Determination of Background Levels of Metals in National Atmospheric Deposition Program/National Trends Network Field Blank Samples and the Central Analytical Laboratory In-House Blank Samples by Inductively Coupled Plasma-Optical Emission Spectroscopy

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Abstract

The NADP/National Trends Network (NTN) collects weekly precipitation samples for the measurement of major ions (SO4, NO3, Cl, NH4, Na, K, Mg, Ca, and ortho-P) and pH. Samples are collected in HDPE buckets without preservative and kept at ambient temperature until analysis is performed. An investigation was made to determine the background levels of trace metals in samples collected via the NTN protocol to evaluate the use of NTN samples for semi-quantitative monitoring for soluble fractions of selected metals. An ICP-OES was used to measure cadmium, cobalt, chromium, copper, iron, manganese, nickel, strontium, vanadium and zinc. The ICP was optimized for the analysis of the softer elements (Na, K, Mg, and Ca), however, low ppb detection limits for selected metals could be obtained under these conditions. A second method was developed and optimized for metals only. A NIST 1643e trace elements in water standard reference solution was used to validate this approach. In addition, the CAL participated in three NWRI trace metal round robin studies using this method. Twenty weeks of CAL internal bucket, sample bottle, and lid blank samples and 118 pairs of USGS external field blank samples were analyzed to identify background concentration levels for the selected metals. Concentrations well above the detection limits were found for copper and zinc in USGS field blank control solutions. Higher levels of copper and zinc were found in the bucket portion of the USGS field blank compared to bottle portion. This finding indicates that copper and zinc are being leached from the bucket. The average concentration for copper in the bucket field blank was 76 ppb compared to 2 ppb for the bottle field blank sample pair. The average concentration for zinc in the bucket field blank was 16 ppb compared to a value <DL for the bottle field blank sample pair. The deionized water matrix USGS bucket/bottle pair resulted in 5 ppb for copper, < 1 ppb for iron, and 2 ppb for zinc. This strongly suggests that these metals are being leached from the buckets when acidic matrices are used. Copper and zinc levels near the DL were found in internal CAL blank samples (buckets, Nalgene 1-liter sample bottles, and bucket lid blank samples). All other metals were <DL for the samples evaluated.

Objective

We obtained a Varian Vista Pro ICP-OES in 2003. After extensive testing, the ICP-OES was approved to go on-line in January of 2004. It's primary use is to analyze sodium, potassium, calcium and magnesium in weekly precipitation samples for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Our primary goal of this research was to expand the use of the ICP-OES. Our ICP-OES is capable of analyzing up to 73 elements simultaneously with one injection of sample. Since our samples are not preserved and are filtered, we acknowledge that we may only see the dissolved fraction of metals, this fraction will also be dependent upon the overall sample pH. By adding additional calibration lines for metals to our current method, we are able to screen all samples semi-quantitatively for metals. We also developed and tested a quantitative method to further evaluate samples that are identified to have metals in them by our semi-quantative method.

Experimental Section

We conducted analyses on a Varian ICP-OES Vista Pro. We have a minerals method in place to analzye sodium, potassium, calcium and magnesium in weekly deposition samples from the NADP/National Trends Network (NTN). To this method, we added calibration lines for cadmium, cobalt, chromium, copper, iron, manganese, nickel, strontium, vanadium, and zinc initially and in the summer of 2006 we also added lines for silver. This method will be referred to as M2. This method is our semiquantitative method. We added an additional method which includes all of the metals for M2, but left out the minerals, this method will be referred to as M1. This method is quantitative. We have participated in three NWRI trace metal round robin studies using this method for verification. The instrument operating parameters shown below are different for each method. M1 has been optimized for metals analysis and M2 has been optimized for minerals analysis. We used cesium added via a metered pump for ionization suppressant and yttrium for an internal standard, this was done for both methods. We analyzed weekly precipitation samples from the NADP/NTN) using M2 in order to screen the samples and observe what dissolved fraction of metals we might see in these samples. These samples are not preserved with acid, they are collected weekly in HDPE buckets and kept at room temperature. Once received by the laboratory, they are filtered through 0.45 micrometer filters into 60 mL HDPE bottles and maintained at room temperature until analysis has been completed and the data validated. We analyzed blanks for buckets, sample bottles prepared in-house and also pairs of external field blanks to determine background levels.

