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## Analysis of hydride-forming elements using ICP-OES

### Authors

Tomoko Vincent and Bhagyesh Surekar

Thermo Fisher Scientific, Bremen, Germany

### Keywords

Accuracy, high sensitivity, hydride, ICP-OES, robust, trace analysis

### Goal

To demonstrate the performance of the Thermo Scientific™ iCAP™ PRO Series ICP-OES equipped with two different hydride generation sample introduction systems. These systems will improve sensitivity of hydride-forming elements, such as arsenic, bismuth, antimony, selenium, and mercury, over that provided by a standard sample introduction system.

### Introduction

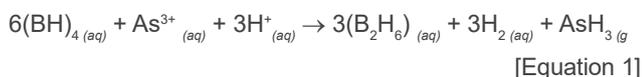
The analysis of antimony, arsenic, bismuth, mercury, and selenium in environmental, biological, and food samples is routine and is typically driven by regulations that require low limits of detection, ensuring that contamination by toxic substances is kept to a minimum. For example, the United States Environmental Protection Agency (EPA) regulates the maximum contamination levels allowed in drinking water to protect public health (Table 1).<sup>1</sup> These specified elements can cause negative health effects with long exposure, it is important to monitor them with accurate analysis techniques.

**Table 1. Maximum contaminant level ( $\mu\text{g}\cdot\text{L}^{-1}$ ) and the main impact on health as detailed in the national primary drinking water regulations by the EPA**

Element	Maximum contaminant level	Health effect from long term exposure
Antimony	6	Increase in blood cholesterol
Arsenic	10	Skin damage
Mercury	2	Kidney damage
Selenium	50	Hair or fingernail loss

Inductively coupled plasma atomic or optical emission spectroscopy (ICP-OES) is a common technique for trace element analysis. The analytical performance required for some elements is challenging to achieve using an ICP-OES with a standard sample introduction configuration (nebulizer, spray chamber, etc.). One such group of elements is the hydride-forming elements, which tend to emit towards the UV end of the spectrum; these wavelengths suffer a higher degree of transmission loss through absorption, further reducing sensitivity. The use of a hydride generation sample introduction system has been shown to improve sensitivity when analyzing hydride-forming elements by ICP-OES.<sup>2</sup> 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 2). If this is not the case, then a pre-reduction reaction will have to be carried out.

**Table 2. 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)

## Experimental

For the analysis of the hydride-forming elements, two hydride-forming sample introduction systems were used—the basic and integrated hydride generator kits were coupled with the iCAP PRO Series ICP-OES instruments. The details of the sample introduction kits and the instrument parameters used are listed in Table 3.

**Table 3. iCAP PRO Series ICP-OES Duo instrument parameters**

Parameter	Integrated hydride generation accessory (iCAP PRO XP ICP-OES and iCAP PRO XPS ICP-OES)	Basic hydride kit (iCAP PRO ICP-OES and iCAP PRO X ICP-OES)
Spray chamber	-	Cyclonic spray chamber
Nebulizer	-	Glass concentric nebulizer
Pump tubing	Sample: Tygon™ green/green i.d., 1.85 mm	Sample: Tygon™ orange/yellow i.d., 0.51 mm
	Drain: Tygon™ black/white i.d., 3.17 mm	Drain: Tygon™ green i.d., 1.85 mm
	Reagent: Tygon™ black/black i.d., 0.76 mm	Reagent: Tygon™ orange/yellow i.d., 0.51 mm
	Acid: Tygon™ orange/yellow i.d., 0.51 mm	-
Pump speed	40 rpm	
Nebulizer gas flow	0.45 L·min <sup>-1</sup>	
Auxiliary gas flow	0.5 L·min <sup>-1</sup>	
Coolant gas flow	12.5 L·min <sup>-1</sup>	
RF power	1,350 W	

(continued)

