

Use of the Agilent Multimode Sample Introduction System (MSIS) for Simultaneous Hydride Determination and Conventional Nebulization Using the PerkinElmer Optima 7/8x00 Series ICP-OES Systems

Application Note

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Introduction

Vapor generation techniques are routinely used with ICP-OES and AAS for the determination of trace levels of environmentally sensitive elements including arsenic (As), selenium (Se), and other elements using the hydride generation technique, plus mercury (Hg) using the cold vapor technique. Determination using hydride generation or cold vapor techniques has advantages including improved sensitivity, simplicity, and reduced interferences, as volatile hydrides are separated from the sample matrix. However, laboratories wishing to use this technique must either dedicate an instrument to hydride determination, or shut down an instrument to change over to hydride determination. Once the instrument has been converted, no other determinations can be performed until it is changed back again.



Figure 1. Agilent Multimode Sample Introduction System (MSIS) for PerkinElmer Optima series ICP OES (p/n 8003-0817)



Agilent Technologies

The Agilent Multimode Sample Introduction System (MSIS) is an innovative option for both PerkinElmer Optima ICP-OES instruments (Figure 1), and Agilent ICP-OES and Agilent MP-AES instruments. The MSIS allows sample determination in three different analysis modes:

- Conventional nebulization (Figure 2)
- Hydride generation (Figure 3)
- Simultaneous nebulization/hydride generation for determination of both hydride and nonhydride-forming elements (Figure 4)

This flexibility eliminates the need to shut down an instrument to swap between a spray chamber and a vapor generation accessory. This saves set-up and analysis time, and helps keep the lab as productive as possible. Using the MSIS for simultaneous hydride generation determination is more convenient and economical. It avoids the need to analyze hydride-forming elements in a separate measurement using a dedicated hydride system. Simultaneous determination also saves time, and simplifies sample analysis by eliminating the need for a second sample digest specifically for hydride determinations.

These unique performance and productivity benefits of the MSIS are achieved using thin-film hydride generation. The MSIS is based on a conventional glass cyclonic spray chamber fitted with vertically opposed tubes in the center. When used for either standalone or simultaneous hydride generation, the sample is pumped into the bottom of the MSIS. A flow of reductant is introduced through the top of the MSIS. The sample and reductant are mixed in a thin film formed at the convergence of the flows. The volatile hydride species formed by the reactions are stripped from the mix, and carried into the plasma by the nebulizer gas flow. The waste liquid flows down the conical ground glass tube, and is continuously pumped to waste. The introduction of volatile hydrides into the plasma ensures that the MSIS achieves significantly better performance for environmentally sensitive elements including Hg, As, Se, and other hydride-forming elements, compared to conventional nebulization. For conventional analysis of routine elements, the sample is introduced through the nebulizer in the usual manner, and the resulting aerosol is carried by the nebulizer gas flow into the plasma.

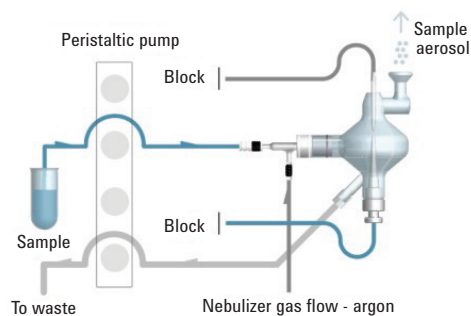


Figure 2. An Agilent MSIS configured for conventional nebulization. The additional tubing for the reductant and the additional flow of sample are temporarily blocked. In this mode, performance is equivalent to a conventional single pass glass cyclonic spray chamber.

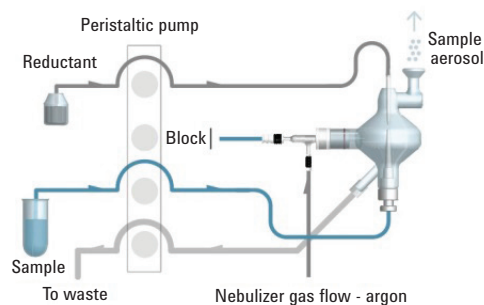


Figure 3. An Agilent MSIS configured for hydride determination only. The nebulizer is left in position, but the tubing for the sample flow to the nebulizer is temporarily blocked.

