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Application News

No. A645

Atomic Absorption Spectrophotometer AA-7000

Leaching Test of Sb and Ge from PET by Graphite Furnace Atomic Absorption Spectrophotometry (GF-AAS)

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User Benefits

- Automatic generation of multi-point calibration curves from a single standard is possible.
- Automatic measurements of samples with concentrations from 1/10 to several times the standard values for leaching are possible.

■ Introduction

Polyethylene terephthalate (PET) has excellent heat resistance and toughness, and is widely used in bottles, tray, packs, and other products. On the other hand, because antimony (Sb) or germanium (Ge) compounds are used as polymerization catalysts in the PET manufacturing process, these elements may remain in the PET. For this reason, Japan's Food Sanitation Act sets Sb and Ge leaching standards for implements, containers, and packaging materials made of synthetic resins consisting mainly of PET. The standard values are no more than 50 µg/L (ppb) for Sb and 100 µg/L (ppb) for Ge as the concentration in the eluate.

Although measurement methods include atomic absorption spectrometry, ICP atomic emission spectrometry, and ICP mass spectrometry, this article introduces an example of measurement using the graphite furnace atomic absorption spectrophotometry (GF-AAS) (electrical heating atomic absorption method), which can measure samples with high sensitivity. The graphite furnace atomic absorption spectrophotometry (GF-AAS) makes it possible to measure concentrations as low as 1/10 of the standard values without sample concentration. Moreover, use of the auto dilution function of a Shimadzu autosampler enables automatic generation of multi-point calibration curves from a single standard and automatic dilution and reanalysis of samples that exceed the set standard values.

■ Instrument Configuration and Measurement Conditions

The instruments used here were a Shimadzu AA-7000/AAC atomic absorption spectrophotometer, GFA-7000A graphite furnace atomizer, and ASC-7000 autosampler.

In the tests, the eluate from samples immersed for a specified time in 20 mL of 4 % acetic acid per 1 cm^2 of the sample surface area was measured.

A standard solution having the same concentrations as the standard values (Sb: 50 µg/L, Ge: 100 µg/L) was prepared by diluting a commercial 1000 mg/L standard solution with 4 % acetic acid. The standard solution and dilute solution (prepared with 4 % acetic acid) were set in the autosampler, and calibration curves for Sb and Ge were prepared by measuring these two solutions while changing the sampled amounts in a stepwise manner.

Simulation samples were prepared by adding Sb and Ge to the 4 % acetic acid at levels from 1/10 to 2 times the standard values.

Table 1 shows the measurement conditions and atomization conditions of the AA-7000, and Table 2 shows the autosampler formulation conditions for the standard solutions for the calibration curves.

Table 1 Measurement Conditions

Element	Sb	Ge
Analytical wavelength	217.6 nm	265.2 nm
Slit width	0.7 nm	
Lighting mode	BGC-D2	
Lamp current	13 mA	18 mA
Incineration temperature	800 ˚C	
Atomization temperature	2300 ˚C	2500 ˚C
Tube type	Platform	
Matrix modifier	Nickel nitrate	
Sample injection volume	Sample: 10 µL + nickel nitrate: 2 µL	
Signal processing	Peak height	
Number of repeated measurements	2 (maximum 3)	

Table 2 Conditions for Formulation of Calibration Curve Standard Solutions by Autosampler

Set concentration (ppb)		Standard solution (Sb: 50 ppb, Ge: 100 ppb)	Dilute solution (4 % acetic acid)	Additive (nickel nitrate)	Total injection volume
Sb	Ge				
0	0	0 µL	10 µL	2 µL	12 µL
10	20	2 µL	8 µL		
25	50	5 µL	5 µL		
50	100	10 µL	0 µL		

■ Additives

In the graphite furnace atomic absorption spectrophotometry (GF-AAS), palladium, nickel, and other elements that are employed as catalysts are used as additives. These elements function as matrix modifiers (interference inhibitors, chemical modifiers). Specifically, formation of a stable compound of the element being measured, which is easily volatilized at low temperature, prevents volatilization in the drying and incineration stages, and enables stable and efficient atomization unaffected by coexistent substances (i.e., the matrix). In this experiment, nickel nitrate was added automatically by using the autosampler.