**Table 3 contd. iCAP PRO Series ICP-OES Duo instrument parameters**

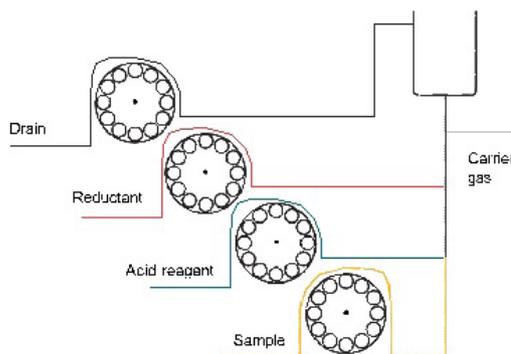
Center tube	2.0 mm	
Exposure time	eUV 10 s, iFR 10 s	
Total analysis time	120 s, including uptake and wash	
Sample volume	12 mL	5 mL

The basic hydride generation kit simply introduces a reducing solution and acidified sample solutions containing 3.6 w/w % HCl via a T-piece connector using three channels of the peristaltic pump of the Thermo Scientific™ iCAP PRO ICP-OES or the iCAP PRO X ICP-OES to the nebulizer. This system has the advantage of allowing additional non-hydride-forming elements to be analyzed simultaneously along with the hydride-forming elements.

The integrated hydride generation kit uses four channels of the peristaltic pump of the iCAP PRO XP ICP-OES or the iCAP PRO XPS ICP-OES. The hydride-forming reaction takes place in a dedicated gas liquid separator. This allows the gaseous product from the hydride-forming reaction [Equation 1] to be separated and introduced into the ICP-OES system directly using argon carrier gas (nebulizer gas) (Figures 1 and 2).



**Figure 1. iCAP PRO XP ICP-OES or iCAP PRO XPS ICP-OES coupled with an integrated hydride generation kit**



**Figure 2. Schematic of pump tube allocation of integrated hydride generation kit**

For automation of the sample introduction process, a Teledyne™ CETAC™ ASX-560 autosampler (Omaha, NE, USA) was used.

## Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to create LabBooks for sample analysis, data acquisition, processing, and reporting. The intuitive wavelength selection tool of the Qtegra ISDS Software, along with inspection of subarray plots and full frame images, was used to select interference-free wavelengths in standard solutions. In addition, the flexibility of the Qtegra ISDS Software allowed for a customized analysis method to be created by selecting the eUV mode for the ultraviolet wavelength range for the sample analysis.

## Sample preparation

Pre-reduction techniques used during sample preparation are summarized in Table 4, and the preparation of the calibration standards is detailed in Table 5. Intermediate standards were prepared from single element solutions (1,000 mg·L<sup>-1</sup>, SPEX™ CertiPrep™, Metuchen, NJ, USA).

The individual solutions were prepared using a mixture of 3.6 w/w % hydrochloric acid (TraceMetal™ grade, 32-36%, Fisher Chemical™), 1 w/v % potassium iodide (>99.5%, Merck) and 1 w/v % ascorbic acid (ACS grade, Merck). Acid reagent used in the study is 3.6 w/w % hydrochloric acid (HCl) and reducing agent used is 0.5 w/v % sodium borohydride (NaBH<sub>4</sub>) stabilized in the 0.5 w/v % sodium hydroxide (NaOH) solution.

**Table 4. Pre-reduction techniques used for sample preparation**

Element	Reagents	Preparation condition
Arsenic/ Antimony	1 w/v % potassium iodide and ascorbic acid in 3.6 w/w % HCl	5 hours at room temperature
Bismuth/ Mercury	No pre-reduction required	N/A
Selenium	18 w/w % HCl	Boiled for 15 minutes

