

# **Evaluation of Inductively Coupled Plasma (ICP) False Positives for Arsenic and Trace Metals Analysis in Coal Ash and Coal Ash Media**

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**KEYWORDS:** arsenic, coal ash, fly ash, SPLP, ICP, ICP/MS, leaching, TCLP, hydride, dynamic reaction cell; DRC

## **ABSTRACT**

The phenomenon of potential bias in EPA Method 6010 analysis of environmental samples via Inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy has long been documented. The potential for biased results, in the case of arsenic, is due to the fact that a relatively weak primary emission wavelength for arsenic is overlapped by one of several strong emission lines for aluminum. Even though a 2001 U.S. Environmental Protection Agency Office of Technical Standards Alert estimated that environmental data reported using ICP may have a false-positive rate for arsenic of 25 to 50 percent, this phenomenon still receives sparse attention. One possible reason is that EPA methods provide language that interelement correction factors and background correction mechanisms should adequately compensate for these 'spectral interferences. As a result, the regulated community has often forgotten or overlooked this issue, and many may be unaware of it at all. Decision making based on data with a false positive bias could result in costly, unnecessary response actions.

This paper presents the results of coal ash, coal ash media, and other environmental sample analysis by EPA Method 6010 and EPA Method 6020 (ICP/MS), as well testing via hydride generation and an Method 6020 modification utilizing a dynamic reaction cell (DRC). An evaluation of potential method bias and consideration of spectral interferences is also included.

## **INTRODUCTION**

Arsenic occurs naturally in trace amounts in rocks, sediments, and coal. Waters in contact with these materials have resulted in the identification of naturally occurring sources of arsenic in groundwater resources in the United States (US). A limited United States Geological Survey (USGS) study of 18,850 wells reported that the highest arsenic concentrations of arsenic in groundwater were generally identified in the West, with parts of the Midwest and Northeast also exceeding 10 ug/L<sup>1</sup>.

Pyrite, a common mineral composed of iron and sulfur, can exhibit some structural replacement of sulfur with small amounts of arsenic, and is a widespread natural source of arsenic. Arsenic is often the most abundant micro element in pyrite and may comprise as high as 10 wt. % on a micro scale<sup>2,3</sup>. Pyrite is the primary source of arsenic in bituminous coal, with lesser contributions from the organic portions<sup>4</sup>.

Arsenic's strong affinity to concentrate in sulfide minerals is well documented in some coals, but it has been reported that its mode of occurrence in fly ash is less predictable<sup>5</sup>. The mode of occurrence of arsenic in fly ash is largely dependent upon the original coal source and the associated coal combustion conditions. At the temperature of coal combustion, arsenic is initially transferred to the gas phase and then deposited on fly ash particles by a mechanism of surface condensation/adsorption<sup>6</sup>. Compared to other elements in ash, arsenic enrichment is strong (5 to 10 times) in the finest (< 10 um) size fractions<sup>6,7</sup>. A comparison of average arsenic content in US coals by basin indicates mean concentrations ranging from 1.4 parts per million (ppm) to 71 ppm<sup>4</sup>. Literature values reported for arsenic in fly ash range from 2 ppm to 440 ppm<sup>8</sup>. Evaluating the relationship between feed coal and its fly ash is complicated by the fact the coal blends are commonly used to fire boilers in the US<sup>9</sup>. Coal fly ash samples evaluated in this study include both US and South American samples that were generated from blended feed coal.

## POTENTIAL ANALYTICAL INTERFERENCES

All methods developed for analytical determinations of trace contaminants in environmental samples are subject to physical, chemical, and/or spectral interferences. For example, extensive spectral wavelength tables have been published from data collected from dc arc, high voltage spark, and discharge tube excitation sources, such as the National Bureau of Standard's tables<sup>10</sup> (39,000 lines) and the Massachusetts Institute of Technology (MIT) Wavelength Tables<sup>11</sup> (approximately 110,000 lines). These tables are invaluable for interpretation of spectra in spectroscopic techniques, although only the more "prominent" lines are generally used in day to day ICP quantification considerations<sup>12</sup>. Nevertheless, it is noteworthy that the author of the comprehensive MIT tables recognized in 1939 as having included "only half of the known spectrum lines in the region covered" and later that "...successor tables should contain information on at least ten times as many lines as are listed herein, grouped both as to parent atom and its stage of ionization, and in order of wavelengths."

