

Using Dynamic Reaction Cell ICP-MS Technology to Determine the Full Suite of Elements in Rainwater Samples

This paper describes how scientists at an environmental and geochemical laboratory utilize dynamic reaction cell ICP-MS technology to study the transport and deposition of the full suite of important trace metals from rainwater. Previously, the presence of spectral interferences necessitated the use of additional techniques to achieve the desired detection limits, but this study shows that the lab can now use a single technique, which has increased sample throughput and dramatically improved their lab productivity.

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It is well-documented that natural and anthropogenic sources can significantly increase trace metal concentrations in the atmosphere. This is compounded by acidic precipitation which potentially can make some trace metals more bioavailable than others. At its inception in 1977, the National Atmospheric Deposition Program (NADP) (1) recognized the need for measuring trace metals in acid rain. However, due to cost issues and the difficulty of measuring such low levels, the only toxic metal that was monitored on a regular basis was mercury as a part of the Mercury Deposition Network (MDN) (2). Recent interest has been fueled by the potential environmental effect of trace metals on aquatic and terrestrial ecosystems and potential human health affects through the consumption of drinking water. The publication of the US EPA's "critical maximum concentration" water quality criteria, designed to protect environmental and human health, has further demonstrated the need for the accurate measurements of trace metals in wet deposition samples (3). As a result in 1998, Frontier GeoSciences (Seattle, WA), which serves as the Hg Analytical Lab (HAL) for the MDN program, in conjunction with the NADP coordinator for air toxics, began to develop and refine the tools needed to support a trace metal

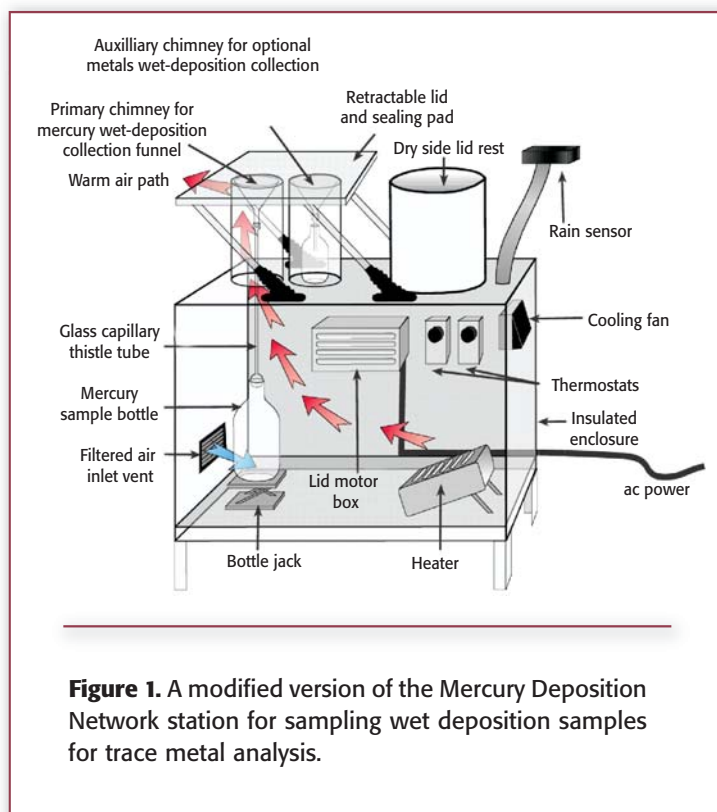


Figure 1. A modified version of the Mercury Deposition Network station for sampling wet deposition samples for trace metal analysis.

Table I. Typical ranges in ng/L (ppt) for trace metals in wet deposition samples.

