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Low Level Analysis of Base Cations in Precipitation Samples: Flame Atomic Absorption Spectroscopy vs. Inductively Coupled Plasma-Atomic Emission Spectroscopy

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Abstract

This study was conducted to evaluate the use of ICP-AES to replace flame-AAS for ppb level base cation analysis in precipitation samples. Sodium, potassium, calcium and magnesium were investigated. A Varian SpectrAA-800 was used for flame-AAS analysis and a Varian VISTA-PRO CCD Simultaneous ICP-AES for ICP analysis. Samples analyzed were from a long-term environmental monitoring program, therefore method changes must be 'equivalent or better' to minimize step function changes in the data set. Samples were filtered through 0.45 µm Gelman polyethersulfone filters and stored at ambient temperature prior to analysis. FAAS required the addition of a releasing agent (lanthanum chloride) for magnesium and calcium, and an ionization suppressant (cesium chloride) for sodium and potassium. ICP-AES did not require a releasing agent for magnesium and calcium due to the high temperature of the plasma, however, an ionization suppressant (cesium chloride) and an internal standard (yttrium) were used. These were combined and metered via a pump into the sample introduction stream to the plasma. For FAAS, 50 µL of either the ionization suppressant or the releasing agent was added to each sample prior to analysis. QA/QC and routine samples were analyzed in parallel by both methods. Alternate wavelengths can also be monitored with ICP to determine interferences. None were observed during this study.

Introduction

The purpose of this study was to conduct a side-by-side analysis of rain samples collected for the National Atmospheric Deposition Program/National Trends Network. The analysis of 212 samples was completed utilizing Flame Atomic Absorption Spectroscopy (FAAS) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Previously, the analysis of calcium, magnesium, sodium and potassium had been performed utilizing Flame Atomic Absorption Spectroscopy. Recent developments in ICP-AES have extended its usefulness for the analysis of minerals. The use of an ICP-AES offers distinct advantages compared to FAAS. First, the linear dynamic range is extended as multiple wavelengths are available for use. Secondly, all four minerals can be analyzed simultaneously with the ICP-AES saving time and sample volume.

Bias #1

	Calcium ICP	Calcium AA	T-Test Pass or No Pass	Potassium ICP	Potassium AA	T-Test Pass or No Pass	Sodium ICP	Sodium AA	T-Test Pass or No Pass	Magnesium ICP	Magnesium AA	T-Test Pass or No Pass
1	0.169	0.162	P	0.115	0.114	P	0.4791	0.490	P	0.076	0.076	P
	0.169	0.169		0.112	0.112		0.483	0.483		0.078	0.078	
	9	9		9	9		9	9		9	9	
2	0.050	0.050	P	0.018	0.019	P	0.038	0.040	P	0.015	0.015	P
	0.05	0.050		0.019	0.019		0.039	0.039		0.015	0.015	
	9	9		9	9		9	9		9	9	
3	0.807	0.750	P	0.293	0.295	P	1.323	1.324	P	0.248	0.243	P
	0.790	0.790		0.290	0.290		1.320	1.32		0.250	0.250	
	9	9		9	9		9	9		9	9	

ata presented reflects the average data for three samples of varying concentration levels which were analyzed in triplicate on three different days on each instrument. The analyses were completed on the same day for both instruments.

Bias #2

Calcium ICP	Calcium AA	T-Test Pass or No Pass	Potassium ICP	Potassium AA	T-Test Pass or No Pass	Sodium ICP	Sodium AA	T-Test Pass or No Pass	Magnesium ICP	Magnesium AA	T-Test Pass or No Pass
0.460	0.437	P	0.061	0.062	P	0.351	0.351	P	0.070	0.069	P
0.46	0.46		0.062	0.062		0.344	0.344		0.070	0.070	
3	3		3	3		3	3		3	3	
0.461	0.439	P	0.061	0.062	P	0.355	0.357	P	0.069	0.069	P
0.46	0.46		0.062	0.062		0.344	0.344		0.070	0.070	
3	3		3	3		3	3		3	3	
0.460	0.433	P	0.061	0.061	P	0.355	0.35	P	0.069	0.068	P
0.46	0.46		0.062	0.062		0.344	0.344		0.070	0.070	
3	3		3	3		3	3		3	3	
0.460	0.438	P	0.062	0.061	P	0.357	0.358	P	0.068	0.067	P
0.46	0.46		0.062	0.062		0.344	0.344		0.070	0.070	
3	3		3	3		3	3		3	3	