In summary, elements analyzed by ICP may be impacted by other elements which have direct spectral overlap, wing overlap, and nearby emission scatter. For conventional trace metal analysis, basic spectral interferences are documented and can impact a potential false positive or false negative bias on the reported results. An EPA Office of Technical Standards Alert reported in 2001 that the use of the ICP analytical method for drinking water samples may result in false positive detections of arsenic, lead, and or thallium above their respective maximum contaminant levels (MCLs)<sup>13</sup>. EPA also estimated that ICP analytical data for arsenic may have a false positive rate of 25 to

50%<sup>14</sup>. False positive biases were also documented in literature in recent (2010) case studies where method quality control was otherwise acceptable<sup>15</sup>.

EPA Method 6010C recommends the 193.696 nm emission wavelength for arsenic and provides for interelement correction considerations for aluminum, chromium, and vanadium. For this study, method optimization resulted in laboratory selection of an alternate ICP arsenic emission wavelength for arsenic quantitation:

$$\lambda = 189.042 \text{ nm (1890.42 \AA)}$$

ICP-MS is also susceptible to spectral interferences which are termed isobars. Isobars have the same mass/charge ratio as the analyte of interest (AOI) but are not the AOI and cannot otherwise be distinguished. For example<sup>15</sup>, ICP-MS suffers from <sup>40</sup>Ar<sup>35</sup>Cl mass interference on the monoisotopic <sup>75</sup>As.

For the past several decades, the ICP method has been the most commonly used analytical method for routine determinations of trace metals in environmental media. The addition of ICP-MS instrumentation has recently become more prevalent in larger commercial environmental labs. While the use of hydride instrumentation and ICP-MS DRC enhancements are less prone to interferences, these methods are less commonly used in routine environmental analysis. ICP and ICP-MS interferences are of special concern since falsely biased results can lead to incorrect environmental decision making. This study focuses in particular on ICP and ICP-MS data.

## SAMPLE PREPARATION AND ANALYTICAL METHODS

Solid samples were homogenized prior to sample digestion, with fly ash sample homogenization enhanced via use of a ball mill. Solid samples were then prepared via acidic digestion using EPA Method 3050<sup>16</sup>. Four analytical methods were used to test samples in this study, for which potential interferences are well documented in the methods. EPA Method 6010<sup>17</sup> was followed for inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. EPA Method 6020<sup>18</sup> was followed for inductively coupled plasma mass spectrometry (ICP-MS) analysis. Instrumentation for hydride generation atomic fluorescence (HGAF)<sup>19</sup> was used for sample analysis via a method modification of hydride generation atomic absorption EPA Methods 206.3<sup>20</sup> and 1632<sup>21</sup>. ICP-MS instrumentation enhanced with a Dynamic Reaction Cell (DRC)<sup>22</sup> was also utilized. In addition, samples were extracted using the Synthetic Precipitation Leaching Procedure (SPLP), EPA Method 1312<sup>23</sup>, prior to analysis of arsenic in the SPLP extracts.

## SAMPLE SELECTION

Seven representative samples of coal ash were obtained from utility companies operating coal burning units in the continental US. Three samples of uncontaminated, natural clay/silty clay deposits and one sample of uncontaminated gravel deposits were also analyzed in this study. The clay and gravel samples were collected in various locations in Central Connecticut and were included because they were expected to be naturally low in arsenic and naturally high in aluminum.

All samples were given “blind” letter designations (e.g., A, B, C,...) and submitted under Chain of Custody to Alpha Analytical Labs (Westborough, Massachusetts, USA and Mansfield, Massachusetts, USA) for analytical testing. Alpha Analytical Labs, a NELAC certified commercial analytical laboratory, has undergone comprehensive third-party audit and is equipped for the four analytical methods contemplated for this study. The sample sources are summarized in Table I:

SAMPLE DESIGNATION	SAMPLE SOURCE
A	Cerro Largo (Columbia):Paso Diablo (Venezuela) – 1:1 blend
B	Paso Diablo - 100%
C	Loveridge (West Virginia eastern bituminous):Paso Diablo - 2:1 blend
D	Bailey (Pennsylvania eastern bituminous):Paso Diablo – 1:1 blend
E	Virginia/Kentucky eastern bituminous
F	clay/silty clay (Central Connecticut)
G	clay/silty clay (Central Connecticut)
H	clay/silty clay (Central Connecticut)
I	gravel (Central Connecticut)
J	La Jagua (Columbia) - 100%
K	Illinois Basin coal – 100%

## DATA QUALITY

A data quality assessment was performed to assess the overall quality of the data and confirm its usability for this study. The assessment included a preliminary review of instrument performance checks, initial and continuing calibrations, method blanks, laboratory control samples (LCS), LCS Duplicates (LCSD), LCS/LCSD Relative Percent Differences (RPDs), internal standard recoveries, and sample data formatting. Three coal ash samples were also designated for matrix spiking and analysis by both ICP-AES and ICP-MS.