**Table 5. Detail of standard preparation methods**

Element	Intermediate standard (mg·L <sup>-1</sup> )	Calibration standard matrix solutions
Arsenic	100 µL of 1,000 mg·L <sup>-1</sup> As in 100 mL of 1% potassium iodide and ascorbic acid in 3.6 w/w % HCl and left for 5 hours at room temperature	Intermediate standard diluted to the required concentrations with 1 w/v % potassium iodide and ascorbic acid in 3.6 w/w % HCl
Antimony	100 µL of 1,000 mg·L <sup>-1</sup> Sb in 100 mL of 1% potassium iodide and ascorbic acid in 3.6 w/w % HCl and left for 5 hours at room temperature	
Bismuth	100 µL of 1,000 mg·L <sup>-1</sup> Bi in 100 mL of 3.6 w/w % HCl	Intermediate standard diluted to the required concentrations with 3.6 w/w % HCl
Mercury	100 µL of 1,000 mg·L <sup>-1</sup> Hg in 100 mL of 3.6 w/w % HCl	
Selenium	100 µL of 1,000 mg·L <sup>-1</sup> Se boiled for 10 minutes in 18 w/w % HCl and made up to 100 mL	

The calibration standard matrix solutions (Table 5) were used to prepare the standards to final concentrations ranging from 0 to 10 µg·L<sup>-1</sup> (Table 6).

**Table 6. Detail of calibration standard concentration**

	Basic hydride generation kit (µg·L <sup>-1</sup> )	Integrated hydride generation kit (µg·L <sup>-1</sup> )
Blank	0	0
Standard-1	2.5	0.1
Standard-2	5	0.5
Standard-3	10	1
Standard-4	-	5
Standard-5	-	10

## Results and discussion

### Sensitivity (LOD), linearity, and accuracy

The wavelengths used for the analysis are shown in Table 6. The intelligent Full Range (iFR) analysis mode can measure wavelengths from 167.021 to 852.145 nm in one simultaneous measurement; this allows a significant reduction of the analysis times, this feature is available on iCAP PRO Series ICP-OES instruments. The enhanced eUV analysis mode can be used to further enhance sensitivity for

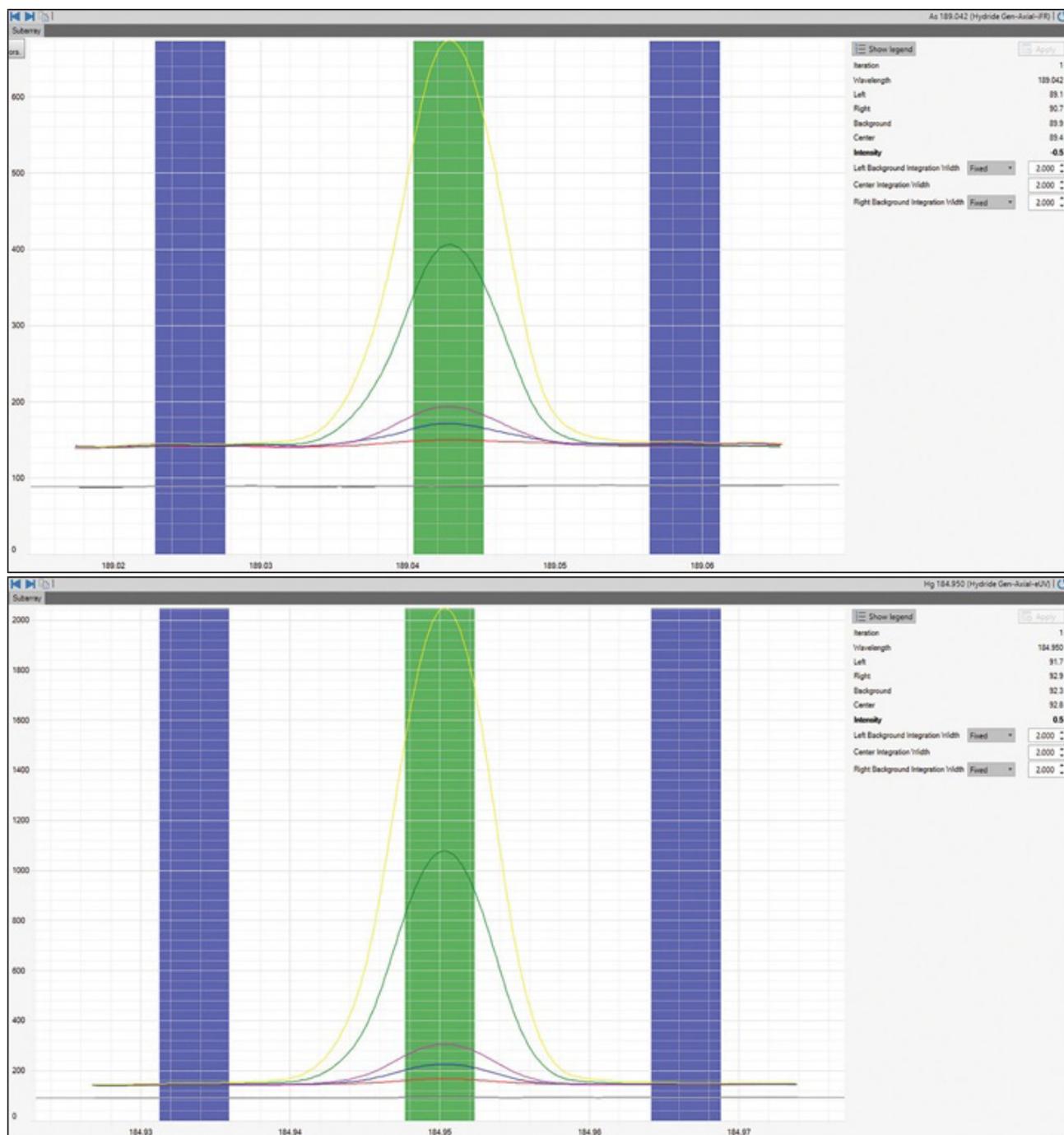
elements that fall in the UV wavelength range. This feature is available on the iCAP PRO XP ICP-OES and iCAP PRO XPS ICP-OES instruments.