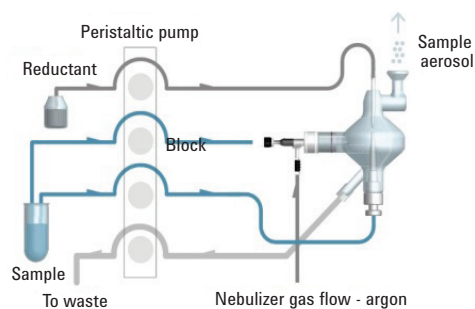


Figure 4. An Agilent MSIS configured for simultaneous hydride generation and conventional nebulization. All lines are unblocked, and the sample is introduced simultaneously through the nebulizer and the bottom of the MSIS.

Experimental

Instrumentation

A PerkinElmer Optima 7300 DV ICP-OES was used for this study. This instrument offers sequential dual view capabilities (axial first, then radial in a separate subsequent measurement). However, all the results presented here were achieved using axial view. The results obtained using the MSIS in conventional nebulization mode were also compared against results obtained using a conventional glass cyclonic spray chamber.

Only Agilent supplies for the PerkinElmer Optima ICP-OES instrument were used in this study. Agilent supplies for PerkinElmer instruments are guaranteed to be fully compatible with the equipment for which they are specified. These supplies are designed and manufactured to meet critical specifications set by Agilent engineers to ensure optimal fit and performance with PerkinElmer instruments.

The inert concentric Agilent OneNeb Series 2 nebulizer was used for all determinations (Figure 5). The performance of the OneNeb Series 2 nebulizer relative to conventional glass concentric and inert nebulizers used with the PerkinElmer Optima Series ICP-OES systems has been described previously [1].



Figure 5. The Agilent OneNeb Series 2 nebulizer (p/n 8003-0951) improves performance compared to conventional glass concentric and inert nebulizers used with PerkinElmer Optima ICP-OES instruments.

Table 1 shows the instrument operating conditions.

As shown in Figure 4, four solutions must be pumped when the MSIS is configured for simultaneous analysis. The peristaltic pump on the PerkinElmer Optima 7300 DV ICP-OES has only three channels. Therefore, a stand-alone external peristaltic pump was used to provide the extra capacity required.

Table 1. Instrument Operating Conditions Used on the PerkinElmer Optima 7300 DV ICP-OES

Instrument parameters	
Plasma power	1,500 W
Torch	Torch, demountable, 1-slot (p/n 8003-0346) Injector, alumina, 2.0 mm id (p/n 8003-0453)
Argon gas flows	18 L/min (plasma) – 0.2 L/min (aux)
Nebulizer	Agilent OneNeb Series 2 nebulizer (p/n 8003-0951)
Nebulizer flow	0.5 L/min
Spray chamber	Agilent MSIS (p/n 8003-0817)
Peristaltic pump	Gilson Minipuls3
Peristaltic pump tubing	PVC, 2 stop, black/black, for sample and reductant (p/n 3710027200) PVC, 2 stop, black/white, for waste (p/n 3710068900)
Pump speed	25 rpm
Number of replicates	5
Read time	Min 5 seconds Max 20 seconds
Stabilization time	25 seconds
Uptake time	15 seconds
Rinse time	120 seconds

Calibration standards and standard reference materials

Six multielement calibration standard solutions were prepared from Agilent aqueous single element certified reference materials. A recent study [2] noted that a matrix of 50% hydrochloric acid (HCl) provided good recoveries for the hydride-forming elements determined in this study. To match the acid matrix used for the samples, all calibration standards were prepared in 50% hydrochloric acid. The calibration range was determined based on the expected concentration of the elements in the Standard Reference Material (SRM) used in this study. The concentrated hydrochloric acid (37%) used for standard and sample preparation was sourced from Merck. Table 2 shows the composition of the calibration standards used.

