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Simultaneous Multi-Element Analysis by Pneumatic Nebulization and Hg by Cold Vapor with the Glass Expansion HydraMist Spray Chamber

While Hg can be determined by Inductively Coupled Plasma Optical Emission Spectrometry, (ICP-OES) with conventional pneumatic nebulization, the low µg/L detection limits typically achieved are not adequate for most environmental applications. The Cold Vapor technique, using an acidified stannous chloride reductant ($SnCl_2$) solution, is a widely-used technique to improve the sensitivity of Hg in atomic spectroscopy. The Cold Vapor process traditionally uses a dedicated instrument, or a Cold Vapor/Hydride Generation accessory connected to the ICP. However, for laboratories that routinely determine Hg and other elements in the same sample, switching between a cold vapor and conventional nebulization modes adds complexity, increases argon (Ar) consumption and reduces laboratory productivity.

Figure 1. HydraMist - Simultaneous Cold Vapor/Pneumatic Nebulization Spray Chamber

Glass Expansion, world leaders in sample introduction systems for ICP-OES and ICP-MS have made a single-pass cyclonic spray chamber with conventional pneumatic nebulization capabilities and a secondary inlet port to inject a stream of $SnCl_2$ into the nebulizer aerosol plume. The aerosol/liquid interaction ensures a rapid mixing of the aerosolized Hg in the nebulizer plume with the acidified $SnCl_2$, efficiently converting Hg into a volatile form to improve Hg sensitivity. In this simple arrangement, the HydraMist gave a 20-fold improvement in Hg detection limits compared to conventional pneumatic nebulization setup, without degrading the precision or sensitivity of the other elements being conventionally nebulized through the SeaSpray nebulizer.

Instrument

The ICP-OES used in this work was an Agilent Technologies® 5100 SVDV ICP-OES, with HydraMist spray chamber and Glass Expansion SeaSpray nebulizer with operating conditions indicated in Table 1 below. To compare the performance of the system without the Cold Vapor process the analysis was repeated using a standard Tracey single-pass spray chamber from Glass Expansion instead of the HydraMist spray chamber.

Table1. Instrumental conditions

Experimental Parameter	Setting
RF power	1.4 kW
Nebulizer gas flow rate	0.60 L/min
Plasma gas flow rate	12 L/min
Auxiliary gas flow rate	1.0 L/min
Read time	30 sec
Number of replicates	3
Peristaltic pump speed	20 rpm
Stabilization time	30 sec
Sample line pump tubing	White/white
$SnCl_2$ line pump tubing	Black/black
Drain tubing	Black/white
Nebulizer	2 mL/min Direct Connection SeaSpray

The instrument was operated at a constant sample uptake with the option of the fast rinse between samples disabled.

$SnCl_2$ Preparation

As $SnCl_2$ can form an insoluble salt when dissolved in water, it is usually dissolved in concentrated HCl acid first and then diluted with H_20 to form a 5% $SnCl_2$ solution in 5% HCl.

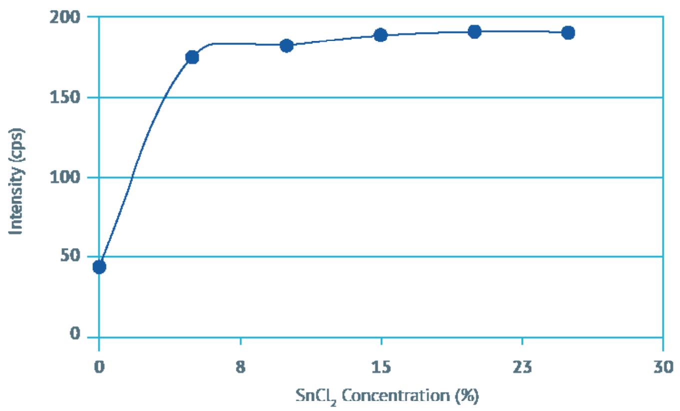
Sample Preparation

The sample was Standard Reference Material 1643f Trace Elements in Water from the National Institute of Standard Technology (NIST) Gaithersburg, MD. SRM 1643f does not naturally have detectable Hg so it was spiked with 5ppb for this work.

