

Analysis of Hydride Forming Elements with the Thermo Scientific iCAP 7000 Plus Series ICP-OES and the Basic Hydride Generator Kit

Nora Bartsch, Application Specialist,
Thermo Fisher Scientific,
Bremen, Germany

Key Words

Accuracy, Hydride, Precision, Trace Elemental

Goal

This application note demonstrates the ability of the Thermo Scientific iCAP 7000 Plus Series ICP-OES to determine hydride forming elements with the Basic Hydride Generator Kit, which significantly improves detection capability, precision and accuracy for arsenic, bismuth, antimony, selenium and mercury compared to standard ICP-OES sample introduction.

Introduction

The analysis of arsenic, bismuth, antimony, selenium and mercury in environmental, biological and food samples is common place, and is driven by regulations which require lower limits of detection year upon year to ensure that contamination by toxic substances is kept to a minimum. The main technique used for the general elemental analysis of these types of samples (along with AA and ICP-MS) is ICP-OES.



The analytical performance required for these elements is often difficult to achieve using a standard sample introduction setup (nebulizer, spray chamber, etc.), as some of these analytes tend to suffer from spectral interference and poor sensitivity because the major emission lines for these analytes lie in complex regions of the spectrum and often produce poor sensitivity due to the high excitation energies of the elements.

Furthermore, many of the primary wavelengths are towards the UV end of the spectrum which undergoes a higher degree of transmission loss through absorption. This serves to further reduce sensitivity. The analytical performance of these elements can be enhanced by the use of a hydride generation sample introduction system. This is due to the chemical properties of these elements, which enable the formation of volatile gaseous hydrides when reacted with reducing agents such as sodium borohydride.

An example of the hydride generation reaction is given below, in this case arsenic is the hydride-forming element:



For the hydride-forming reaction to take place the hydride-forming element must be present in the test solution in the correct oxidation state (Table 1). If this is not the case then a pre-reduction will have to be carried out.

For online hydride generation with the standard sample introduction assembly an additional tube is added to the sample pump to add sodium borohydride solution to an acidified sample via a T piece prior to the nebulizer.

The nebulizer and spray chamber act as a gas liquid separator preferentially aspirating the hydride gases, this leads to an improvement in the sensitivity and detection limits.

Table 1. Common oxidation states of the hydride forming elements and oxidation states required for the hydride reaction to take place.

| Element | Most common oxidation state | Oxidation state needed for the reaction |
|----------|-----------------------------|---|
| Arsenic | As (V) | As (III) |
| Antimony | Sb (V) | Sb (III) |
| Bismuth | Bi (III) | Bi (III) |
| Mercury | Hg (II) | Hg (II) |
| Selenium | Se (VI) | Se (IV) |

Instrumentation

For the analysis of hydride forming elements with the Basic Hydride Generator Kit the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo and Radial instruments (Figure 1) were used. The sample introduction kit components and the instrument parameters used are listed in Table 5.



Figure 1. The iCAP 7000 Plus Series ICP-OES.

Sample preparation

Pre-reduction techniques used during sample preparation are summarized in Table 2 and the preparation of the calibration standard is detailed in Table 3. Intermediate standards were prepared from single element solutions (1000 mg·l⁻¹, SPEX CertiPrep Group). The individual solutions were made with 18 MΩ ultra-pure water and hydrochloric acid (trace metal grade 32-36%, Fisher Chemical) as well as with potassium iodide (≥99.5%, Sigma Aldrich) and ascorbic acid (ACS grade, Merck). The reducing agent was prepared from sodium borohydride powder (99%, ACROS organics™) and sodium hydroxide pellets (ACS grade, Merck).

Table 2. Pre-reduction techniques used for sample preparation.

| Element | Reagents | Time |
|----------|--|-----------------------------|
| Arsenic | 1% potassium iodide and ascorbic acid in 10% hydrochloric acid | 5 hours at room temperature |
| Antimony | 1% potassium iodide and ascorbic acid in 10% hydrochloric acid | 5 hours at room temperature |
| Bismuth | No pre-reduction required | - |
| Mercury | No pre-reduction required | - |
| Selenium | 6 molar hydrochloric acid | Boil the sample 15 minutes |

Table 3. Standard preparation methods.