Table 2. Calibration Standards (Concentrations in $\mu\text{g/L}$)

Element	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6
Al				62.5	125	250
Cd	62.5	125	250			
Cr	62.5	125	250			
Co	62.5	125	250			
Cu	62.5	125	250	25	50	100
Li	62.5	125	250			
Mn	62.5	125	250	25	50	100
Ni	62.5	125	250			
Pb	62.5	125	250			
Zn	62.5	125	250	25	50	100
Fe				62.5	125	250
Mo				62.5	125	250
V				12.5	25	5
Mg				125	250	500
Ca				125	250	500
As	20	60	100	5	10	15
Hg	5	15	25	1.25	2.5	3.75
Se	5	15	25	1.25	2.5	3.75

To validate the performance of the MSIS, an SRM from the National Institute of Standard and Technology (NIST) was used. The SRM selected for this study was NIST SRM 1643f "Trace elements in water", sourced from Graham B. Jackson (Aust.) Ltd. Table 3 lists the certified concentrations and the valid range for the elements in NIST SRM 1643f determined in this study. There are a number of other elements with certified concentrations, but the method used did not allow for determination of all the elements. For example, it is not possible to determine either sodium or boron, because of the excess introduced in the reductant solution. The chemistry

used for hydride generation (optimized for simultaneous determination of As, Se, and Hg with the non-hydride elements) is not recommended for determination of antimony or tin, where best performance is achieved using a 4% acid solution with addition of 1% L-Cysteine [2]. Treating the sample with alternate chemistry, or measuring some hydride elements individually with the MSIS, can improve achieved detection limits, but this was not investigated in this study. Determination of tellurium was not attempted because the concentration in the prepared sample, after allowing for the dilution applied during sample preparation, is close to the detection limit. This analysis was also not intended to be a complete analysis of all the elements in this SRM. The measured elements were selected to ensure this covered the most toxic (As, Se, Hg, Cd and Pb) and the most common elements, as well as covering both a wide wavelength range and a wide concentration range (four orders of magnitude).

Table 3. Certified Concentrations for the Elements in the NIST SRM 1643f "Trace Elements in Water" Determined in This Study

Element	Certified concentration ($\mu\text{g/L}$)	Element	Certified concentration ($\mu\text{g/L}$)
Al	133.8 ± 1.2	Mg	$7,454 \pm 60$
As	57.42 ± 0.38	Mn	37.14 ± 0.60
Ca	$29,430 \pm 330$	Mo	115.3 ± 1.7
Cd	5.89 ± 0.13	Ni	59.8 ± 1.4
Co	25.3 ± 0.17	Pb	$18,488 \pm 0.084$
Cr	18.5 ± 0.10	Se	$11,700 \pm 0.081$
Cu	21.66 ± 0.71	V	36.07 ± 0.28
Fe	93.44 ± 0.78	Zn	74.4 ± 1.7
Li	16.59 ± 0.35		

The sample preparation procedure for the NIST SRM 1643f SRM consisted of a simple 1:2 dilution using concentrated hydrochloric acid. This dilution ensured the best recovery, and matched the acid matrix used for the calibration standards. The SRM was allowed to reach ambient temperature before analysis.

The reductant used to generate the hydride vapor was 1% (w/v) sodium borohydride (NaBH_4) in 0.5% (w/v) sodium hydroxide (NaOH).

Results and discussion

Limits of detection and sensitivity

Limits of detection (LODs) were calculated as a three-sigma value, that is, three times the standard deviation. The LODs were based on the concentration of 10 replicate readings for a hydrochloric acid blank (50% HCl), measured after completing a full calibration. The LODs listed for the hydride-forming elements have been corrected for the two times dilution factor.

LODs were also determined using a conventional glass concentric nebulizer (SeaSpray), enabling a direct performance comparison with the OneNeb Series 2. To ensure a valid performance comparison, the optimum gas flow for each nebulizer was determined, and the performance tests were completed using the optimum gas flow. For this study, the SeaSpray glass concentric nebulizer was operated using a nebulizer flow of 0.7 L/min. Table 4 shows the measured LODs. The measured LODs obtained using the OneNeb Series 2 nebulizer are equivalent, and for many elements, better than those achieved using the SeaSpray nebulizer.