Analyte	Range
As	20–340
Cd	10–330
Cr	10–380
Cu	50–2670
Pb	10–1390
Ni	20–500
Se	20–430
Zn	100–5420

network. This involved taking separate samples from almost 20 of the 90 current sampling sites across the US, using a modified version of MDN sampling station. The focus of the HAL initiative was to identify and develop both sampling and analytical methodology to accurately measure a group of critical elements including Ag, As, Be, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Se, V and Zn in addition to total and methyl Hg. The first step was to design a modified version of the MDN sampling station to take wet deposition samples for trace metal analysis. This modified sampling station is shown in Figure 1.

Initial Analytical Issues

One of the major reasons why Frontier GeoSciences began to develop a trace metal wet deposition program in 1998 was that the company had recently invested in inductively coupled plasma mass spectrometry (ICP-MS) technology. This technique's extremely low detection capability and high sample throughput enabled most of the impor-

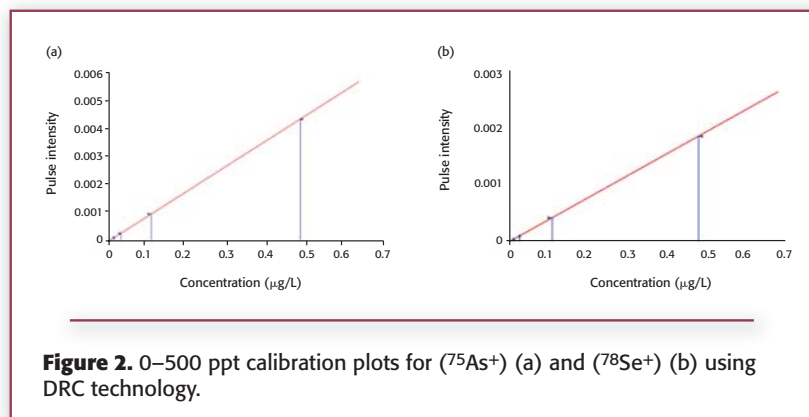
tant elements to be determined in one sample run. With many of the trace metal contaminants below 50 ng/L (ppt), method detection limits for flame atomic absorption (AA) and ICP atomic emission spectrometry (AES) wouldn't have been low enough, while electrothermal atomization would have struggled to keep up with the sample workload generated from the multitude of sampling sites. Table I shows typical concentration ranges for eight of the trace metals found in MDN wet deposition samples.

Even though many of the analytes were at low ppt levels, the detection capability of ICP-MS enabled a majority of the elements to be determined with relative ease. However, normal levels of two of the most critical elements, arsenic and selenium, were lower than the detection limits for ICP-MS due to polyatomic spectral interferences derived from the plasma gas and the sample matrix. The major isotope of selenium at mass 78 and 80 were overlapped by a massive argon dimer peaks ($^{40}\text{Ar}^{40}\text{Ar}^+$, $^{40}\text{Ar}^{38}\text{Ar}^+$) generated by the plasma gas, while arsenic, which is mono isotopic ($^{75}\text{As}^+$) suffered a major $^{40}\text{Ar}^{35}\text{Cl}^+$ interference from the chloride matrix at mass 75.

To get around this problem, hydride generation atomic fluorescence spectrometry (HG-AFS) was used to determine both selenium and arsenic. Similar in principle to hydride generation AA, this extremely sensitive technique involves the reduction of the metal to its

Table II. Method detection limits (MDL) and reporting limits (RL) generated by Frontier GeoSciences in both 2% HNO_3 and a composite (n = 15) rainwater sample (RW), in a HNO_3 /HF matrix.

Element	Frontier GeoSciences			Industry Standard (IS)	DCR-ICP MS RL Improvement over IS
	DRC-ICP-MS in 2% HNO_3 (ng/L)	DRC-ICP-MS in RW/ HNO_3 /HF(ng/L)	DRC-ICP-MS RL in RW/ HNO_3 /HF(ng/L)	Conventional ICP-MS RL (ng/L)	
Cd	2	3	10	200	20
Cr	2	6	10	500	50
Cu	4	16	50	500	10
Fe	9	383	500	20000	40
Mn	2	13	20	500	25
Ni	3	9	20	500	25
Pb	1	7	10	1000	100
Se	8	15	30	500	17
V	2	16	30	200	7
Zn	9	38	100	4000	40
As	3	9	30	500	17



gaseous hydride, but instead of detection by absorption it uses atomic fluorescence (4). Although this technique solved the detection capability issue, it significantly affected lab productivity, because three separate sample preparation methods and three separate analytical runs had to be carried out: one for the ICP-MS multielement suite and another two for the determination of selenium and arsenic by HG-AFS.