Results & Discussion

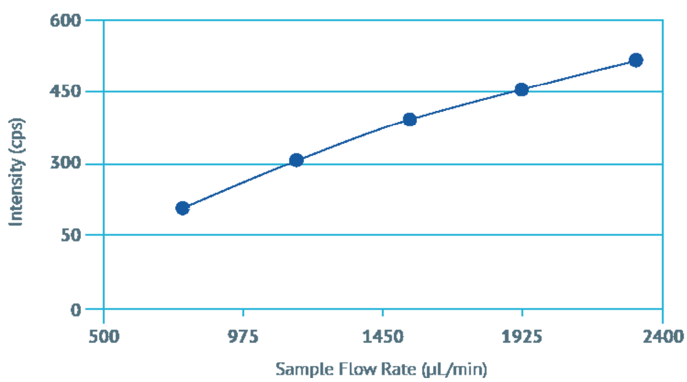
As can be seen in Figure 2, the optimum concentration of $SnCl_2$ reaches a maximum at about 5% and plateaus after that.

Figure 2. Sensitivity of Hg 194 with $SnCl_2$ concentration



In Figure 3, the intensity of Hg at 194nm is measured as a factor of sample uptake rate. The sample uptake rate is adjusted by varying the instrument peristaltic pump speed. The intensity of Hg increases as the volume of sample aspirated is increased, indicating the Cold Vapor process is sample limited, not reductant limited.

Figure 3. Hg 194nm intensity versus sample uptake rate.



In Figure 4, the Signal to Root Background Ratio (SRBR) and Net Intensity of Hg at 194nm were evaluated as a function of nebulizer flow. The nebulizer gas flow not only aspirates the analyte solution, but it is also used to transport the sample aerosol and Hg Cold Vapor into the plasma. SRBR is used to optimize nebulizer flow, as it is a good proxy for detection limit performance in a solid-state detector based ICP-OES. As can be seen in Figure 4, optimum nebulizer flow rate is around the 0.6 L/min Ar.

Figure 4. SRBR and Net Intensity of Hg 194nm versus Nebulizer gas flow rate (L/min)

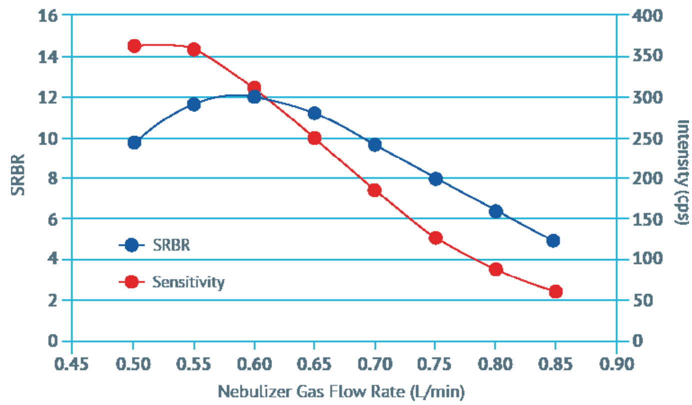


Figure 5 shows a comparison of blank intensity, and 5ppb and 10ppb Hg intensities with and without $SnCl_2$ showing Hg sensitivity enhancements due to cold vapour generation using this $SnCl_2$ - HydraMist method.

