Improved Detection of Arsenic, Antimony and Selenium Using the CETAC HGX-200 Hydride Generator with ICP-AES

Arsenic, antimony and selenium are noteworthy as being more difficult to detect than other elements by conventional pneumatic nebulization with inductively coupled plasma atomic emission spectrometry (ICP-AES). One option for improving As, Sb and Se detection by ICP-AES is the use of hydride generation.

An acidified aqueous sample containing arsenic, antimony and selenium can be mixed with a reducing agent such as sodium borohydride ($NaBH_4$). The general sequence of reactions is:

1. $NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_4 + NaCl + 8H^+$
2. $E^{m+} + 8H^+$ ad EH_n (g) + H_2 (g)

where E is the volatile hydride forming element. The species EH_n is then swept by the nebulizer gas to the ICP-AES for detection. Note that hydrogen gas (H_2) is generated as a by-product of the reaction.

The hydride generation reaction can be nearly 100% efficient, enabling greatly enhanced detection of As, Sb, and Se versus much less efficient conventional solution nebulization. The As, Sb, and Se are also separated from any non-hydride forming matrix components.

CETAC HGX-200 Hydride Generator

The CETAC HGX-200 Hydride Generator (Figure 1) is equipped with solution mixing blocks and a specialized gas-liquid separator (GLS) with a “frosted” glass post. This post provides a high surface area for release of volatile hydrides. The GLS also features a porous polytetrafluoroethylene (PTFE) membrane and a droplet separator for complete gas/liquid separation and reduction of signal noise.

An integrated gas flow meter allows improved control of the argon gas flow through the GLS; a second argon gas flow above the membrane helps transport any hydrides to the ICP.

Two peristaltic pumps (user provided) are recommended: one pump for sample and reagent addition and one pump to remove liquid waste from the GLS. One peristaltic pump with three or four channels may be used, but care must be taken to prevent liquid waste buildup in the GLS. A general experimental setup is given in Figure 2.

Important Notes

When using the HGX-200, the ICP-AES nebulizer gas (or carrier gas) is added to the gas port at the top of the gas-liquid separator. A separate mass flow controller is used to add the additional Ar gas after the PTFE membrane.

Dedicated reagent bottles ($NaBH_4$, acid) supplied with the HGX-200 are all equipped with porous filters in the lids to allow outgassing. This is especially important for the $NaBH_4$ solution, as the buildup of H_2 in a sealed bottle can cause it to explode.

The As, Sb and Se standard solution (100 μg/L) was prepared in 4% HNO_3. The sodium borohydride solution was 1% (w/v) $NaBH_4$ in 0.1 M NaOH (which acts as a stabilizing agent).

Figure 1. CETAC HGX-200 Hydride Generator

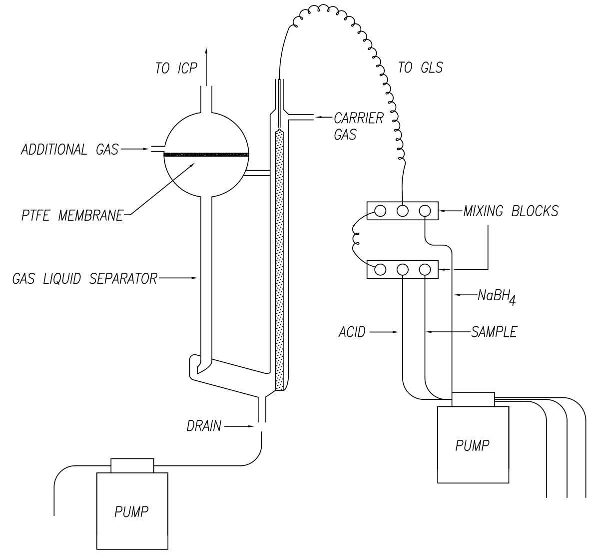

Figure 2. HGX-200 Experimental Setup

Operating Conditions

ICP-AES Instrument: Thermo iCAP 6500

Hydride Generator: CETAC HGX-200

Operating Parameters	**Pneumatic Nebulization**	**HGX-200**
RF Power	1150 W	1150 W
Coolant gas	14 L/min.	14 L/min.
Auxiliary gas	0.5 L/min.	0.5 L/min.
Nebulizer	glass concentric	NA
Spray chamber	cyclonic	NA
Solution(s) uptake	3.0 mL/min.	0.8 mL/min.
Carrier Ar gas	0.55 L/min.	0.35 L/min.
Additional Ar gas	NA	0.10 L/min.
Element viewing	axial	axial
Integration time	30 sec.	30 sec.

NA = Not Applicable

Results

A comparison of instrument detection limits (IDLs) for As, Sb and Se is given below. The IDLs are given in units of μg/L.

Element	Wavelength (nm)	Pneumatic Nebulization	HGX-200	IDL Improvement Factor
As	189.04	1.3	0.12	11
Sb	206.83	2.9	0.18	16
Se	196.09	3.3	0.15	22

The IDLs are based on 3 times the standard deviation of the reagent blank concentration. The IDL improvement factors show that detection of As, Sb and Se can be easily below 1 μg/L using hydride generation. Impurities in reagents and signal noise are the most likely limitations to further IDL reduction.