Although the absorbance of Sb does not differ significantly due to the addition of nickel nitrate, the absorbance of Ge is increased by addition of nickel nitrate, and as shown in Fig. 1, stable absorbance could be obtained in the range of 700 ˚C to 1000 ˚C, even as the incineration temperature increased.

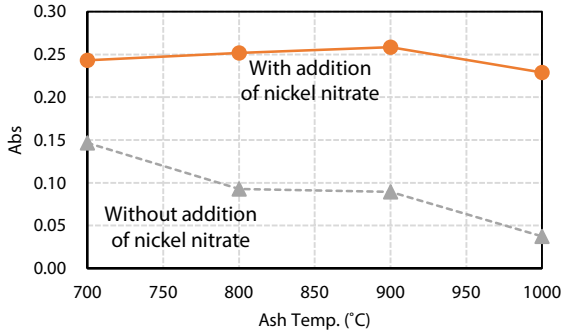

Fig. 1 Effect of Nickel Nitrated Addition on Absorbance and Incineration Temperature Dependence of Ge (Atomization Temperature: 2400 ˚C)

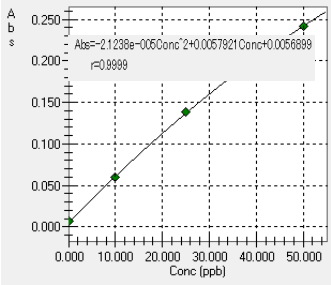

Fig. 2 Calibration Curve of Sb

Table 3 Measurement Results of Sb Simulation Samples

Spiked conc. (ppb)	Abs.	Measured conc. (ppb)	%RSD (n=2)	Auto dilution rate	Actual conc. (ppb)	Recovery rate
5	0.0354	5.2	1.2	1	5.2	105 %
10	0.0616	10.0	1.2	1	10.0	100 %
25	0.1326	24.0	2.2	1	24.0	96 %
40	0.2051	40.4	1.7	1	40.4	101 %
100	0.1143	20.3	6.2	5	101	101 %

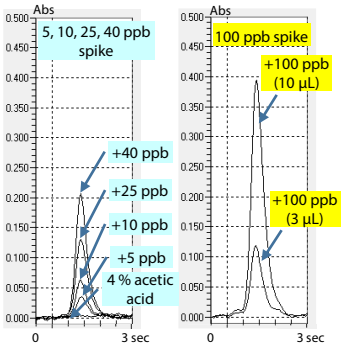

Fig. 4 Peak Profiles of Simulation Samples (Sb)

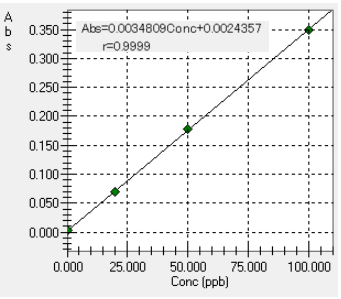

Fig. 3 Calibration Curve of Ge

Table 4 Measurement Results of Ge Simulation Samples

Spiked conc. (ppb)	Abs.	Measured conc. (ppb)	%RSD (n=2)	Auto dilution rate	Actual conc. (ppb)	Recovery rate
10	0.0358	9.58	4.2	1	9.58	96 %
20	0.0696	19.30	1.4	1	19.30	97 %
50	0.1801	51.04	0.3	1	51.04	102 %
80	0.2822	80.37	0.2	1	80.37	101 %
200	0.2032	57.68	0.9	3.333	192.25	96 %

