Hydride Generation for the Determination of As, Sb, Se and Bi Using the Teledyne Leeman Lab's Prodigy 7 ICP-OES

Introduction

The combination of hydride generation with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is an extremely effective and inexpensive sample introduction technique. Because hydride forming elements have high transport efficiency (separation of the hydride from the sample matrix) as well as efficient atomization/excitation, greater sensitivity and thus lower detection limits can be achieved in comparison to conventional ICP nebulization. To produce the hydrides, a sample that has been diluted in an acid solution is mixed with a reducing agent (usually a solution of sodium borohydride in dilute sodium hydroxide). The reaction of sodium borohydride with the acid produces hydrogen which subsequently reduces the analyte ions to hydrides, which are gaseous at ambient temperature. An example of the hydride generation reaction is given below:

$$6BH_4^-{}_{(aq)} + As^{3+}{}_{(aq)} + 3H^+{}_{(aq)} \rightarrow 3B_2H_{6(aq)} + 3H_{2(g)} + AsH_{3(g)}$$

This application note will use hydride generation in combination with the Teledyne Leeman Labs Prodigy7 Inductively Coupled Plasma (ICP) Spectrometer equipped with a dual-view torch. Experimental conditions were optimized for the determination of As, Sb, Se and Bi.

Instrument

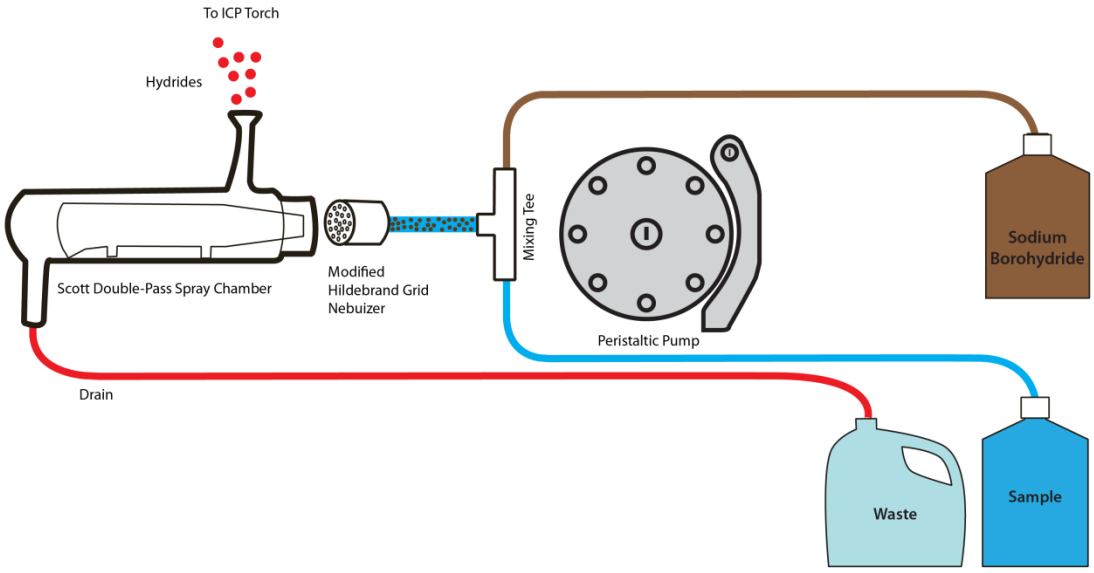
The Prodigy7 is a compact bench-top simultaneous optical emission instrument featuring a 500 mm focal length Echelle optical system coupled with a mega-pixel large format CMOS detector. At 28 mm^2, the active area of the CMOS detector is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows the Prodigy7 to achieve higher optical resolution than other solid-state detector based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm permitting measurement over the entire ICP spectrum in a single reading without sacrificing wavelength range or resolution. This detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than six orders of magnitude. The Prodigy7's 40.68 MHz rugged, water cooled, free-running RF Generator, allows it to handle the most difficult sample matrices, as well as common organic solvents.