In order to develop a major trace metals deposition network, especially with the projected sample workload, a critical question had to be answered: How could lab productivity be improved without negatively affecting detection capability and analytical accuracy? It became clear that the only realistic solution was to use ICP-MS to determine all the analytes including selenium and arsenic. So in the Spring of 2001 it was decided to

carry out an evaluation of collision/reaction cell technology. It was well-documented in the literature that this exciting new development could reduce argon-based interferences like $^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ar}^+$ and $^{38}\text{ArH}^+$ in the determination of elements like iron ($^{56}\text{Fe}^+$), calcium ($^{40}\text{Ca}^+$) and potassium ($^{39}\text{K}^+$) (5). But it was unclear whether it was as efficient in reducing the argon-dimer and argon-chloride based interferences for the determination of Se and As.

Instrument Investigation

After a careful evaluation, the instrument chosen for the investigation was an ELAN DRC (PerkinElmer SCIEX, Concord, Ontario), which utilized the principles of dynamic reaction cell technology. There are many references in the public domain describing this approach, which uses a highly reactive gas such as ammonia (NH_3) to react with the interference but not the analyte (6, 7, 8). Through a number of different ion-molecule reaction mechanisms, the gaseous molecules react with the interfering ions

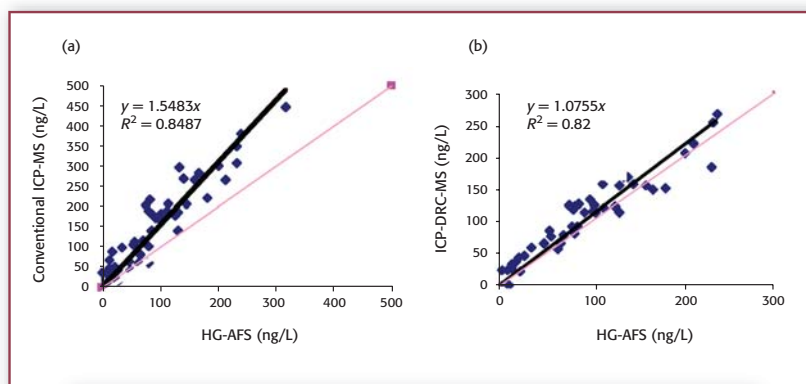


Figure 3. Determination of arsenic in rainwater samples by HG-AFS and compared with both conventional ICP-MS (a) and DRC-ICP-MS (b).

to convert them into species that will not interfere with the analyte. The analyte mass then emerges from the dynamic reaction cell free of its interference and enters the analyzer quadrupole for conventional mass analysis.

By careful optimization of the DRC quadrupole electrical fields, unwanted reaction by-products, which potentially could lead to new interferences, are eliminated. This cleansing process, known as “chemical resolution,” means that every time an analyte and interfering ions enter the dynamic reaction cell, the bandpass of the quadrupole can be optimized for that specific problem and then changed on-the-fly for the next analyte. The added benefit of this approach for multielement analysis is that the instrument can be operated in both DRC and normal modes. By incorporating stabilization times in the method, different gases (and gas flows) can be used for the DRC elements, while

the normal mode can be used for the other elements in the same multielement run.