| Element | Intermediate standard (mg·l ⁻¹) | Calibration standard |
|----------|--|--|
| Arsenic | 100 µl of 1000 mg·l ⁻¹ As in to 100 ml of 1% potassium iodide and ascorbic acid in 10% hydrochloric acid and left for 5 hours at room temperature | Intermediate standard diluted to the required concentrations with 1% potassium iodide and ascorbic acid in 10% hydrochloric acid |
| Antimony | 100 µl of 1000 mg·l ⁻¹ Sb in to 100 ml of 1% potassium iodide and ascorbic acid in 10% hydrochloric acid and left for 5 hours at room temperature | Intermediate standard diluted to the required concentrations with 1% potassium iodide and ascorbic acid in 10% hydrochloric acid |
| Bismuth | 100 µl of 1000 mg·l ⁻¹ Bi in to 100 ml of 10% hydrochloric acid | Intermediate standard diluted to the required concentrations with 10% hydrochloric acid |
| Mercury | 100 µl of 1000 mg·l ⁻¹ Hg in to 100 ml of 10% hydrochloric acid | Intermediate standard diluted to the required concentrations with 10% hydrochloric acid |
| Selenium | 100 µl of 1000 mg·l ⁻¹ Se boiled for 10 minutes in 6 molar hydrochloric acid and made up to 100 ml | Intermediate standard diluted to the required concentration with 10% hydrochloric acid |

Table 4. Calibration concentration in µg·l⁻¹ used on iCAP 7400 ICP-OES Radial with Basic Hydride Generator Kit.

| Element | View | Blank | Standard 1 | Standard 2 | Standard 3 |
|----------|--------|-------|------------|------------|------------|
| Arsenic | Radial | 0 | 0.5 | 5 | 10 |
| Antimony | Radial | 0 | 0.5 | 5 | 10 |
| Bismuth | Radial | 0 | 0.5 | 5 | 10 |
| Mercury | Radial | 0 | 0.5 | 5 | 10 |
| Selenium | Radial | 0 | 0.5 | 5 | 10 |

Method development and analysis

Various instrument parameters were applied to reach stable plasma conditions. A high nebulizer gas flow was used to allow the sample to penetrate the plasma efficiently and to reduce stabilization time. The parameters used for the analysis are shown in Table 5. The concentrations of reductant and acid in the sample was investigated, and the optimum concentration for the elements investigated was 10% hydrochloric acid for the samples and 0.5% sodium borohydride stabilized with 0.5% sodium hydroxide as the reducing agent.

A 10 $\mu\text{g}\cdot\text{l}^{-1}$ solution of each element was used during the optimization and analysis. A detection limit study was carried out by analyzing the calibration blank three times with ten replicates and multiplying the standard deviation of this analysis by three. To ensure freedom from interferences, the subarray plots were examined and background correction points were set appropriately. In addition a calibration was performed on the Radial instrument using the concentrations shown in Table 4.

Table 5. Sample introduction kit components and instrument parameters.

| Parameter | Setting | |
|-----------------------|------------------------------|-------------------|
| Pump tubing | Sample: Tygon™ white/white | |
| | Drain: Tygon™ blue/yellow | |
| | Reagent: Tygon™ orange/green | |
| Pump speed | 50 rpm | |
| Spray chamber | Baffled cyclonic | |
| Nebulizer | V-groove | |
| Nebulizer gas flow | 0.50 L min ⁻¹ | |
| Auxiliary gas flow | 0.5 L min ⁻¹ | |
| Coolant gas flow | 12 L min ⁻¹ | |
| RF power | 1300 W | |
| Center tube | Duo instrument | Radial instrument |
| | 2.0 mm | 1.5 mm |
| Radial viewing height | N/A | 10 mm |
| Exposure time | UV 15 s, Vis 15 s | UV 15 s, Vis 15 s |

Results

The results displayed in Table 6 show that the use of the Basic Hydride Generator Kit improves detection limits compared to the standard sample introduction system. Even though the sensitivity is slightly lower than the dedicated hydride generation sample introduction system, the Basic Hydride Generator Kit is a good and cost efficient option for the analysis of hydride forming elements.

The results also show that both, the iCAP 7400 Duo as well as the iCAP 7400 Radial instrument can detect sub ppb concentrations of hydride forming elements. Figure 2 shows the difference of detection limits of the inlet systems and the instruments. The linearity of the calibration curves is good. An example calibration curve for Bi 223.061 nm is shown in Figure 3 with R² value of 1.000.