For this application note the sample introduction system consisted of the following:

1. Four-channel peristaltic pump
2. Scott Double-Pass spray chamber
3. Demountable quartz torch
4. Modified Hildebrand Grid nebulizer

The modified Hildebrand Grid nebulizer was used as an efficient hydride generator. The Prodigy7's four-channel peristaltic pump was used to deliver both the sample and a sodium borohydride solution to a tee junction where they were mixed and then allowed to flow over the inner platinum screen. The design of the modified Hildebrand Grid nebulizer results in an efficient liquid-gas separator which facilitates the release of the hydride species from the sample solution. A diagram of the sample introduction system is shown in Figure 1.

Figure 1 Hydride Generation Sample Introduction Diagram



Method

Sample Preparation

The technique was applied to the analysis of the hydride forming elements in standard reference waters (NIST 1643f and 1640a) obtained from the National Institute of Standards and Technology (NIST). Sodium borohydride ($NaBH_4$) was used as the reducing agent to produce gaseous hydrides, and was freshly prepared at a concentration of 2% (w/v) in 0.01% of sodium hydroxide.

To guarantee the efficient hydride generation reduction reaction, analytes have to be pre-reduced to the lower oxidation states prior to analysis. As and Sb were pre-reduced with 5% KI/ascorbic acid and concentrated HCl. Se and Bi were pre-reduced with concentrated HCl. The pre-reduction procedures are summarized in the Table I.

Table I Pre-Reduction Procedures		
Element	**Oxidation State**	**Pre-reduction Procedures**
As	V → III	0.2% KI/ascorbic acid/2M HCl → >30 minutes at room temp
Sb	V → III	0.2% KI/ascorbic acid/2M HCl → >30 minutes at room temp
Se	VI → IV	6M HCl → 90°C heat for 60 minutes
Bi	V → III	6M HCl → 90°C heat for 60 minutes

Calibration Standards

Calibration standards were made from single-element stock solutions (VHG Labs). Standards and blanks were treated in the same manner as the samples and were carried through the pre-reduction procedures described above. Concentrations of the calibration standards are listed in Table II.

Table II Calibration Standards, ppb		
Element	**STD1 (ppb)**	**STD2 (ppb)**
As, Sb	0	200
Se, Bi	0	200

Instrument Operating Conditions

The Prodigy7 operating parameters are listed in Table III.

Table III Instrument Operating Parameters	
Instrument*	
RF Power	1.20 kW
Coolant Flow	15 L/min
Auxiliary Flow	1.0 L/min
Nebulizer Pressure	1.0 L/min
Uptake Rate**	25 rpm
Sample Introduction	
Nebulizer Type	Hildebrand Grid
Spray Chamber	Scott Double-Pass
Torch	Quartz Demountable
Injector	2.5 mm bore
Uptake Tubing Sample	Inner diameter 0.76 mm
Uptake Tubing $NaBH_4$	Inner diameter 0.51 mm
Drain Tubing	Inner diameter 1.5 mm
Sample	
Integration Time	30 seconds

* The analytical viewing zone was set by using a 200 ppb As standard. The optimum viewing position is automatically selected by the Prodigy7's Salsa software.
** Flow rate (determined by tubing diameter) for sample and borohydride solution is different.
*** Contact Teledyne Leeman Labs for the appropriate sample introduction component part number.

Wavelength Parameters

The Prodigy7 typically uses a 29 pixel wide subarray, centered on the wavelength of interest, to collect data for each analyte. However, subarrays can be up to 57 pixels in width if needed. The analytical peaks and background correction points are defined in each subarray with pixel position and width values. In Table IV below, wavelength and background correction position data are listed. Where possible, two wavelengths were used for each element. All data in the subarrays is collected simultaneously and all pixel data are saved, permitting recalculation of results at a later time.