Table 4. Measured LODs Using MSIS in Simultaneous Vapor Generation/Nebulization Mode

Element and wavelength (nm)	Measured LOD using Agilent OneNeb (µg/L)	Measured LOD using SeaSpray (µg/L)
Al 394.401	8	5
As 188.979	1.7*	1.8*
Ca 317.933	3.3	2.6
Cd 226.502	0.24	0.40
Co 230.786	0.98	0.82
Cr 357.869	6.9	2.5
Cu 324.752	2.1	0.7
Fe 259.939	1.5	0.46
Hg 194.168	0.23*	0.35*
Li 670.784	0.03	0.04
Mg 279.553	0.35	0.30
Mn 257.610	0.27	0.05
Mo 204.597	1.7	2.4
Ni 231.604	11	5
Pb 220.353	3.7	3.3
Se 196.026	0.30*	0.90*
V 292.402	1.5	0.9
Zn 202.548	0.42	0.45

* Measured using vapor generation and corrected for the 2x dilution factor applied during preparation

The benefits of using the hydride generation technique are demonstrated when comparing the LODs using the MSIS in simultaneous mode to those obtained using conventional nebulization. Table 5 shows this comparison. In simultaneous mode, the LODs for As, Se, and Hg using vapor generation were improved to low ppb levels. The LODs for the other elements measured in simultaneous mode are equivalent to those achieved using conventional nebulization [2].

Table 5. Measured LODs for Mercury and the Hydride-forming Elements Using MSIS in Simultaneous Mode

Element and wavelength (nm)	Measured LOD using hydride generation (µg/L)	Measured LOD using conventional nebulization (µg/L)
As 193.696	1.7	13
Hg 194.168	0.23	1.3
Se 196.026	0.30	12

The OneNeb Series 2 nebulizer has been shown to achieve superior efficiency, with up to four times more sensitivity than other nebulizers used with the PerkinElmer Optima Series ICP-OES [1]. This improvement in sensitivity is also evident when comparing the calibration curves obtained with the OneNeb Series 2 nebulizer with calibration curves from the SeaSpray nebulizer using the MSIS in simultaneous mode. The OneNeb Series 2 nebulizer was up to three times more sensitive than the SeaSpray for both hydride-forming and routine elements measured using conventional nebulization (Figure 6).

Precision

The precision was determined as the % RSD from five replicate readings for a low-mid range calibration standard. Table 6 shows that excellent precision was observed for all 18 elements examined in this study. The achieved precision was below 1% RSD for most elements, based on the standard solutions with concentrations 0.25 µg/L and below.

