HGX-200 Technical Note

Enhanced Detection of Arsenic and Selenium Using the CETAC HGX-200 Hydride Generator with Quadrupole ICP-MS Detection

Introduction

The metalloids arsenic and selenium are noteworthy as being more difficult to detect than other elements by conventional pneumatic nebulization with quadrupole inductively coupled plasma mass spectrometry (ICP-MS) detection. Difficulties for detection of both elements include spectroscopic interferences and higher ionization energies. One option for improving As and Se detection by ICP-MS is the use of hydride generation.

An acidfied aqueous sample containing arsenic 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. $E^{m+} + 8H^+ \rightarrow EH_n\,(g) + H_2\,(g)$

where E is the volatile hydride forming element. The species EH_n is then swept by the nebulizer gas to the ICP-MS 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 and Se versus much less efficient conventional solution nebulization. The As and Se is also separated from any non-hydride forming matrix components.

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 droplet separator for complete gas/liquid separation and reduction of signal noise. An integrated gas flow meter allows the addition of a second argon gas flow after the PTFE membrane; this second gas enables the best optimization of washout time and further reduction of signal noise.

Two peristaltic pumps (user provided) are recommended: one pump for sample and reagent addition and one pump to remove liquid waste from the GLS. A general experimental setup is given in Figure 2.

Figure 1. HGX-200 Hydride Generator

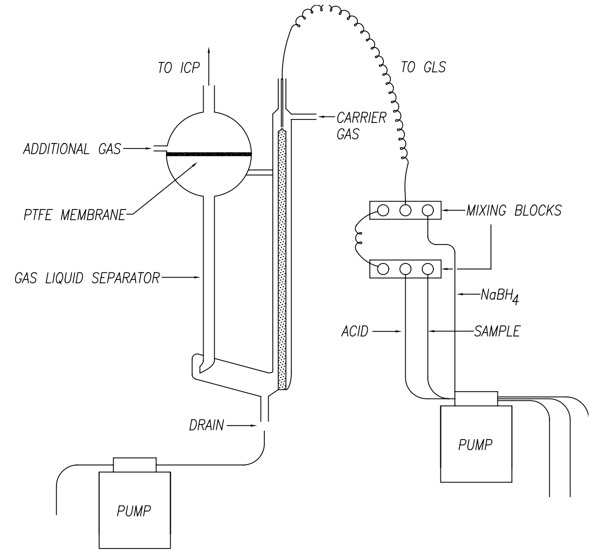

Figure 2. Experimental Setup

Operating Conditions

ICP-MS Instrument: PerkinElmer ELAN 9000
Hydride Generator: CETAC HGX-200

	Pneumatic Nebulization	CETAC HGX-200
RF power	1400 W	1400 W
Nebulizer	crossflow	NA
Spray chamber	cylindrical	NA
Solution(s) uptake	2.2 mL/min	1.5 mL/min
Nebulizer gas	0.70 L/min	0.72 L/min
Additional Ar gas	NA	0.28 L/min
Integration time	3 s	3 s
Replicates	20	20

NA = not applicable

Important Notes

When using the HGX-200, the nebulizer gas was added to the gas port after the PTFE membrane. A separate mass flow controller was used to add the 0.28 L/min additional Ar gas through the GLS (just above the “frosted” glass post). Dedicated reagent bottles ($NaBH_4$, acid) that are 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 and Se standard solution (100 ug/L) was in 1% HNO_3 and mixed with a 5% HNO_3 for further acidification to help drive the hydride reaction. The sodium borohydride solution was 1% $NaBH_4$ with 0.1 M NaOH (which acts as a stabilizing agent).

Arsenic signal was measured at m/z = 75, the only isotope for that element. The major isotopes for Se are at m/z = 78 (23.8% abundance) and m/z = 80 (49.6% abundance), but both of these isotopes are overlapped by argon dimer interferences ($^{38}Ar^{40}Ar^{+}$, $^{40}Ar^{40}Ar^{+}$). Selenium signal was thus measured at m/z = 77 (7.6% abundance) and m/z = 82 (8.7% abundance).

Results

A comparison of instrument detection limits (IDLs) for As and Se is given in Table 1 below; the IDLs are given in units of ng/L.

Element	m/z	Pneumatic Nebulization	HGX-200	Improvement Factor
As	75	4	0.8	4
Se	77	70	4	17
Se	82	70	4	17

The IDLs are based on 3 times the standard deviation of the reagent blank concentration. The improvement factors show that detection limits can be significantly improved, particularly for the lower abundant isotopes used for Se detection. Impurities in reagents and signal noise are the most likely limitations to further IDL reduction.