Table IV Wavelength Parameters

Element	Wavelength, nm	Left Background Correction		Right Background Correction	
		Position	Width	Position	Width
As	189.042	2	2	27	2
	197.262	2	2	27	2
Sb	206.833	2	2	27	2
	217.581	2	2	27	2
Se	196.090	2	2	27	2
Bi	223.061	2	2	27	2

Figure 2 illustrates the element parameters for the Se 196.090 nm line as an example. The left and right background regions begin at pixel positions 2 and 27, respectively. The width of both positions is 2 pixels. The analytical region of interest, where the "Se" peak is found, begins at pixel position 13 and has a width of 5 pixels. Figure 3 illustrates a typical calibration curve.

Figure 2 Se 196.090 nm Wavelength Parameter Example

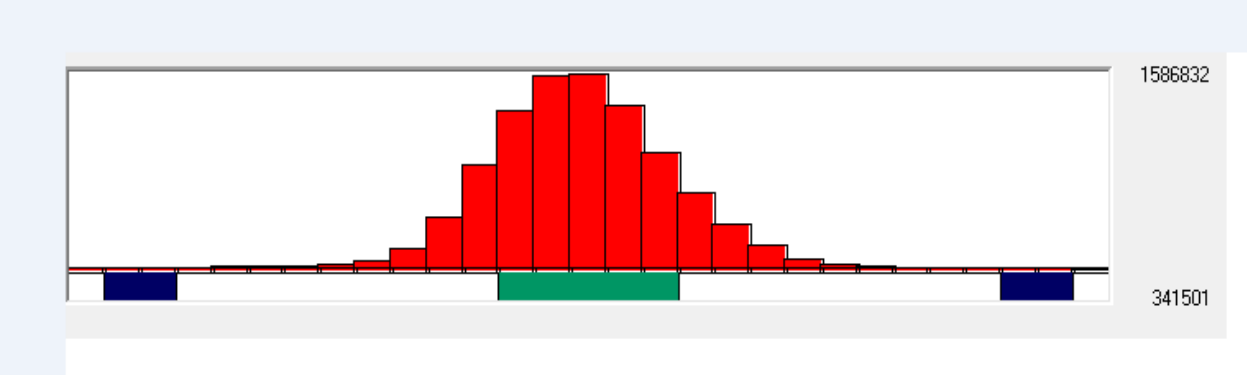
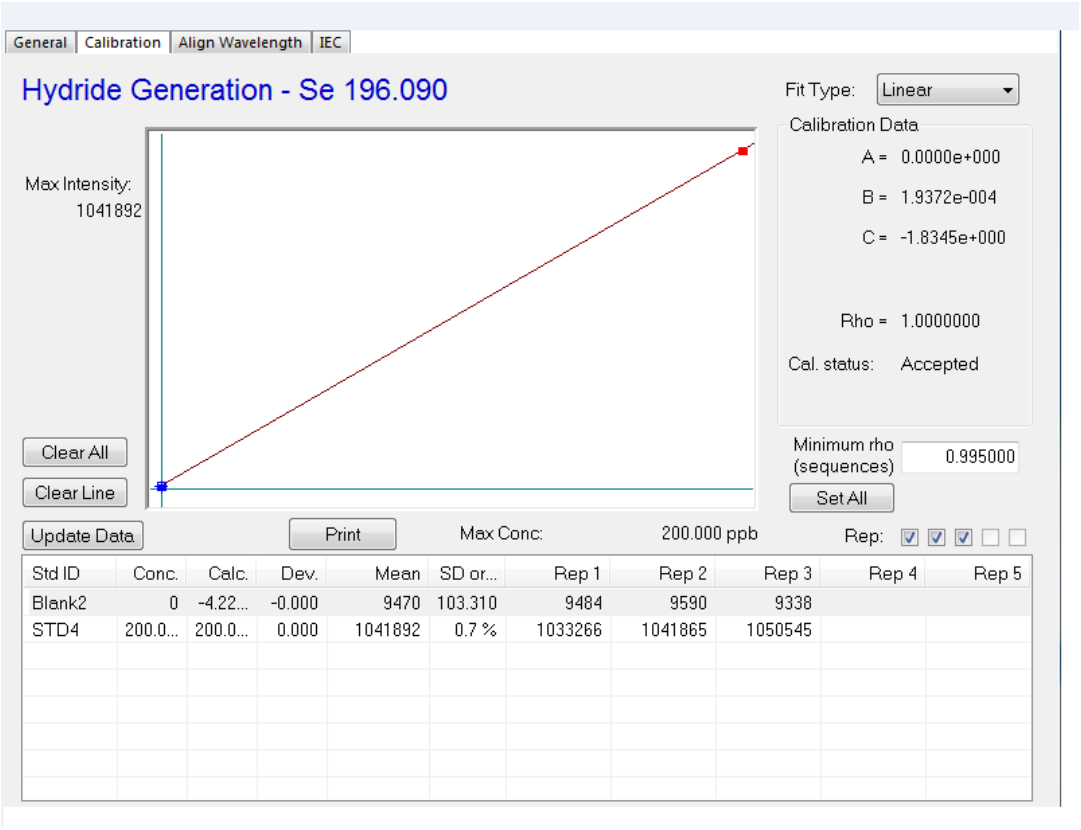


