

Intercomparison Of Aeolian Dust Elemental Concentrations Via PIXE And ICP-AES

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Abstract. In this study we compare elemental concentrations of aeolian dust samples obtained via PIXE with elemental concentrations obtained via ICP-AES. Bulk dust samples were collected at Owens (dry) Lake, California during a sequence of three separate wind events in March 1993 along a 1.2km north-south transect. The samples were analyzed by Proton Induced X-ray Emission (PIXE) as solid pressed pellets and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) after digestion. PIXE analyses revealed the presence of 19 elements; additional trace elements were detected at ppm levels by ICP-AES. Al, K, Ti, Mn, Fe, Ni, Cu, Zn, As, and Sr were detected by both analytical techniques. Ba, Pb, Cr, Co, Mo and Cd were detected by ICP-AES only and Na, Si, Ca, S, Mg, Cl, Rb, Br, Ga were detected by PIXE only. PIXE revealed higher concentrations in most of the elements than ICP-AES. For instance, Al was at least 75% higher via PIXE than ICP-AES and for lower concentration elements such as As, PIXE was at least 27% higher than ICP-AES. Scatter plots and correlation factors depict the differences obtained from each method. The best correlations between the two methods were for Ti, Sr, Zn, and Mn with an R^2 of 0.71, 0.73, 0.79 and 0.86, respectively. Al, Ni, and K presented no correlation with $R^2 = 0.007$, 0.006, and 0.0018, respectively. As and Cu concentrations were predominantly higher in the third dust storm when analyzed by PIXE while Ni was predominantly higher in the third dust storms when analyzed by ICP-AES. Ni was detected by PIXE in 28% of the samples and 100% via ICP-AES. Outliers and variability may be explained by differences in the established detection limits for each analytical method, difference in analytical conditions, differences in sample preparation, and/or cross-contamination from sampling instruments.

Keywords: quality assurance, ICP-AES, detection limits, dust, California.

INTRODUCTION

Elemental concentrations of aeolian dust samples measured via Proton- Induced X-Ray Emission (PIXE) and Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) were intercompared to determine the association and strength of elemental concentrations obtained by the two different analytical techniques and to explore possible causes of variability in data results.

METHODOLOGY

Airborne dust samples were collected at Owens (dry) Lake, California, during an international aerosol campaign. Elemental analysis of these samples was performed via PIXE and ICP-AES.

Sample collection

Samples were collected during three sequential wind storms at Owens Lake, California at six heights in seven locations along a 1.2 km long transect (1,2). Refer to the paper in these proceedings titled "Particle Size/Composition Relationships Of Wind-Eroding Sediments, Owens Lake, California, USA" for the detailed sample collection method.

PIXE sample preparation and analysis

Samples for PIXE analysis were first pulverized in a corundum mortar and pestle. An aliquot of approximately 1 gram of each pulverized sample was pelletized into a 2.5 cm disk between two Kapton films. PIXE analysis was performed by a General

Ionex 4 MV tandem accelerator with a duoplasmatron source capable of producing beam currents in the range of a few nanoamps to tens of microamps, a dual quadrupole focusing lens, an x-y beam scanner to insure beam homogeneity, a beam pulser with 50 ns response time and a vacuum/helium chamber with internal dimensions of 20" w x 16" l x 8" h. Data acquisition was accomplished by use of a computer driving a CAMAC crate front ended with a 150 eV resolution, 30 mm² Si(Li) detector for X-ray collection and Au surface barrier detector to monitor scattered protons. Samples were irradiated using a 1.6 cm collimator to enhance overall response for elements and to reduce potential for homogeneity issues. Each pellet was subjected to irradiation such that it was subjected to a minimum number of proton counts (typically 1 million per sample).

Data reduction was accomplished with a modified version of software developed at the University of Guelph (3). The efficacy of the analyses was verified using USA National Institute of Standards and Technology Standard Reference Material 2711, Montana II Soil, which was pelletized and analyzed under the same conditions during the same run.