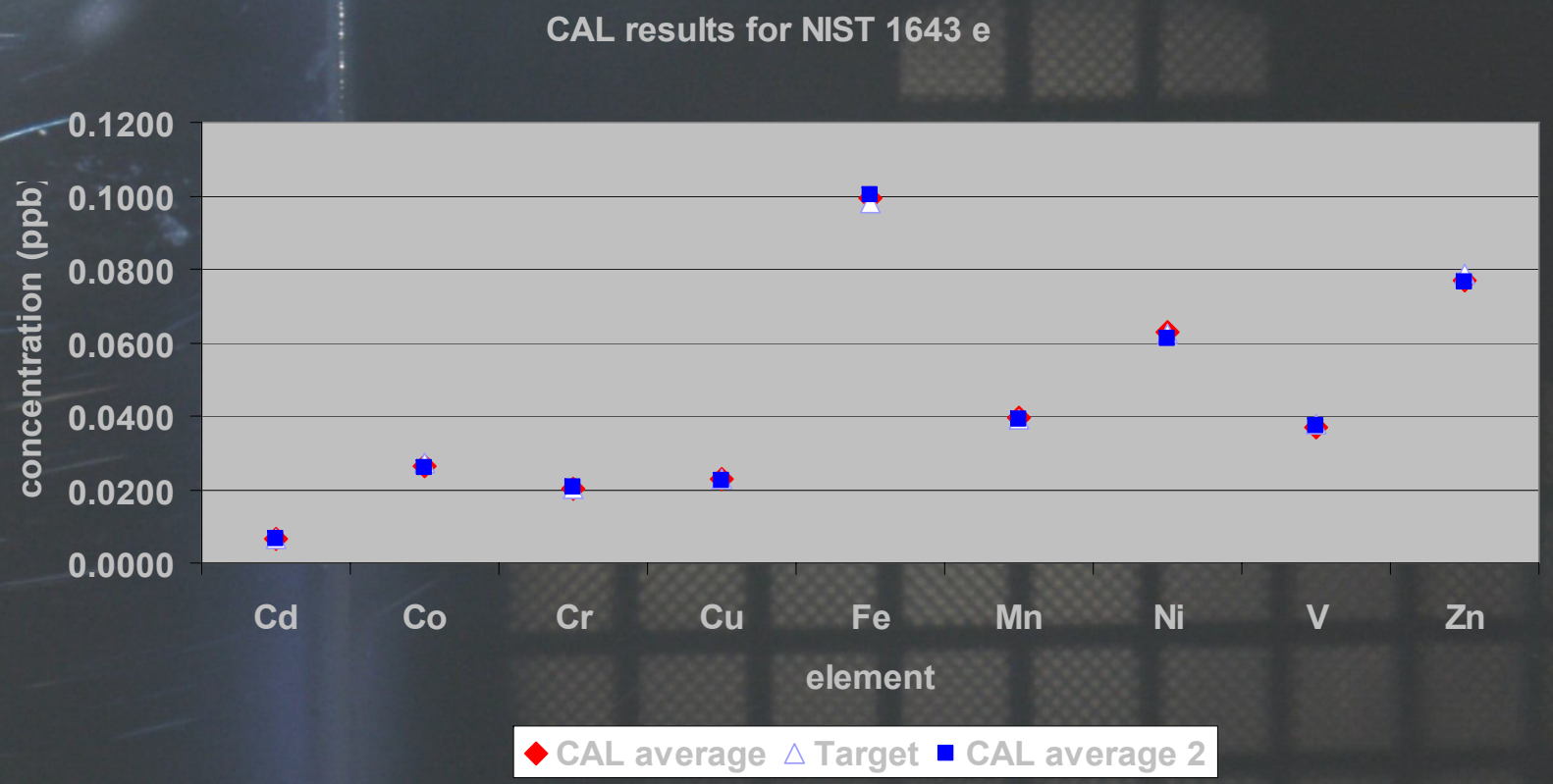
Instrument parameters

- Power 1.00 kW
- Plasma flow 15.0 L/min
- Auxiliary flow 1.50 L/min
- Neb flow 1.15 L/min

- Power 1.25 kW
- Plasma flow 15.0 L/min
- Auxiliary flow 1.50 L/min
- Neb flow 0.75 L/min

Metal	Detection limits with M2 (ppm)	Detection limits with M1 (ppm)
Silver	0.002	Undetermined
Cadmium	0.003	0.001
Cobalt	0.003	0.001
Chromium	0.003	0.002
Copper	0.003	0.002
Iron	0.002	0.001
Manganese	0.001	0.0008
Nickel	0.010	0.002
Strontium	0.0001	0.001
Vanadium	0.003	0.0008
Zinc	0.004	0.0009

Instrument detection limits determined by analyzing blank samples 7 times over a period of several days with varying instrumental conditions.



The CAL has used a NIST 1643 e trace elements in water to validate it's metals only method. This graph shows the average results obtained by the CAL for validation when participating in two NWRI trace metal round robin studies.

NWRI sample #1	Cd	Co	Cr	Cu	Fe	Mn	Ni	Sr	V	Zn
upper warning limit	0.00227	0.00428	0.00615	0.00755	0.0234	0.00762	0.01193	0.0797	0.00384	0.0347
M1 average	0.00198	0.00322	0.00437	0.00499	0.0162	0.00709	0.00906	0.0719	0.00249	0.0300
M2 average	0.00212	0.00375	0.00526	0.00627	0.0193	0.00735	0.0105	0.0758	0.00317	0.0324
assigned value	0.00190	0.00353	0.00490	0.00611	0.0175	0.00697	0.00978	0.0700	0.00307	0.0282
lower warning limit	0.00153	0.00278	0.00365	0.00467	0.0116	0.00632	0.00763	0.0603	0.00230	0.0217

The CAL has participated in three NWRI trace metals studies, results obtained from the M1 method were sent. We are awaiting for the most recent evaluation to be completed, but have received an overall rating of good and satisfactory for the 1st and 2nd study that we participated in. The table above compares our results from both methods for one of the NWRI samples The results are shown with 3 significant figures just for comparison purposes.