calibration mode	Standard additions
Sample volume	20 µL
Modifier volume	5 µL
Modifier injection type	Co-injection
Total volume	30 µL
Hot injection temperature	60 °C
Injection speed	3

Table 2. Furnace Settings.

Step	Temp (ºC)	Time (s)	Argon Flow (L/min)	Read
1	80	60	0.3	
2	120	30	0.3	
3	925	20	0.3	
4	925	10	0.3	
5	925	1	0	
6	2200	0.6	0	Yes
7	2200	2	0	Yes
8	2600	2	0.2	
9	40	21.5	0.3	

Reagents

The following reagents were used for preparation of calibration solutions and for sample preparation:

- Antimony standard solution, 1000 mg/L
- High-purity HCl, HNO_3, $HClO_4$, HF
- Class 1 Water (18 MΩ/cm)
- 0.1 % palladium nitrate, Agilent partnumber: 5190-8335
- 1 % magnesium nitrate, Agilent partnumber: 5190-8338

The PSD 120 autosampler rinse solution was 2 % v/v of high purity nitric acid.

1 g/L $Mg(NO_3)_2$, $6H_2O$ + 0.9 g/L $Pd(NO_3)_2$ mixed modifier was prepared.

Standards additions were prepared by the autosampler for each sample with different volumes of a master standard of 200 µg/L. Spiked concentrations are 10, 20, 40 µg/L. The automixing capabilities of the sampler were utilized.

Sample collection and preparation

10 L of river waters were filtered at < 0.45 µm porosity to collect the particulate phase of water: Suspended Particulate Matters (Sample 1).

Integrative samples collected during four to five days by sediment traps to get long term Suspended Particulate Matters. Then centrifuged (375 g) and freeze-dried. Sediments were dried and sieved at 2 mm (Sample 2).

Road soil samples specific from urban areas, called Road Deposited Sediments (RDS), were sampled in the gutter of a street (Samples 3 and 4). The RDS were dried and sieved at 200 µm to keep the contaminants bound to finer fraction and discard gravels.

All sediments and RDS were ground in an agate mortar. Approximately 100 mg of SPM was mineralized in PTFE beakers and heated by DigiPREP block under an exhaust hood. A three-phase-digestion was performed. First, 4 mL of HF (30 %) and 2 mL $HClO_4$ (67 %) were left at ambient temperature for 2 hours then heated at 150 °C for 6 hours. The second digestion phase saw the addition of 3.75 mL of HCl (30 %) and 1.25 mL of HNO_3 (67 %). The solution was then kept at ambient temperature for 8 hours before heating at 120 °C during 3 hours and 20 minutes. Finally, three successive evaporations of 1 hour at 110 °C after addition of 1 mL of HNO_3 (67 %) were performed. The dry evaporated residue was then redissolved in 50 mL of HNO_3 at 2 % v/v.

Results and discussion

Optimization

The Agilent 240Z instrument features a furnace viewing camera, Tube-CAM. This provided real time viewing inside the graphite Omega tube and was used to optimize drying steps.

Ash and atomization temperatures were optimized using SRM (Surface Response Methodology) Wizard, within the instrument software. By choosing initial ash and atomize temperatures and steps for each (Table 3), the software automatically derived the experiments needed.

Table 3. SRM Parameters.

Step	Target Temperature (°C)	Step (°C)
Ash	1000	200
Atomization	2100	200

Figure 2 shows the 3D shape and the optimum temperatures :

- Ash temperature: 932 °C
- Atomization temperature: 2195 °C

In the furnace program, the ash and atomize temperatures were rounded to 925 and 2200 °C respectively.
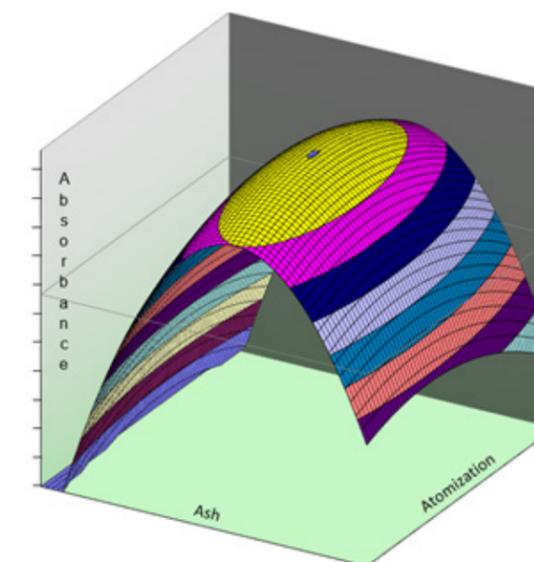
Figure 2. SRM ash and atomization optimization.