Table 6: Instrument detection limits in $\mu\text{g}\cdot\text{l}^{-1}$ with different sample introduction systems on the Thermo Scientific iCAP ICP-OES Duo and Radial instrument

| Element and wavelength (nm) | Radial Instrument with Basic Hydride Generator Kit | Duo instrument with Basic Hydride Generator Kit | Duo instrument with integrated hydride generation accessory | Duo instrument with Standard sample introduction kit |
|-----------------------------|--|---|---|--|
| As 189.042 | 1.40 | 0.20 | 0.07 | 2.9 |
| Sb 206.833 | 0.62 | 0.21 | 0.07 | 3.3 |
| Bi 223.061 | 0.78 | 0.16 | 0.08 | 3.8 |
| Hg 184.950 | 0.13 | 0.06 | 0.013 | 0.14 |
| Se 196.090 | 0.64 | 0.20 | 0.12 | 3.1 |

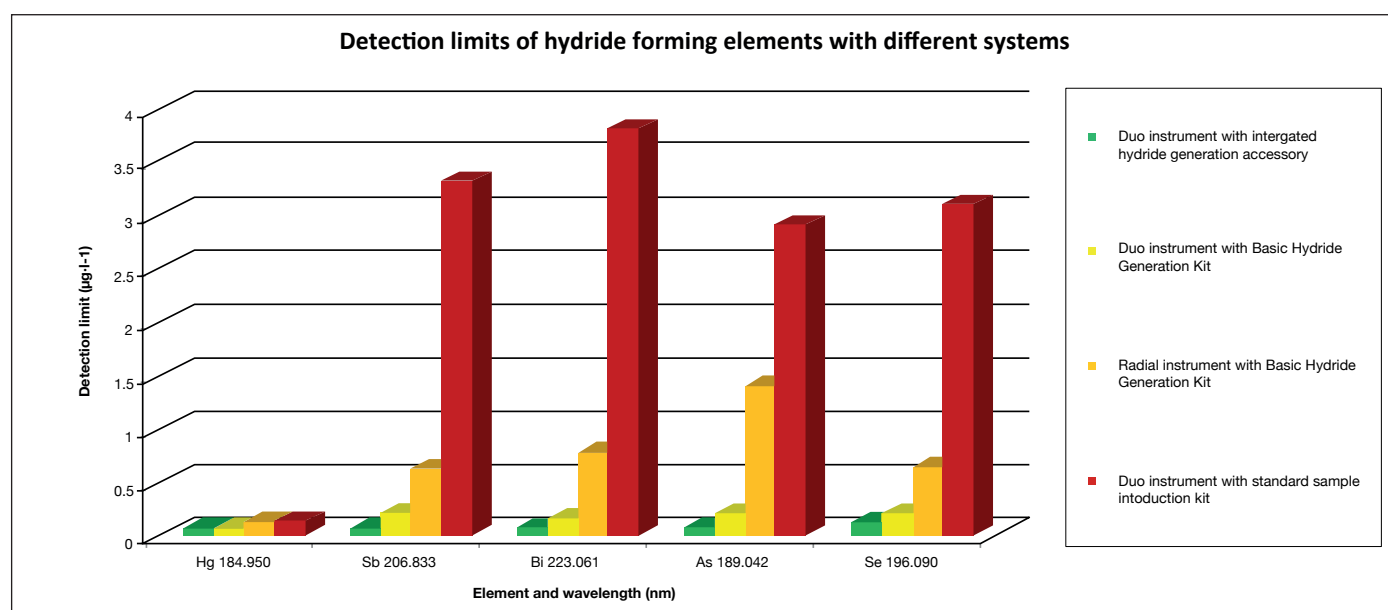


Figure 2. Detection limits of hydride forming elements with different systems.

Conclusion

With the simple addition of the Basic Hydride Generator Kit, the lower working range of the iCAP 7400 ICP-OES can be extended to sub $\mu\text{g}\cdot\text{l}^{-1}$ levels for the hydride-forming elements. It is an easy and cost efficient solution for laboratories which occasionally require improved detection limits for hydride forming elements.

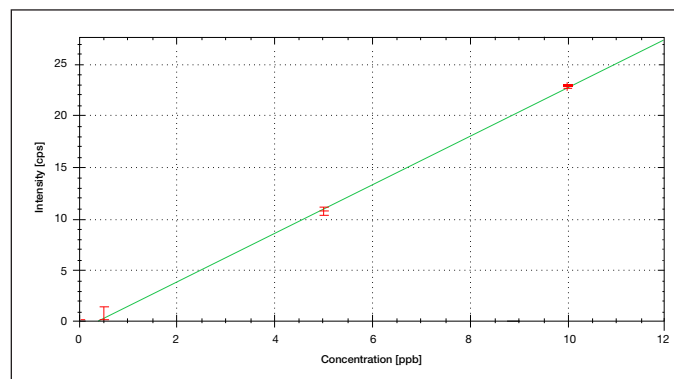


Figure 3. Calibration curve for Bi 223.061 nm.

Find out more at thermofisher.com/ICP-OES