Figure 3 Se 196.090 nm Calibration Curve



Results

After igniting the plasma and allowing a 15 minute warm-up period, the Prodigy7 was calibrated. Once the calibration was complete, a 40 ppb QC standard was analyzed with an acceptance criteria of ±10%. Upon successful completion of the QC standard analysis, the reference samples were analyzed.

Results from the analysis are shown in Table V and Table VI. Results for each reference sample are reported in units of parts per billion (ppb) and are corrected for the 1:2.5 dilution. Results are also presented for the recoveries of the 10 ppb spikes, along with %RSD values for the measured spike concentrations. The values measured by the Prodigy7 are contained in the column labeled “Found ppb” while the certified values are in the column labeled “Certified ppb”.

Table V NIST 1643f					
Element	Wavelength (nm)	Certified (ppb)	Found (ppb)	Spike Recovery, %	RSD %
As	189.042	57.42 ± 0.38	54.42	92.9	0.7
As	197.262		54.34	87.3	0.1
Sb	206.833	55.45 ± 0.40	53.54	88.1	0.1
Sb	217.581		53.33	89.2	0.2
Se	196.090	11.700 ± 0.081	11.473	96.0	0.4
Bi	223.061	12.62 ± 0.11	11.90	87.7	1.4

Table VI NIST 1640a					
Element	Wavelength (nm)	Certified (ppb)	Found (ppb)	Spike Recovery, %	RSD %
As	189.042	8.075 ± 0.070	8.138	95.4	0.7
As	197.262		8.563	96.6	0.5
Sb	206.833	5.105 ± 0.046	4.599	97.0	0.5
Sb	217.581		4.447	98.0	1.5
Se	196.090	20.13 ± 0.17	20.30	93.3	0.6
Bi	223.061	-	-	-	-

Detection Limits

Detection limits were calculated based on three times the standard deviation of 10 replicate measurements of the blank solution that was taken through the pre-reduction procedures. This was repeated three times for each element and the average was calculated. Results for the detection limit study are listed in Table VII.

Table VII Detection Limits (DLs)		
Element	Wavelength (nm)	DL (ppb)
As	189.042	0.4
As	197.262	0.4
Sb	206.833	0.5
Sb	217.581	0.4
Se	196.090	0.3
Bi	223.061	0.3

Conclusion

The results presented in this application note demonstrate that the use of hydride generation as a method of sample introduction permits the trace analysis of hydride forming elements that is not typically possible using conventional ICP nebulization. Spike recovery data was within an acceptable range and indicated that the method is free from matrix interferences. Combining the Prodigy7 ICP with hydride generation exhibited high sensitivity and low detection limits making it a simple and accurate means to determine As, Sb, Se and Bi.