ICP-AES sample preparation and analysis

The sample analysis was conducted with a Leeman Labs inductive coupled plasma – atomic emission spectrometer. Samples were prepared as per U.S. Environmental Protection Agency (EPA) Method 3050B and analyzed per EPA Method 6010B.

RESULTS

The elements detected by PIXE and ICP-AES analyses are presented in Table 1.

TABLE 1. Reported elements by PIXE and ICP-AES.

PIXE Only	ICP-AES Only	Both analytical techniques
Bromine	Barium	Aluminum
Calcium	Cadmium	Arsenic
Chlorine	Chromium	Copper
Gallium	Cobalt	Iron
Magnesium	Lead	Manganese
Rubidium	Molybdenum	Nickel
Silicon		Potassium
Sodium		Strontium
Sulfur		Titanium
		Zinc

Possible Causes for Variability

1. Detection limits (DLs): DLs for PIXE are established on a per sample basis and are dependent upon the atomic number, matrix interferences, detector efficiency, proton beam intensity and irradiation time. DL for ICP-AES are based on EPA Method 200.8
2. Differences in analytical conditions
3. Differences in sample preparation:
 - a. solid pressed pellets for PIXE
 - b. acid digestion for ICP-AES per EPA Method 3050B
4. Cross-contamination from instruments
5. Data manipulation

Assessment of DL based on atomic number and ICP-AES measurements

In PIXE, X-ray production cross-sections decrease with increasing atomic number, influencing DLs. Table 2 shows the reported elements by increasing atomic number.

TABLE 2. Reported elements atomic number.

Method	Element	Atomic #	Method	Element	Atomic #
PIXE	Sodium	11	both	Nickel	28
PIXE	Magnesium	12	both	Copper	29
both	Aluminium	13	both	Zinc	30
PIXE	Silicon	14	PIXE	Gallium	31
PIXE	Sulfur	16	both	Arsenic	33
PIXE	Chlorine	17	PIXE	Bromine	35
both	Potassium	19	PIXE	Rubidium	37
PIXE	Calcium	20	both	Strontium	38
both	Titanium	22	ICP-AES	Molybdenum	42
ICP-AES	Chromium	24	ICP-AES	Cadmium	48
both	Manganese	25	ICP-AES	Barium	56
both	Iron	26	ICP-AES	Lead	82
ICP-AES	Cobalt	27			

Table 2 shows a possible correlation with increasing atomic number and decrease in X-ray production cross-sections, therefore impacting the established detection limits. This, however, does not necessarily infer that high atomic numbers are the culprit for non-detection of some of the elements detected by ICP-AES.

Elements present in low concentrations may not be detected when higher DLs are established, as in Fig. 1 – Fig 3. These charts compare PIXE DLs with actual ICP-AES measurements for Mo, Cr and Ni. In general, the minimum DLs for PIXE were higher than the concentrations measured by ICP-AES. This coupled with high atomic numbers may better explain non-detection of these elements by PIXE.

Assessment of EPA Method 3050B

Determinative techniques under this method, used for ICP-AES sample preparation, do not account for bromine, chlorine, gallium, rubidium and sulfur. This explains non-detection of these elements by ICP-AES. Calcium, sodium, magnesium and silicon are major elements and may require different sample preparation. These elements were purposefully omitted in the analysis. Other elements such as Be, V, Se, Na and Mg were also detected by ICP-AES, but were dropped due to poor calibration readings.

Association and strength of PIXE and ICP-AES measurements

Scatter plots and correlation factors depict the differences obtained from each method. The best correlations between the two methods were for Ti, Sr, Zn, and Mn with an r^2 of 0.76, 0.86, 0.84 and 0.87, respectively (see Fig 4 and Fig. 5). Nickel presented no association with an r^2 of .06.