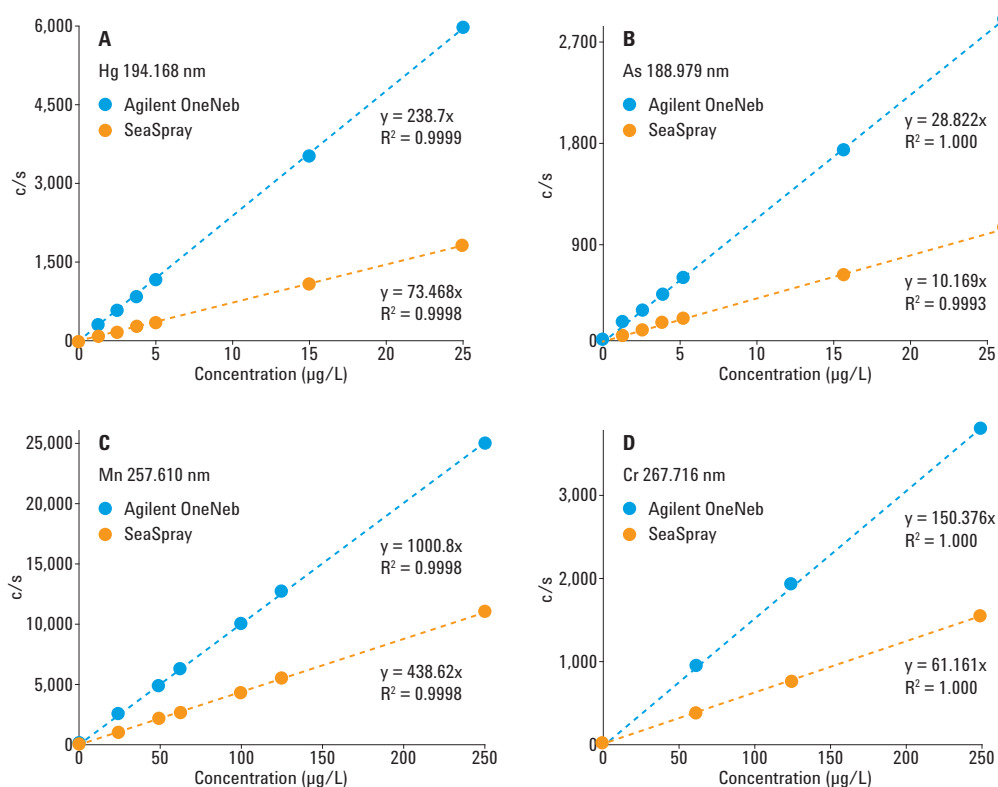


Figure 6. Comparison of calibration curves generated using the Agilent OneNeb Series 2 and SeaSpray nebulizers for selected hydride and routine elements measured using the Agilent MSIS in simultaneous mode.

Table 6. Achieved Precision (% RSD) for the Low-mid Range Calibration Standard Measured Using the Agilent OneNeb Series 2 with the Agilent MSIS in Simultaneous Mode

Element	Standard concentration (µg/L)	Precision % RSD	Element	Standard concentration (µg/L)	Precision % RSD	Element	Standard concentration (µg/L)	Precision % RSD
Al	125	0.61	Cu	50	0.27	Mo	125	0.64
As	10	1.4	Fe	125	0.74	Ni	125	0.63
Ca	250	1.2	Hg	15	0.55	Pb	125	0.38
Cd	125	0.40	Li	125	0.72	Se	15	0.67
Cr	125	0.96	Mg	250	0.85	V	25	0.55
Co	125	0.28	Mn	50	0.60	Zn	50	0.90

Performance of the Agilent MSIS as a conventional spray chamber

When used with the ICP-OES instrument, the MSIS provides the flexibility for the analyst to switch quickly between conventional nebulization, hydride generation, or simultaneous analysis mode. The performance of the MSIS in conventional nebulization mode was compared with the performance achieved using a conventional single pass glass cyclonic spray chamber (SPSC) and a double pass glass cyclonic spray chamber (DPSC). Table 7 shows the LODs achieved. The instrument conditions used for this study were the same as those listed in Table 1.

The MSIS used in conventional nebulization mode is able to achieve comparable LODs to those achieved with a conventional DPSC (Table 7). Those LODs are also usually better than those achieved with a SPSC.

The MSIS in conventional nebulization mode provides comparable sensitivity to the SPSC, and better sensitivity to the DPSC for routine elements. This is best demonstrated by comparing the calibration curves obtained (Figure 7). The average difference between the sensitivity achieved with the MSIS and the DPSC is approximately 40%.