Except in instances where low levels of aluminum in the laboratory spikes were overwhelmed by native sample concentrations, the laboratory reports otherwise indicate that non-conformance issues were not identified for these data. Based on a review of

the method criteria for the laboratory data for precision and accuracy, no data were rejected from consideration and the data are usable without qualification.

### ANALYTICAL RESULTS FOR TOTAL METALS

Average arsenic results in units of mg/kg (dry) for the analysis of the coal ash, clay, and gravel samples by the four analytical methods are shown in Figure 1.

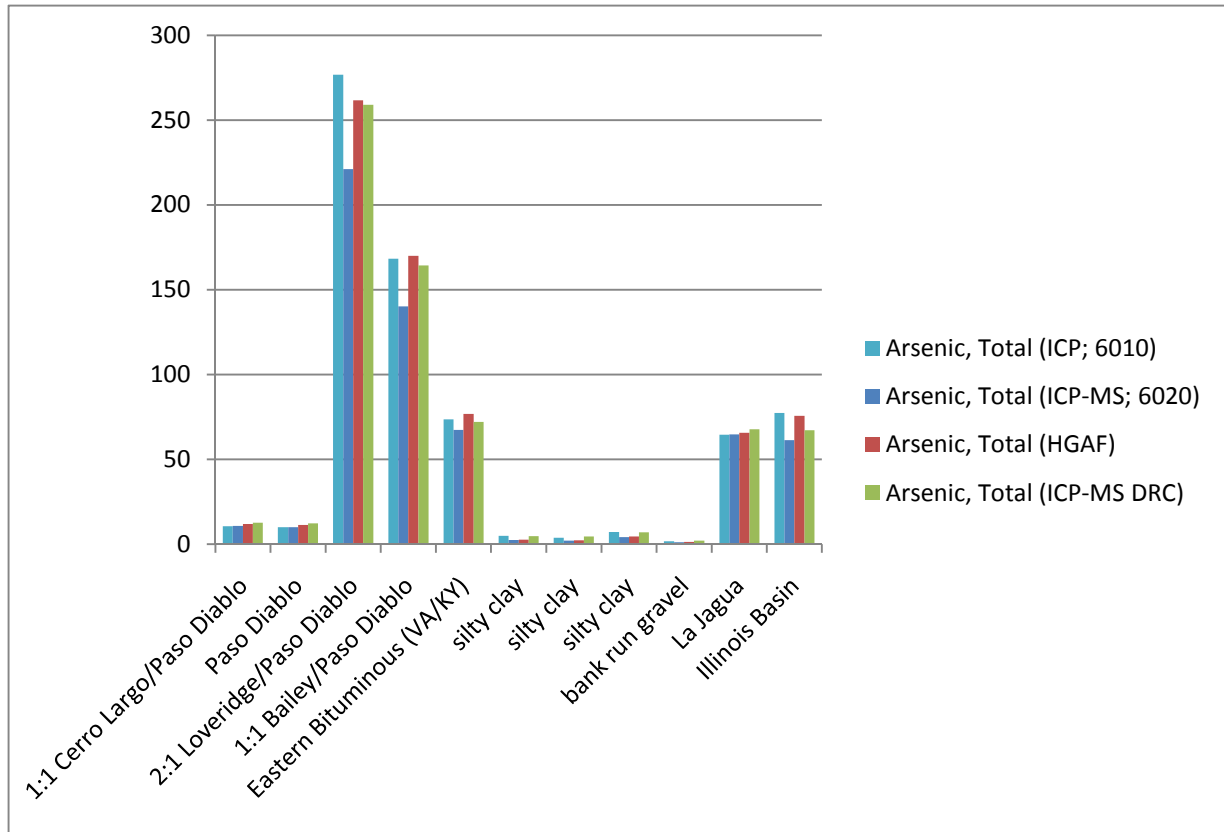


FIGURE 1: AVERAGES OF REPORTED ARSENIC RESULTS (mg/kg, dry)

Reported arsenic concentrations in the coal ash samples ranged from 9.29 mg/kg to 290 mg/kg, with aluminum concentrations ranging from 6,100 mg/kg to 44,000 mg/kg. Reported arsenic concentrations in the clay and gravel samples ranged from 1.09 mg/kg to 7.6 mg/kg, with aluminum concentrations ranging from 9,400 mg/kg to 40,000 mg/kg. Individual sample arsenic and aluminum analytical results are summarized by sample in Tables II through XII.