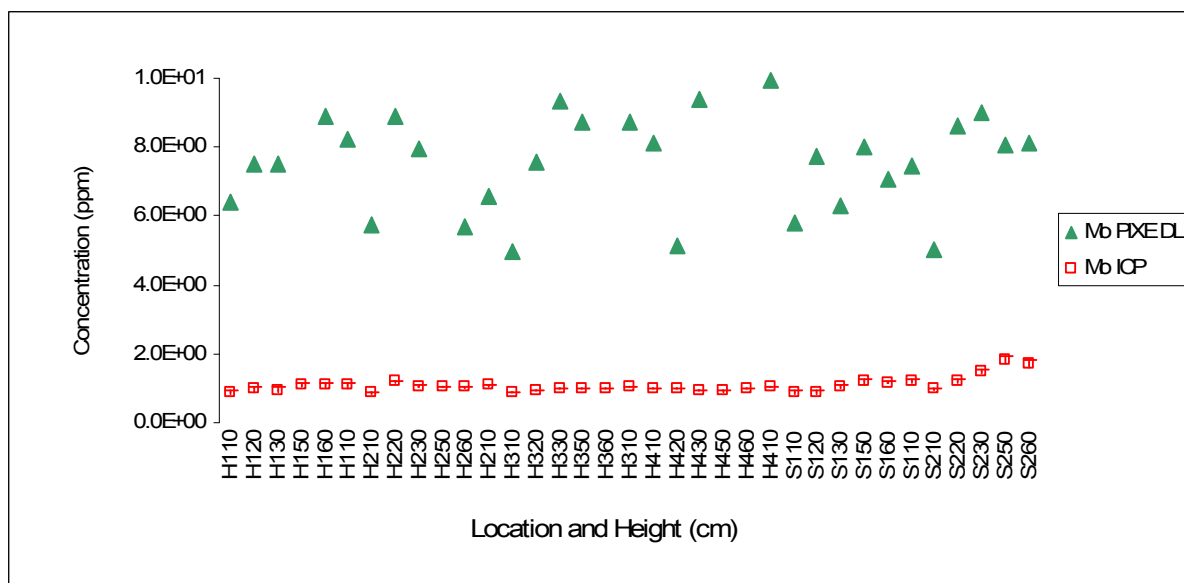


Figure 1. PIXE DLs vs. ICP-AES concentrations for Mo.

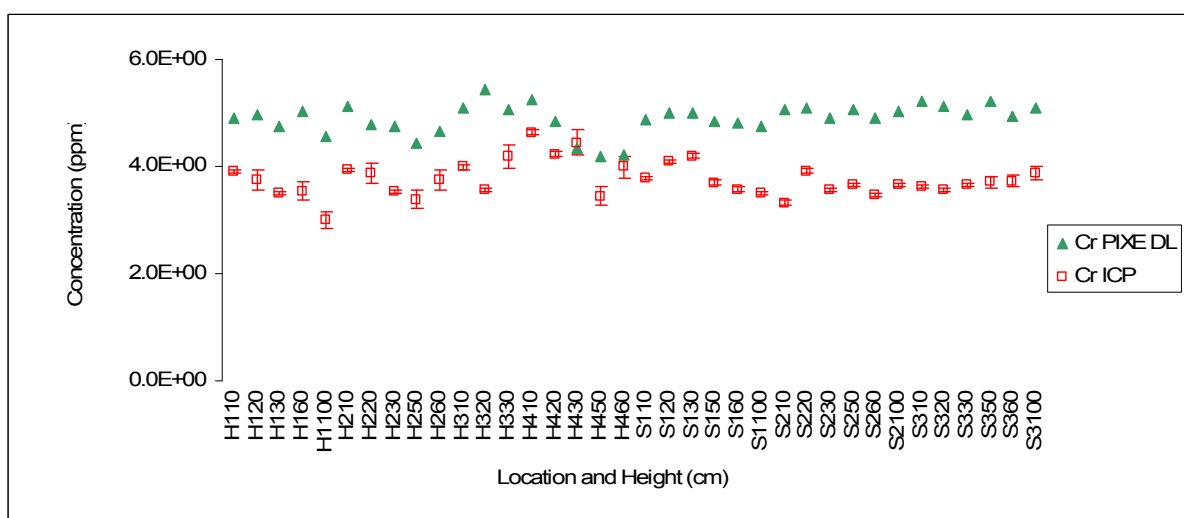


Figure 2. PIXE DLs vs. ICP-AES concentrations for Cr.