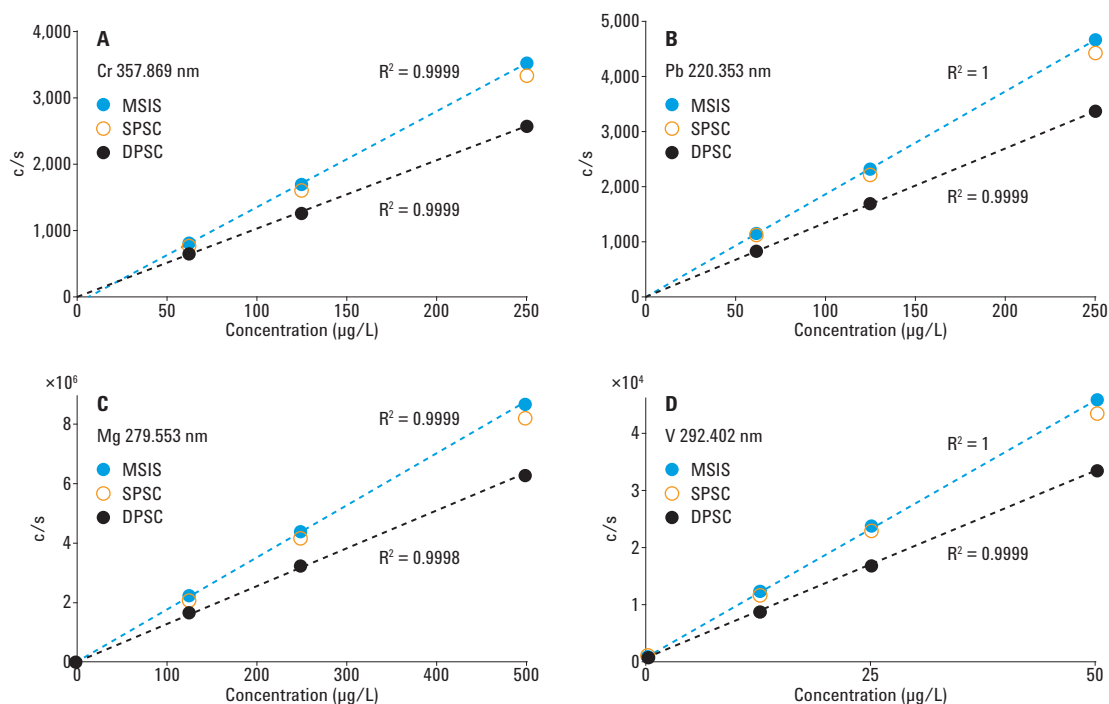


Figure 7. Calibration curves generated using the Agilent MSIS in conventional nebulization mode are compared with those achieved using the single pass (SPSC) and double pass (DPSC) spray chambers.

Table 7. Measured LODs Comparing Performance of the MSIS with Conventional Spray Chambers

Element and wavelength (nm)	MSIS in conventional nebulization mode (µg/L)	Single pass glass cyclonic spray chamber (µg/L)	Double pass glass cyclonic spray chamber (µg/L)	Element and wavelength (nm)	MSIS in conventional nebulization mode (µg/L)	Single pass glass cyclonic spray chamber (µg/L)	Double pass glass cyclonic spray chamber (µg/L)
Al 394.401	4	7	3	Mg 279.553	0.05	0.06	0.04
Ca 317.933	0.4	1.4	0.8	Mn 257.610	0.04	0.06	0.05
Cd 226.502	0.08	0.06	0.07	Mo 204.597	1.2	1.2	1.7
Co 230.786	0.2	0.7	0.8	Ni 341.476	4	4	4
Cr 357.869	2	1.5	2.4	Pb 220.353	3	2	3
Cu 324.752	0.5	0.4	0.6	V 292.402	0.4	0.5	0.8
Fe 259.939	2	0.2	0.3	Zn 202.548	0.1	0.1	0.2
Li 670.784	0.04	0.09	0.05				

SRM recoveries

The performance of the MSIS was validated using the NIST SRM 1643f "Trace elements in water". The results are shown in Table 8. Excellent recoveries were achieved for all 18 elements determined in this study, being within $\pm 10\%$ of the certified value. These recoveries demonstrate the suitability of the MSIS to achieve accurate results for both hydride-forming and routine elements when used in simultaneous mode.

Spike recoveries

Accuracy was further checked by spiking an aliquot of the NIST SRM 1643f with the hydride-forming elements. For all three analytes, spike recoveries ranged from 98 to 100% (Table 9), even with a low concentration spike. There is no certified value for mercury in NIST SRM 1643f. The excellent spike recoveries for mercury and the hydride-forming elements demonstrate the ability of the MSIS when used in simultaneous mode, to accurately determine hydride-forming elements at low concentrations, such as those found in the water-based NIST SRM.