Method Development and Validation

After reviewing the literature and carrying out optimization studies, the decision was made to use oxygen gas to chemically-resolve argon chloride and argon dimers from the arsenic and selenium ions. In the case of arsenic, advantage was taken of the DRC’s ability to measure the arsenic oxide ionic species ($^{75}\text{As}^{16}\text{O}^+$) at mass 91, where the argon-chloride interference at mass 75 does not pose a spectral problem. This has been well-documented and has proven to be a clever way of determining arsenic in a chloride matrix (9). In the case of selenium, the oxygen gas is used to react with the argon dimers to produce non-interfering species so selenium can be determined at its major isotope of $^{80}\text{Se}^+$ or

Table III. 100 ng/L spike recovery and precision data on a composite rainwater sample.

Analyte	Unspiked Conc. in RW (ng/L)	Determined Conc. (ng/L)	Spike (ng/L)	% Spike Recovery	%RSD (n=9)
As	31	114	100	83	5.8
Cd	5	93	100	88	3.1
Co	8	110	100	101	3.4
Cr	28	128	100	101	3.1
Cu	102	208	100	106	8.4
Fe	9407	9522	100	115	2.1
Mn	435	550	100	115	1.6
Ni	66	169	100	103	3.0
Pb	132	234	100	102	2.7
Se	50	144	100	94	5.1
V	157	268	100	111	2.6
Zn	649	751	100	102	2.9

$^{78}\text{Se}^+$. It's also worth emphasizing that in addition to oxygen, ammonia also was used as a reaction gas to minimize the formation of other polyatomic spectral interferences such as $^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ar}^{12}\text{C}^+$ and $^{37}\text{C}^{18}\text{O}^+$ for the determination of elements like $^{56}\text{Fe}^+$ and $^{52}\text{Cr}^+$ and $^{55}\text{Mn}^+$ respectively.

Once the gas flows and ion-molecule chemistry of the DRC were optimized

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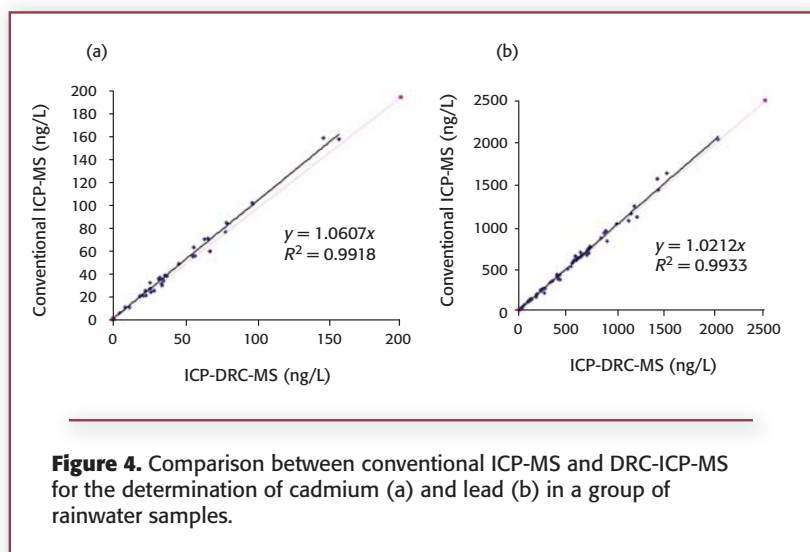
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for the full suite of elements, it was decided to validate the performance of the analytical method by comparing HG-AFS data with both standard ICP-MS and DRC-ICP-MS data for arsenic and selenium in rainwater samples. For the other suite of trace metals, results from conventional ICP-MS were compared with DRC-ICP-MS results. Unfortunately no standard reference materials were available for these types of samples, so method detection limits and spike recovery studies were carried out on various archived rainwater samples.