Sensitivity and linearity of the target elements were determined from the analysis of the calibration blank and standards. The excellent linearity with coefficient of determination R<sup>2</sup> > 0.9987 over the calibration range 0.1 to 10 µg·L<sup>-1</sup> and limits of detection are shown in Table 7. The LODs were calculated as three times the standard deviation of ten replicate measurements of the calibration blank. The LODs for all the elements of interest are significantly below the expected levels required for environment safety allowance (Table 1). The detection performance of the two- hydride generation sample introduction systems is significantly improved compared to the performance of the standard sample introduction system<sup>3</sup>. The details are given in Table 7.

The subarray plot for arsenic and mercury shows interference-free analysis (Figure 3). The calibration plots (Figure 4) show excellent linearity of the range analyzed. The detection limits obtained for some elements such as arsenic (0.015 µg·L<sup>-1</sup>) using the integrated hydride generation kit are excellent, where the detection limit achieved for mercury is close to that of ICP-MS performance, with a BEC of 0.004 µg·L<sup>-1</sup> and an LOD of 0.004 µg·L<sup>-1</sup>. All measured analytes met the maximum allowance of the environment water criteria (Table 1).

**Table 7. Linearity (coefficient of determination, R<sup>2</sup>) and sensitivity (LOD as µg·L<sup>-1</sup>) data for five hydride-forming elements using three different introduction systems**

Analyte	Wavelength (nm)	iCAP PRO ICP-OES and iCAP PRO X ICP-OES equipped with basic hydride kit			iCAP PRO XP ICP-OES and iCAP PRO XPS ICP-OES equipped with integrated hydride kit			Standard sample introduction system <sup>3</sup>	
		Mode	R <sup>2</sup>	LOD (µg·L <sup>-1</sup> )	Mode	R <sup>2</sup>	LOD (µg·L <sup>-1</sup> )	Mode	LOD (µg·L <sup>-1</sup> )
Hg	184.950	Axial-iFR	0.9987	0.019	Axial-eUV	0.9998	0.004	Axial-eUV	1.1
As	189.042	Axial-iFR	0.9985	0.203	Axial-eUV	1.0000	0.015	Axial-eUV	1.8
Se	196.090	Axial-iFR	0.9999	0.252	Axial-eUV	0.9996	0.035	Axial-eUV	2.4
Sb	206.833	Axial-iFR	0.9989	0.210	Axial-iFR	0.9999	0.036	Axial-iFR	3
Bi	223.061	Axial-iFR	0.9987	0.096	Axial-iFR	0.9998	0.042	Axial-iFR	2.5