Calibration

Standard addition calibration graphs are shown for each sample in Figure 3. Excellent correlation coefficients were obtained as shown in Table 4.
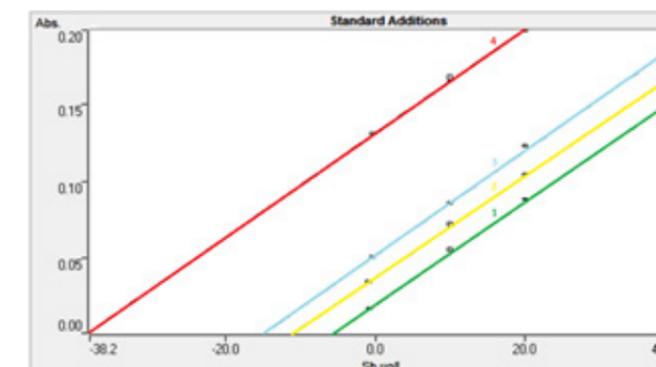
Figure 3. Standard addition calibrations on sample 1 to 4.

Table 4. Slopes and correlation coefficients.

Sample	Slope	Correlation coefficient
1	**0.00337**	0.9992
2	**0.00332**	0.9996
3	**0.00343**	0.9995
4	**0.00341**	0.9990

As shown in Table 4, the slope of the four samples is similar. That means that all samples had a similar signal response. Therefore, instead of running standard additions on each sample, standard additions were performed on the first sample only. More samples could thus be measured according to the first sample calibration.

Figure 4 shows Sb peak profiles of three replicates of Sample 4 (low peaks) and one standard addition (high peaks). These overlays signals show the benefit of the platform in delaying atomization of Antimony as described by the work done by Boris L'Vov in 1978 (*4*) and by Walter Slavin et al in 1981 (*5*) in the Stabilized Temperature Platform Furnace (STPF) concept.
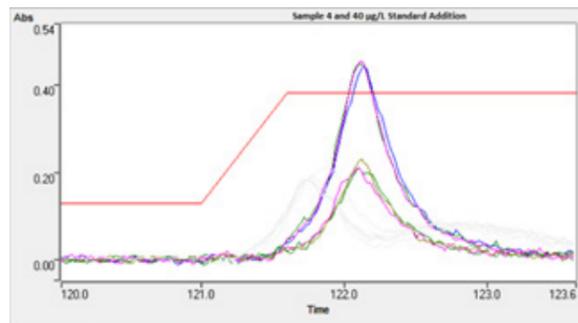
Figure 4. Sb furnace signal on sample 4 and 40 µg/L standard addition.

Repeatability

To check repeatability, the four digested soil samples were analyzed three times. Table 5 shows measured concentrations results of the four samples, mean concentration and %RSD.

Table 5. Repeatability results.

Sample	Analysis 1	Analysis 2	Analysis 3	Mean	Std dev	C.V. %
1	2.4	2.2	2.17	2.257	0.125	5.5
2	4.05	3.96	3.9	3.970	0.075	1.9
3	7.38	6.93	7.32	7.210	0.244	3.4
4	20.3	20.81	18.83	19.980	1.028	5.1

Accuracy

To check accuracy, digested soil samples were first analyzed once using ICP-MS. As shown in Table 6, recovery results using this method were within ±10 % of the results obtained by ICP-MS.

Table 6. ICP-MS comparison.

Sample	Analysis 1	Analysis 2	Analysis 3	Mean	Std dev	%
1	2.40	2.20	2.17	2.257	0.125	5.5
2	4.05	3.96	3.90	3.970	0.075	1.9
3	7.38	6.93	7.32	7.210	0.244	3.4
4	20.3	20.81	18.83	19.980	1.028	5.1

Long term stability

Long term stability was tested by analyzing a sample over 50 times during more than 6 hours. The 240Z AA showed excellent stability over the 6 hour run with RSD values of less than 3.5 %.

Figure 5 shows that conditions remain stable during the 6-hour sequence.
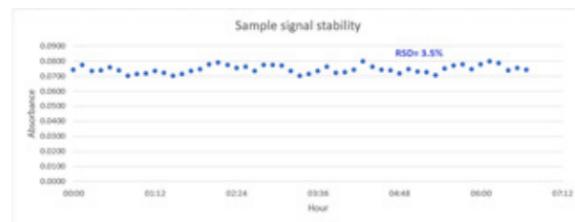
Figure 5. Sample stability over 6.5 hours

Detection and quantification limits

The detection and quantification limit expressed as the concentration equal to three and 10 (respectively) times the standard deviation of the 10 concentration measurements of a blank are shown in table 7. LOD and LOQ in mg/kg have been calculated based on sample preparation (100 mg weight in 50 mL volume).

Table 7. Detection and quantification limits.

	In solution µg/L	In soil mg/kg
LOD	1	0.5
LOQ	2.9	1.4

Characteristic Mass

The Characteristic Mass (m_0) expressed as the absolute mass of analyte giving a peak area of 0.0044 absorbance was 24 pg for Antimony.

Conclusions

The method using the Agilent 240Z graphite furnace AA provided accurate results for the determination of low levels (ppm) of antimony in soils and sediments. The results obtained were within ±10 % of the results obtained on an ICP-MS instrument.

The instrument's transverse Zeeman background correction and the chemical modifier, Omega tube design, and temperature optimization by Surface Response Methodology allowed the development of a robust method. This meant single standard addition calibration was possible, saving time and reducing gas costs.

References

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