TABLE II - SUMMARY OF ANALYTICAL RESULTS CERRO LARGO (COLUMBIA):PASO DIABLO (VENEZUELA) – 1:1 BLEND					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
A REP 1	11	10.6	11.7	12.7	7,000
A REP 1	11	11.4			7,300
A REP 2	10	10.2	11.6	12.9	6,900
A REP 2	10	11.0			7,000
A REP 3	11	10.1	12.4	12.6	7,000
A REP 3	10	11.0			7,200
AVERAGE	10.5	10.7	11.9	12.73	7,067

All results in mg/kg, dry.

TABLE III - SUMMARY OF ANALYTICAL RESULTS PASO DIABLO (100%)					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
B REP 1	10	9.43	10.8	12.6	6,100
B REP 1	10	10.40			6,600
B REP 2	10	9.50	11.4	12.2	6,400
B REP 2	10	10.40			6,600
B REP 3	10	9.29	11.7	12.3	6,400
B REP 3	10	10.50			6,600
AVERAGE	10	9.92	11.3	12.37	6,450

All results in mg/kg, dry.

TABLE IV - SUMMARY OF ANALYTICAL RESULTS LOVERIDGE (WEST VIRGINIA EASTERN BITUMINOUS):PASO DIABLO - 2:1 BLEND					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP-MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP-MS DRC)	Aluminum, Total (ICP; 6010)
C REP 1	270	178	252	255	40,000
C REP 1	290	259			44,000
C REP 2	270	186	264	260	40,000
C REP 2	270	268			42,000
C REP 3	280	173	269	262	42,000
C REP 3	280	262			44,000
AVERAGE	277	221	262	259	42,000

All results in mg/kg, dry.

TABLE V - SUMMARY OF ANALYTICAL RESULTS BAILEY (PENNSYLVANIA EASTERN BITUMINOUS):PASO DIABLO – 1:1 BLEND					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
D REP 1	170	120	174	163	21,000
D REP 1	170	163			22,000
D REP 2	170	115	169	168	21,000
D REP 2	170	163			22,000
D REP 3	160	122	167	162	20,000
D REP 3	170	158			21,000
AVERAGE	168	140	170	164	21,167

All results in mg/kg, dry.

TABLE VI - SUMMARY OF ANALYTICAL RESULTS VIRGINIA/KENTUCKY EASTERN BITUMINOUS					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
E REP 1	74	59.3	76.8	71.4	9,700
E REP 1	74	74.0			10,000
E REP 2	74	59.8	74.2	71.7	9,800
E REP 2	74	73.7			10,000
E REP 3	73	61.2	79.1	73.0	10,000
E REP 3	73	76.4			11,000
AVERAGE	74	67	76.7	72	10,083

All results in mg/kg, dry.

TABLE VII - SUMMARY OF ANALYTICAL RESULTS CLAY/SILTY CLAY (CENTRAL CONNECTICUT)					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
F REP 1	5.0	2.63	2.31	4.22	22,000
F REP 2	4.7	2.43	2.8	4.93	22,000
F REP 3	4.8	2.53	2.78	4.96	20,000
AVERAGE	4.8	2.5	2.63	5	21,333

All results in mg/kg, dry.



TABLE VIII - SUMMARY OF ANALYTICAL RESULTS CLAY/SILTY CLAY (CENTRAL CONNECTICUT)					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
G REP 1	3.7	2.06	2.16	4.48	23,000
G REP 2	3.5	2.04	2.1	4.40	21,000
G REP 3	3.9	2.31	2.44	4.64	26,000
AVERAGE	3.7	2.1	2.2	4.5	23,333

All results in mg/kg, dry.

TABLE IX - SUMMARY OF ANALYTICAL RESULTS CLAY/SILTY CLAY (CENTRAL CONNECTICUT)					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
H REP 1	7.60	4.04	4.46	7.12	36,000
H REP 2	6.90	4.15	4.68	6.91	34,000
H REP 3	7.20	4.03	4.45	6.73	40,000
AVERAGE	7.23	4.07	4.53	6.92	36,667

All results in mg/kg, dry.