ta presented reflects the average data for the analysis of samples from the USGS Interlaboratory Comparision Study. The samples were analyzed in triplicate on the same day on each of the instruments.

Bias #3

Calcium ICP	Calcium AA	T-Test Pass or No Pass	Potassium ICP	Potassium AA	T-Test Pass or No Pass	Sodium ICP	Sodium AA	T-Test Pass or No Pass	Magnesium ICP	Magnesium AA	T-Test Pass or No Pass
0.012	0.010	P	0.049	0.051	NP	0.19	0.196	P	0.020	0.020	P
.014 ±.001	.014 ±.001		.050 ±.002	.050 ±.002		.20 ±.01	.20 ±.01		.022 ±.001	.022 ±.001	
8	8		8	8		8	8		8	8	
0.054	0.054	P	0.102	0.102	P	0.397	0.39	P	0.050	0.050	P
.055 ±.001	.055 ±.001		.093 ±.003	.093 ±.003		.40 ±.01	.40 ±.01		.051 ±.001	.051 ±.001	
8	8		8	8		8	8		8	8	
0.169	0.168	NP	0.031	0.032	P	0.068	0.068	P	0.030	0.029	NP
.164 ±.035	.164 ±.035		.030 ±.028	.030 ±.028		.067±.021	.067±.021		.030 ±.0096	.030 ±.0	
8	8		8	8		8	8		8	8	

e data presented is the average for three NIST traceable reference samples. The samples were ran on various days on each of the instruments.

Recovery

	Calcium	Potassium	Sodium	Magnesium
ay 1	100%	88%	98%	100%
ay 2	104%	96%	102%	99%
ay 3	101%	94%	96%	99%
verage ecovery	**101%**	**93%**	**99%**	**99%**

Four 20 mL precipitation samples were each spiked at the 25th percentile level and measured three times on different days. The background concentration (subtracted from the results) was determined by analyzing the precipitation sample without spiking

MDL

	MDL for FAAS	MDL for ICP-AES
Calcium	0.015	0.001
Potassium	0.006	0.001
Sodium	0.003	0.002
Magnesium	0.003	0.0004

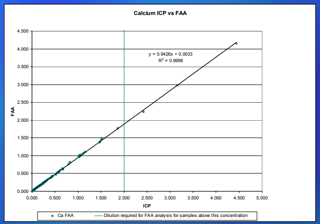
This table shows the MDL's determined in accordance with the NADP CAL Quality Assurance Plan (2002). FAAS results were determined in 2002 and ICP-AES results were determined in 2003. 8

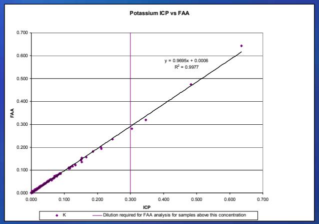
Method

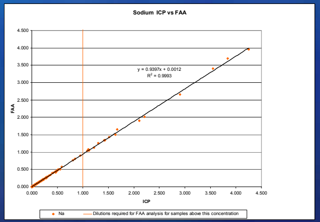
- The samples to be analyzed were determined by selecting sites from each of the 18 USGS hydrologic regions. Sites from Alaska, Hawaii, Puerto Rico, Virgin Islands and AIRMon site (IL11) were added as additional regions. Sites were selected from each of the four NADP site classifications: I (isolated) R (rural), S (suburban) and U (urban) in addition to coastal sites whenever possible and were selected to allow for an even distribution of each of the four seasons. Ultimately samples that were pulled for analysis came from both the current sample inventory as well as the archived samples.
- 212 samples were analyzed on the same day on each instrument.
- Method Detection and Control Limits for the instrument were determined prior to sample analysis.
- In addition to detection and control limits, bias, precision, and recovery encompassed the parameters evaluated during this study.