Table 8. Achieved Recoveries for 18 Elements Determined in the NIST SRM 1643f "Trace Elements in Water" Using the Agilent MSIS in Simultaneous Mode

Element and wavelength (nm)	Measured Concentration ($\mu\text{g/L}$)	Certified Value for NIST SRM 1643f $\mu\text{g/L}$	Recovery (%)
Al 394.401	128.4	133.8 ± 1.2	96
As 188.979	58.09	57.42 ± 0.38	101
Ca 422.673	31,064	$29,430 \pm 330$	106
Cd 226.502	5.78	5.89 ± 0.13	98
Co 228.616	26.5	25.3 ± 0.17	105
Cr 357.869	18.5	18.5 ± 0.10	100
Cu 324.752	23.13	21.66 ± 0.71	107
Fe 259.939	97.50	93.44 ± 0.78	104
Li 670.784	15.28	16.59 ± 0.35	92
Mg 279.553	7,387	$7,454 \pm 60$	99
Mn 257.610	38.21	37.14 ± 0.60	103
Mo 204.597	119.1	115.3 ± 1.7	103
Ni 341.476	58.7	59.8 ± 1.4	98
Pb 220.353	17.676	18.488 ± 0.084	96
Se 196.026	10.814	11.700 ± 0.081	92
V 292.402	38.31	36.07 ± 0.28	106
Zn 202.548	75.1	74.4 ± 1.7	101

Table 9. Spike Recoveries for Low Concentration Spike of the NIST SRM 1643c.

Sample	As 188.979	Hg 194.168	Se 196.026
Sample result (with 2x dilution)	30.27	n.d.	5.45
Spiked sample result	38.15	1.94	9.32
Measured concentration difference	7.88	1.94	3.87
Spike concentration	7.92	1.98	3.92
Spike recovery	99.5%	97.8%	98.7%

Concentrations in $\mu\text{g/L}$

Conclusions

The results obtained in this study demonstrate the flexibility and performance of the Agilent MSIS. When used with the PerkinElmer Optima ICP-OES instrument, it enables simultaneous determination of routine elements using conventional nebulization as well as mercury and the hydride-forming elements using vapor generation. This eliminates the need to shut down the instrument to swap between a spray chamber and a vapor generation accessory. This saves set-up and analysis time and helps keep your lab as productive as possible. This flexibility also saves time and simplifies your sample analysis workflow by eliminating the need for a second sample digest specifically for hydride determinations.

The performance and dynamic range of the MSIS were demonstrated by the excellent recoveries obtained for the simultaneous analysis of 18 elements (including mercury and two hydride-forming elements) in NIST SRM 1643 "Trace elements in water". Sample concentrations in this SRM covered four orders of magnitude. Excellent spike recoveries were achieved for mercury and the hydride-forming elements, further demonstrating the robustness and sensitivity of the MSIS. Excellent precision was achieved for most elements, with less than 1% RSD for low concentration calibration standards of 0.25 mg/L and below.

In conventional nebulization mode, the MSIS is able to achieve comparable detection limits to those achieved with a conventional double pass spray chamber. However, the sensitivity is equivalent to that achieved using a conventional single pass spray chamber.

The Agilent OneNeb Series 2 nebulizer contributes to the superb performance of the MSIS, improving sensitivity by up to three times compared with a conventional glass concentric (SeaSpray) nebulizer for both hydride-forming and routine elements.

References

1. A. Amorin, Evaluating the performance of the OneNeb Series 2 Nebulizer with PerkinElmer Optima 7/8x00 Series ICP-OES systems, *Agilent Technologies Competitive Comparison*, publication number 5991-6664EN (2016).
2. J. Cauduro, Simultaneous analysis of hydride and non-hydride-forming elements via ICP-OES, *Agilent Technologies White Paper*, publication number 5991-6445EN (Published ahead of print 2016).

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