TABLE X - SUMMARY OF ANALYTICAL RESULTS GRAVEL (CENTRAL CONNECTICUT)					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum , Total (ICP; 6010)
I REP 1	1.80	1.10	1.19	2.08	10,000
I REP 2	1.80	1.21	1.38	2.05	9,400
I REP 3	1.80	1.09	1.22	2.07	10,000
AVERAGE	1.80	1.13	1.26	2.07	9,800

All results in mg/kg, dry.

Table XI LA JAGUA (COLUMBIA) – 100%					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
J REP 1	66	59.7	67.8	67.9	8,500
J REP 1	61	71.1			8,200
J REP 2	68	59.6	65.7	68.6	8,600
J REP 2	64	69.1			8,400
J REP 3	66	58.9	63.5	66.8	8,200
J REP 3	62	70.2			8,100
AVERAGE	65	64.8	65.66667	68	8,333

All results in mg/kg, dry.

Table XII ILLINOIS BASIN COAL – 100%					
SAMPLE	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
K REP1	80	62.6	76	69.5	19,000
K REP1	78				19,000
K REP2	79	60.5	75.8	65.2	18,000
K REP2	76				20,000
K REP3	75	61.1	75.3	67.0	17,000
K REP3	76				19,000
AVERAGE	77.3	61.4	75.7	67.2	18,667

All results in mg/kg, dry.

#### ANALYTICAL RESULTS FOR SPLP ARSENIC

Two coal ash samples were submitted for SPLP arsenic analysis by ICP and ICP-MS. These included the 1:1 Bailey:Paso Diablo blend coal ash (blind sample “D”) and the La Jagua coal ash (blind sample “J”). SPLP results for sample D by ICP and ICP-MS were consistent (0.033 mg/L and 0.03 mg/L, respectively). SPLP results for sample J by ICP and ICP-MS were also in the same range (0.011 mg/L and 0.0062 mg/L, respectively). The total and SPLP results for these samples indicate comparably low arsenic leaching by this method.

Individual sample SPLP and total (average) arsenic analytical results are summarized in Tables XIII and XIV.

TABLE XIII - SUMMARY OF SPLP AND TOTAL (AVERAGE) ANALYTICAL RESULTS BAILEY (PENNSYLVANIA EASTERN BITUMINOUS):PASO DIABLO – 1:1 BLEND							
	Arsenic, SPLP (ICP; 6010)	Arsenic, SPLP (ICP; 6020)	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
RESULT	0.033	0.03	168	140	170	164	21,167

SPLP results in mg/L. Total (average) results in mg/kg, dry.

TABLE XIV - SUMMARY OF SPLP AND TOTAL (AVERAGE) ANALYTICAL RESULTS LA JAGUA (100%)							
	Arsenic, SPLP (ICP; 6010)	Arsenic, SPLP (ICP; 6020)	Arsenic, Total (ICP; 6010)	Arsenic, Total (ICP- MS; 6020)	Arsenic, Total (HGAF)	Arsenic, Total (ICP- MS DRC)	Aluminum, Total (ICP; 6010)
RESULT	0.011	0.0062	65	64.8	65.7	68	8,333

SPLP results in mg/L. Total (average) results in mg/kg, dry.

## EXAMINATION OF DATA

In order to assess the ICP and ICP-MS data, basic statistical tests were performed. These calculations were conducted to assess differences between the paired data for the two study groups.

### Null Hypothesis

The natural, variable presence of arsenic in coal and soil has resulted in variable concentrations of arsenic in the samples tested for this study. For the statistical assessment herein, the null hypothesis states that there is no difference between the paired ICP and ICP-MS data sets for arsenic.

### Wilcoxon Signed-Rank Test

The Wilcoxon signed-rank test is a non-parametric statistical hypothesis test for comparing two related sample sets (or repeated measurements on single samples) to assess whether the population means differ. It has long been used for assessing whether two samples are from the same distribution<sup>24,25</sup>. Like the t-test for correlated samples, the Wilcoxon signed-rank test applies to two-sample designs involving repeated measures or matched pairs.

Wilcoxon examination of the entire data set indicates that there is not a significant difference between the ICP and ICP-MS data for arsenic, and that the null hypothesis cannot be rejected. This suggests that the laboratory instrumentation is generally optimized for ICP interelement correction.