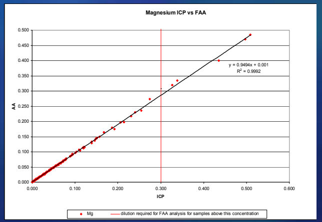
Results

- The data sets from the FAAS and ICP-AES were subjected to the Wilcoxon-Mann-Whitney Rank Sum Test. The results show that there was not a statistically significant difference between the data.
- The data from the ICP-AES was plotted vs. the data from the FAAS for each of the four analytes. The correlation coefficients are .999 for calcium, sodium and magnesium, and .998 for potassium.









Instrumentation

FAAS vs. ICP-AES

- Atomic Absorption Spectroscopy
- Air/Acetylene Flame 2300 K
- Each analyte analyzed separately
- CsCl modifier for sodium and potassium and $LaCl_3$ modifier added for calcium and magnesium
- Modifier added via pipette to each sample.
- Samples poured twice
- Samples above calibration range diluted and reanalyzed

- Atomic Emission Spectroscopy
- Argon Plasma 6000-7000 K
- Simultaneous analysis of all four elemen
- CsCl modifier for all analytes
- Modifier added via pump
- Samples poured once, so consuming less sample volume
- Expanded linear range eliminates the ne dilute most samples
- Lower detection limits
- Faster analysis time
- Unattended analysis possible

Linear Range

FAAS	ICP-AES
Ca 0 - 2.0 ppm	Ca 0 - 25 ppm
K 0 - 0.30 ppm	K 0 - 25 ppm
Na 0 - 2.0 ppm	Na 0 - 25 ppm
Mg 0 - 0.30 ppm	Mg 0 - 25 ppm

Precision

These tables contains the average, standard deviation (s), number of analyses (n), and lower and upper control limits calculated as 3σ for our in-house QC solution. These solutions represent the 10th, 25th, & 75th percentile concentration level for NADP/NTN rain samples.

10th Percentile	Parameter	- Control	Mean	+ Control	s	n
	Calcium AA	0.011	0.026	0.041	0.005	10
	Calcium ICP	0.030	0.031	0.032	0.0004	21
	Potassium AA	- 0.001	0.005	0.011	0.002	10
	Potassium ICP	0.003	0.004	0.006	0.0004	2
	Sodium AA	0.015	0.018	0.021	0.001	10
	Sodium ICP	0.016	0.018	0.021	0.001	21
	Magnesium AA	0.003	0.006	0.009	0.001	10
	Magnesium ICP	0.006	0.007	0.008	.0002	21

25th Percentile	Parameter	- Control	Mean	+ Control	s	n
	Calcium AA	0.060	0.069	0.078	0.003	10
	Calcium ICP	0.073	0.076	0.079	0.001	16
	Potassium AA	0.008	0.014	0.020	0.002	10
	Potassium ICP	0.011	0.013	0.015	0.001	16
	Sodium AA	0.040	0.046	0.052	0.002	10
	Sodium ICP	0.043	0.046	0.050	0.001	16
	Magnesium AA	0.013	0.016	0.019	0.001	10
	Magnesium ICP	0.016	0.017	0.018	0.0003	16

75th Percentile	Parameter	- Control	Mean	+ Control	s	n
	Calcium AA	0.270	0.288	0.306	0.006	10
	Calcium ICP	0.291	0.302	0.313	0.004	16
	Potassium AA	0.049	0.055	0.061	0.002	10
	Potassium ICP	0.049	0.055	0.061	0.002	16
	Sodium AA	0.174	0.186	0.198	0.004	10
	Sodium ICP	0.171	0.187	0.202	0.005	16
	Magnesium AA	0.059	0.065	0.071	0.002	10
	Magnesium ICP	0.066	0.070	0.073	0.001	16