Figure 5. Mercury sensitivity with and without $SnCl_2$

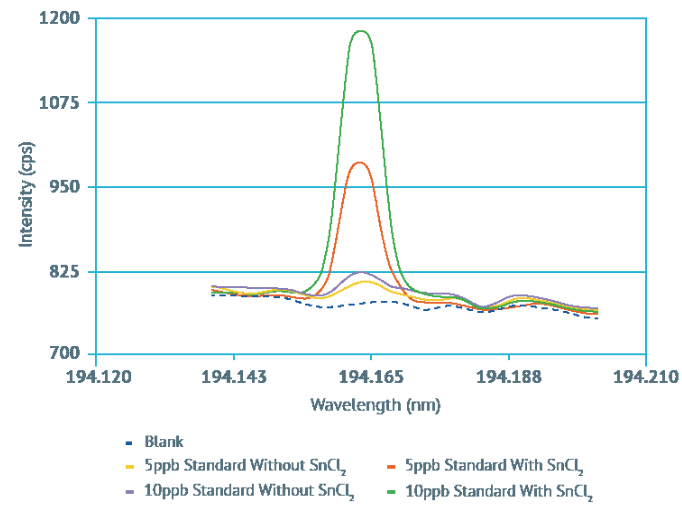


Table 2 presents 3σ Detection Limits (ppb) comparison between HydraMist and Tracey spray chambers.

Table 2. 3σ method detection limits using a HydraMist spray chamber with SeaSpray nebulizer simultaneously determined using pnuematic nebulization and Cold Vapor analysis. The results are an average of 3 separate runs, measured using 3 replicates per sample of 10 blank samples.

Analyte λ (nm)	HydraMist 3σ Detection Limits (ppb)	Tracey 3σ Detection Limits(ppb)
As 188	2.3	2.5
Be 313	0.01	0.01
Cd 214	0.1	0.1
Co 233	0.6	0.6
Cr 268	0.3	0.3
Cu 327	0.7	0.5
Hg 194	0.2	4.2
Mn 257	0.03	0.03
Mo 202	0.5	0.6
Ni 232	0.6	0.8
Pb 220	2.1	2.4
Sb 217	2.8	2.6
Se 196	3.6	3.5
Tl 191	2.4	2.4
V 292	0.4	0.4
Zn 231	0.2	0.2

The measured concentration of 16 elements in SRM 1643f "Trace Elements in Water" using the HydraMist spray chamber and SeaSpray nebulizer under the conditions listed in Table 1 are shown in Table 3 below. As the SRM does not contain measurable concentrations of Hg, a 50 mL aliquot of the SRM was spiked with 25 µL of 10 ppm Hg, for a 5 ppb spike concentration.

Table 3. Measured concentration of 16 elements in SRM 1643f spiked with 5 ppb Hg using the HydraMist spray chamber and SeaSpray nebulizer.

Analyte λ (nm)	SRM 1643f Found (ppb)	SRM 1643f Certified (ppb)	Recovery %
As 188	60.5	57.4	105
Be 313	13.6	13.7	100
Cd 214	5.8	5.9	99
Co 233	25.5	25.3	101
Cr 268	18.5	18.5	100
Cu 327	22.9	21.7	106
Hg 194	5.3*	5.0	106
Mn 257	37.1	37.1	100
Mo 202	121.9	115.3	106
Ni 232	65.1	59.8	109
Pb 220	19.0	18.5	103
Sb 217	56.3	55.5	102
Se 196	11.9	11.7	103
Tl 191	6.3	6.9	91
V 292	37.3	36.1	103
Zn 231	74.8	74.4	101

The 5.3 ppb measured value for the 5 ppb Hg spike, represents a 106% recovery using the cold vapor mode of the HydraMist spray chamber. The measured values of all 15 naturally occurring elements were within 10% of the certified values, indicating the HydraMist spray chamber is not only sensitive for Hg by cold vapor, but also suitable for measuring trace elements in waters using conventional pneumatic nebulization mode.

Conclusion

When using the Agilent Technologies® 5100 SVDV ICP-OES with HydraMist spray chamber in cold vapor mode, the 3σ detection limits of Hg were found to be 0.2 µg/L compared to the 4.2 µg/L detection limits with a conventional Tracey single-pass spray chamber. The measured results for the "naturally occurring" elements and the 5 µg/L Hg spike in ***SRM 1643f Trace Elements in Water*** were all found to be within 10% of the expected values, demonstrating the HydraMist spray chamber is a simple and sensitive sample introduction system suitable for the simultaneous detection of Hg using Cold Vapor and other trace elements by conventional pneumatic nebulization.