Analysis and Results

The calibration graphs for arsenic ($^{75}\text{As}^+$) and selenium ($^{78}\text{As}^+$) using DRC technology are shown in Figure 2. Good linearity has been achieved for both arsenic (Figure 2A) and selenium (Figure 2B) between 0 and 500 ppt. The data also shows that both calibration plots pass through zero, which indicates that the DRC technology success-



fully has removed or avoided the interfering species. It should be noted that the method detection limits obtained from these calibration plots are in the order of 10 ppt for both elements, which is about 3 times lower than achievable by HG-AFS.

To further validate the method, a number of rainwater samples were analyzed by HG-AFS and compared with both conventional ICP-MS and DRC-ICP-MS. The results for arsenic are shown in Figure 3. It can be seen in Figure 3A that the HG-AFS/conventional ICP MS comparison shows poor correlation ($y = 1.5483x$), primarily because of the impact of the $^{40}\text{Ar}^{35}\text{Cl}$ polyatomic interference on the analysis. Whereas in Figure 3B, which shows the HG-AFS/DRC-ICP-MS comparison, the correlation of the data is much better because the impact of the interference has essentially been removed ($y = 1.0755x$). Although it is not shown in this paper, the HG-AFS/DRC data for selenium exhibits even better correlation than arsenic (slope = 0.9933 for Se compared to 1.0755 for As).

To confirm that the other elements in the multielement suite also exhibited good correlation, a comparison was made between conventional ICP-MS and DRC-ICP-MS for the same set of rainwater samples. These elements were determined in the same multielement suite as arsenic and selenium, but using different dynamic reaction cell condi-

tions. Data for two of the elements, cadmium and lead, are shown in Figure 4. It can be seen that there is extremely good correlation between ICP-MS and DRC-ICP-MS for both elements. The lead results are especially encouraging because they were generated by two different analysts, running the same set of samples on different days, using two different instruments.

Table II shows some typical method detection limits (MDL) and reporting limits (RL) in ng/L for a group of the most important trace metals in a composite rainwater sample digested in HNO_3/HF . It's worth emphasizing that MDLs are calculated in a similar manner to instrument detection limit (IDL) except that the blank solution is taken through the entire sample preparation procedure before the analyte concentration is measured multiple times. For this particular methodology, sample preparation closely followed the procedure set out in EPA Method 1638 (10).

The MDL values in Table II represent DRC method detection limits generated by Frontier's laboratory in both 2% HNO_3 and composite rainwater (RW) sample, while the RL values represent real-world reporting limits. On average the RLs are 2–5 times worse than the MDL values and are based primarily upon what an experienced analyst is comfortable with reporting. Of particular interest is the comparison between RL values from this study and typical

industry standard (IS) RL values (average taken from a population of conventional ICP-MS instruments used by environmental labs).

It can be seen that these industry standard values would not be low enough to measure many of the analyte concentrations shown in Table I. The DRC RLs reported in this study are 10–100 times lower than the industry standard values and in most cases are all within the concentration range requirements. It also

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should be noted that the analyte levels in the composite rainwater sample were much higher than in 2% HNO₃. As a result, it can be seen that the MDLs in 2% HNO₃ generally are much lower than in the RW sample.

Table III shows 100 ng/L spike recovery and precision data on the composite rainwater (RW) sample. It can be seen that just about all values are within the recovery limits of 85–115% as defined in EPA Method 200.8 (11). The % RSD values are based upon the analysis of nine separate samples of the original composite sample.

Summary

The study has shown that all the environmentally significant elements, including arsenic and selenium, can be determined successfully in one analytical method using dynamic reaction cell ICP-MS. Because each rainwater sample is not being split into three to determine arsenic and selenium by HG-AFS, only one simple digestion is needed for the

entire suite of elements.

The findings of this investigation together with comprehensive field data have convinced our laboratory to implement this sampling and analytical methodology for the routine monitoring of trace metals in precipitation samples generated by the Mercury Deposition Network. As a result, this more efficient and economic approach to determine the full suite of elements has driven down costs approximately 2–3 fold, improved lab productivity and increased the feasibility of a long-term, nationwide trace metals' monitoring network.

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