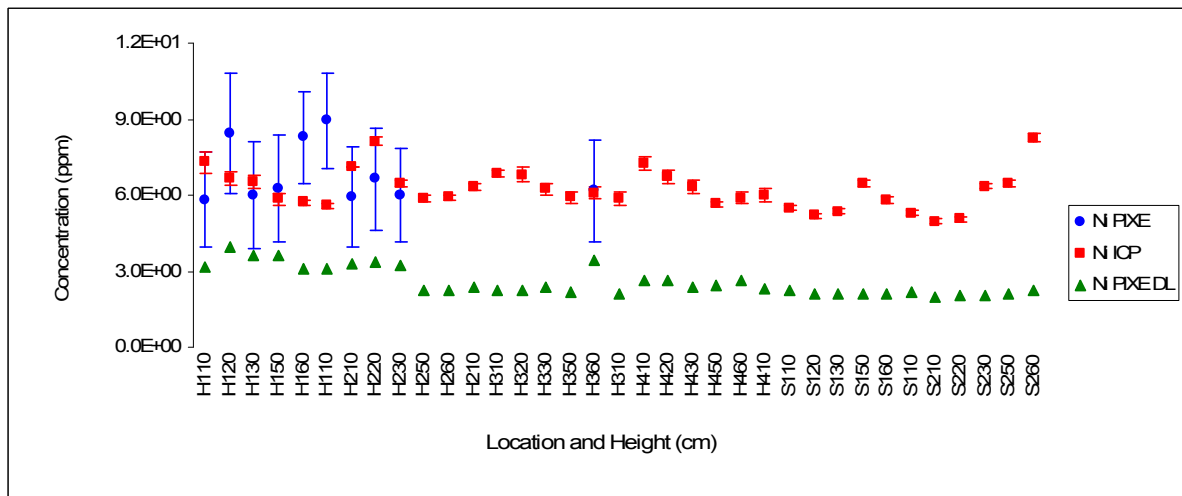


Figure 3. PIXE DLs vs. ICP-AES concentrations for Ni.

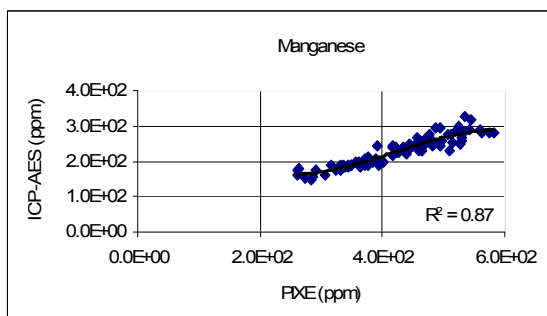


Figure 4. Mn correlation (ppm).

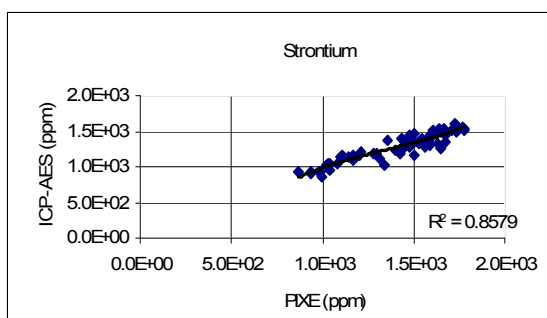


Figure 5. Sr correlation (ppm).

DISCUSSION

The exploration of possible causes of variability and inter-comparison of data results have established quality assurance techniques that will further assist in data interpretation and will provide a stronger understanding of the differences in analytical

techniques. This evaluation has also exposed the importance of proper data manipulation to assure data integrity and proper data comparison to include percent error, adequate concentration units, and consideration of detection limits. When economically feasible, the use of more than one technique may serve as quality assurance and may yield valuable results. It is of essence however, to clearly define the scope and purpose of the study and to become familiar with the capabilities and limitations of each analytical technique prior to sample analysis.

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