**Figure 3. Subarray window for As 189.042 nm and Hg 184.950 nm, indicating the peak (center), right and left background within the Qtegra ISDS Software**

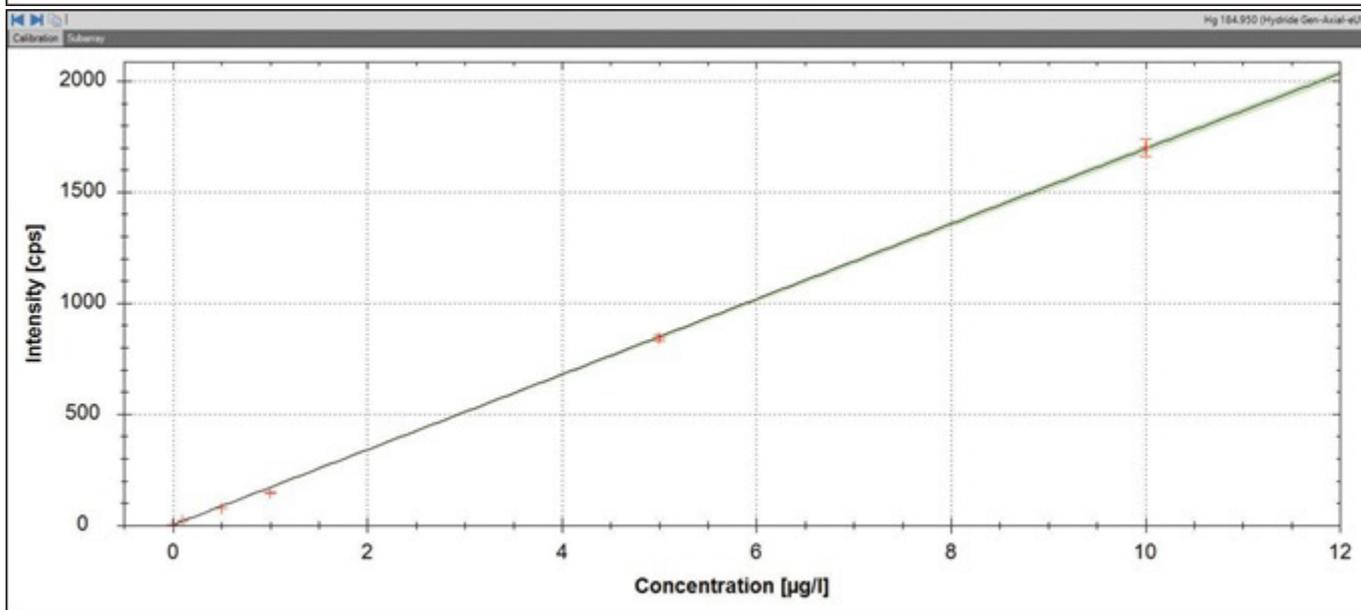
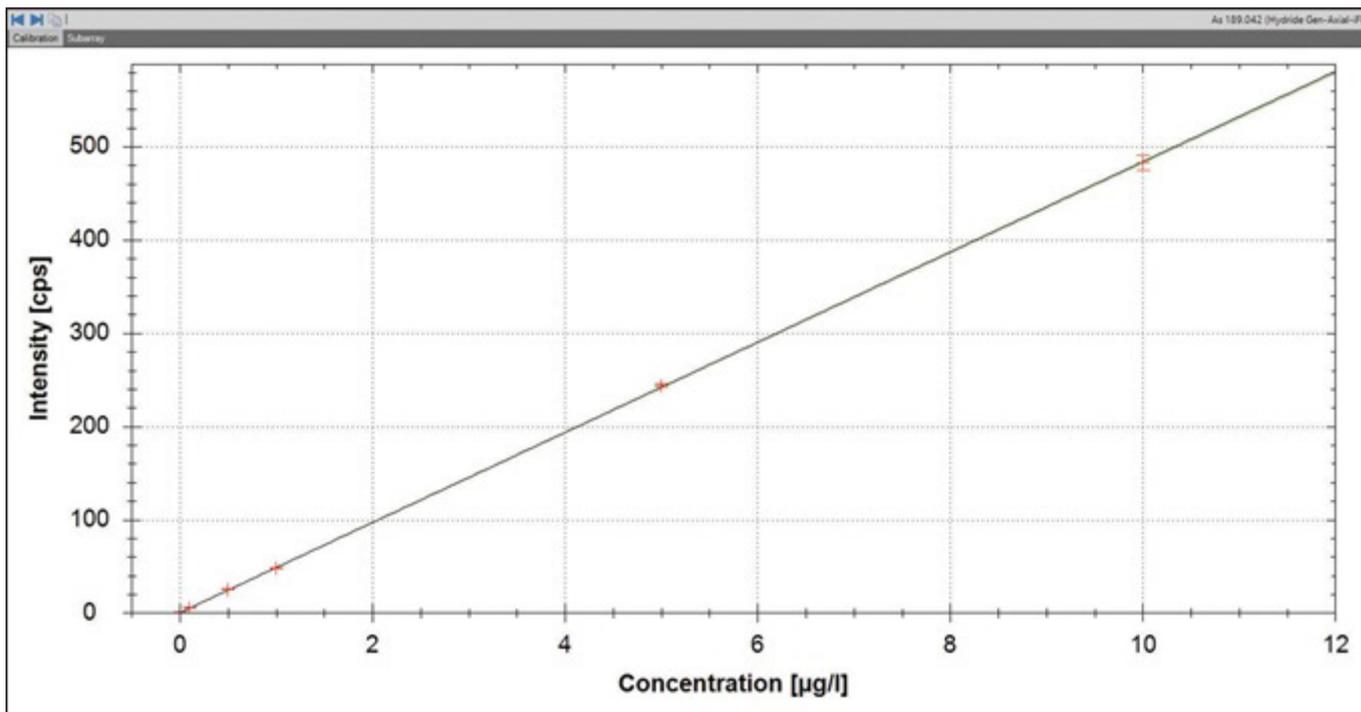


Figure 4. Calibration curve for As 189.042 nm in Axial viewing mode and Hg 184.950 nm in Axial viewing mode assessed over a concentration range of 0.1–10 µg·L<sup>-1</sup>

## Conclusion

The iCAP PRO Series ICP-OES Duo system with basic and integrated hydride generation kits were employed in separate experiments to analyze five hydride-forming elements. These accessories were shown to dramatically improve analysis sensitivity. This analytical method was rigorously tested, and the results obtained clearly demonstrate the following analytical advantages:

- Enhanced sensitivity helps achieve detection limits below 0.05 µg·L<sup>-1</sup> for hydride-forming elements including arsenic, bismuth, antimony, selenium, and mercury using the integrated hydride generation kit.
- The basic hydride generation kit performed ten times better for the LOD compared to the standard introduction system,

allowing the analysis of non-hydride-forming elements simultaneously.

- The performance achieved with the basic hydride kit indicates that achievable detection limits for hydride forming elements are equivalent or better than those with AAS equipped with hydride generation accessory, enabling multi-element determination simultaneously.
- The flexibility of the Qtegra ISDS Software allows creation of a customized analysis method by selecting the eUV analysis mode, which provides enhanced analytical performance.

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