Figure 2 presents a log-log plot of the individual ICP and ICP-MS data for arsenic. It is noteworthy that some samples fall above the 1:1 trend line, reflecting that the reported ICP data are higher for these samples. Closer examination of the data sets indicates that these samples contain aluminum at concentrations greater than 20,000 mg/kg.

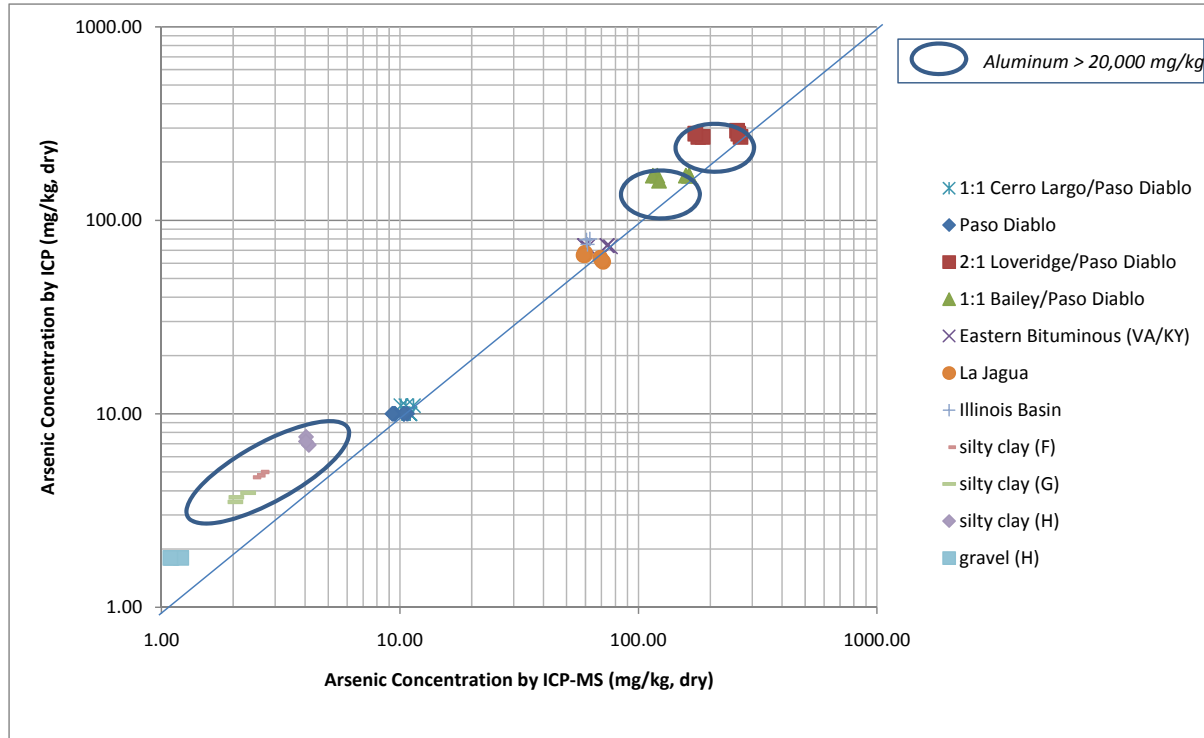


FIGURE 2: PLOT OF INDIVIDUAL ARSENIC RESULTS (mg/kg, dry)

Wilcoxon examination of the data set for samples with greater than 20,000 mg/kg aluminum indicates that there is a significant difference between the ICP and ICP-MS data for arsenic (the ICP data are statistically higher), and that the null hypothesis should be rejected. This suggests that the laboratory instrumentation ICP interelement correction may not adequately compensate for very high native aluminum concentrations (or that some other spectral interference is present). It is also possible that the more sensitive ICP-MS may be subject to greater matrix effects and signal suppression.

## DISCUSSION

Variable concentrations of arsenic are naturally present in certain coal feedstocks and the resulting coal ash. ICP interferences in the analysis of arsenic are well documented and were apparent in the study samples. In this study, a potential false positive bias was observed in the ICP data for samples that were also elevated in naturally occurring aluminum. Statistically elevated concentrations of arsenic were observed for these samples as compared to the ICP-MS data. Since falsely biased results can lead to incorrect environmental decision making, careful review of ICP and ICP-MS results should be undertaken when arsenic is a contaminant of concern.

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