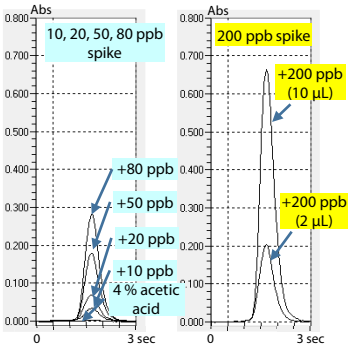

Fig. 5 Peak Profiles of Simulation Samples (Ge)

Table 5 Example of Auto Dilution and Reanalysis (Sb)

Sample ID	X	Conc. (ppb)	Abs.	Pos.	VOL	Acetic Acid 4% 1	Ni1 0ppm 31	Total Volume	ASC DF	Actual Conc.	Actual Conc. Unit
+5ppb		5.1758	0.0351	3	10	0	2	12		5.18	ppb
+5ppb		5.2656	0.0356	3	10	0	2	12		5.27	ppb
+5ppb		**5.2296**	**0.0354**	**3**	**10**	**0**	**2**	**12**		**5.23**	**ppb**
+10ppb		9.9464	0.0612	4	10	0	2	12		9.95	ppb
+10ppb		10.1141	0.0621	4	10	0	2	12		10.11	ppb
+10ppb		**10.020**	**0.0616**	**4**	**10**	**0**	**2**	**12**		**10.02**	**ppb**
+25ppb		23.6719	0.1309	5	10	0	2	12		23.67	ppb
+25ppb		24.4054	0.1344	5	10	0	2	12		24.41	ppb
+25ppb		**24.027**	**0.1326**	**5**	**10**	**0**	**2**	**12**		**24.03**	**ppb**
[illegible]		40.9094	0.2071	6	10	0	2	12		[illegible]	
[illegible]		39.9279	0.2031	6	10	0	2	12		[illegible]	ppb
+40ppb		**40.417**	**0.2051**	**6**	**10**	**0**	**2**			**40.42**	**ppb**
+100ppb	*X*	*118.46*	*0.3938*	*7*	*10*	*0*	*2*	*12*		*118.46*	*ppb*
+100ppb		19.3669	0.1099	7	2	8	2	12	5.000000	96.83	ppb
+100ppb		21.1513	0.1187	7	2	8	2	12	5.000000	105.76	ppb
+100ppb		**20.255**	**0.1143**	**7**	**2**	**8**	**2**	**12**	**5.00000**	[illegible]	

Automatically excluded as concentration exceeded the upper limit.

Auto dilution and reanalysis were conducted with a smaller injection volume.

Auto dilution rate

■ Calibration Curves

Fig. 2 and Fig. 3 show the calibration curves of the respective elements, where the standard value was used as the upper limit.

■ Measurement Results of Simulation Samples

Table 3 and Table 4 show the measurement results of the simulation samples spiked with Sb and Ge in the range of 1/10 to 2 times the standard values. Satisfactory results were obtained, as the recovery rates were 100 ± 10 % for both elements at all spiked concentrations.

The auto dilution and reanalysis function was used in the measurements of the simulation samples spiked with 2 times the standard values. Use of this function enables reanalysis with an automatically reduced sampled volume in cases where the sample concentration exceeds the set upper limit concentration. Because the sample injection volume in this experiment was 10 µL, auto dilution and reanalysis were possible with a maximum concentration of 5 times the standard value when using the minimum injection volume of 2 µL. Table 5 shows an example of the results of auto dilution and reanalysis.

Fig. 4 and Fig. 5 show the peak profiles obtained by measurement of the simulation samples of Sb and Ge, respectively. The profiles on the right side were obtained by auto dilution and reanalysis.

■ Conclusion

Satisfactory results of recovery rates of 100 ± 10 % were obtained in the range from 1/10 to 2 times the standard values for leaching of Sb and Ge.

Automatic generation of calibration curves and automatic dilution and reanalysis of samples that exceed the upper limit concentration are possible by using the auto dilution function and the auto dilution and reanalysis function of the autosampler. Because constant monitoring of the analysis results by the measurement technician is not necessary, even in case of multiple analyses of samples with concentration variations, labor saving and improved efficiency are possible.

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