A COMPARISON OF TRACE ELEMENT ANALYSES OF NORTH DAKOTA LIGNITE LABORATORY ASH WITH LURGI GASIFIER ASH AND THEIR USE IN ENVIRONMENTAL ANALYSES

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Abstract

A series of analyses of laboratory prepared ashes of Dunn County, North Dakota, lignite are compared with analyses of Mercer County, North Dakota, lignite gasifier ash from SASOL gasification test for 73 elements. The analyses demonstrate that a need for laboratory ashing technique that simulates gasifier ash probably exists. Of the 73 elements, 33 were found to be common to the leachate of both the gasifier and laboratory ash samples; nine of the 33 were more leachable in the gasifier ash. Approximately 50 of the 73 elements are found in both coals while approximately 20 elements were below the detection limit of 0.1 ppm in both coals.

The use of this data for environmental assessment of groundwater impact is analyzed. It is concluded that this data probably cannot be used to support existing analytical groundwater models due to system complexities and unknowns. An alternative worst case environmental analysis is presented. It is recommended that worst case analyses be pursued rather than sophisticated analytical modeling techniques.

INTRODUCTION

The continuing energy problem is gradually forcing the major investors and industries of the United States to turn to coal conversion technologies for the development of sources of supply of liquid and gaseous fossil fuels and feedstocks. Although the time scale and extent of this development are unknown, it is likely in the author's view, that several coal conversion facilities will be operable by the end of the century. These facilities will probably include major 250 MMSCFD dry ash Lurgi gasification facilities.

Presently, plans for four such facilities are at the detailed design stage. These facilities are El Paso Gasification Company, Wesco Coal Gasification Company, ANG Coal Gasification Company, and Natural Gas Pipeline Company of America. El Paso and Wesco are located in New Mexico while ANG and Natural are located North Dakota. All four have filed Environmental Assessment Reports. The Department of the Interior (DOI) has issued final Environmental Impact Statements for El Paso and Wesco. DOI has issued a draft Environmental Impact Statement for ANG. Natural has issued only an Environmental Assesment Report. All of the companies have studied, to varying degrees, the environmental impacts associated with disposal of the gasifier ash and its entrained water. This paper addresses one of those impacts.

The work reported here deals with the possible leaching of the trace elements from disposed gasifier ash. Although it may be possible to mitigate this potential impact to within acceptable limits through the use of disposal techniques, it is difficult, if not impossible, to conclusively demonstrate that the disposed ash and sludges will behave in a given manner once actually disposed of in the mined area. This is true, in spite of the current mathematical models that exist, largely because of widely varying boundary conditions and the very complex chemical systems that may exist in the post-mining environment.

Because of these difficulties it is probably advisable to attack the question of potential environmental imact utilizing a worst case approach. This approach does not address the question of actual impact, but does allow one to estimate the maximum impact that can reasonably be expected.

The fate of trace and major constituents during gasification has been addressed by Somerville, et al. (1977)[1], (1976)[2], and by Attari, et al. (1976)[3], (1973)[4]. At the conclusion of the work cited above, the authors noted that the analyses of the laboratory prepared ashes and its leachates were considerably different than those of the Lurgi generated ashes and its leachates.

Data are presented below which specifically compare laboratory and actual gasifier ash and their leachates.

It should be pointed out that the data collected were for the purpose of supporting two different Environmental Assessment Reports which at the time of the data collection were unrelated. Consequently, the authors did not have the opportunity to gather all the control data that are desirable.

OBJECTIVES

The study, under which this data was generated, was made to assess the environmental impact associated with a 250 MMSCFD Lurgi dry ash coal gasification facility utilizing Dunn County, North Dakota lignite. This paper assesses the applicability and use of laboratory ashing techniques to determine the probable trace element emissions from a coal gasification facility.

METHODS

General

Two different lignites, Mercer County and Dunn County, North Dakota, were analyzed for major and minor elemental constituents. The Mercer lignite sample was obtained from the coal gasified as part of an operational test at Sasolburg, South Africa (SASOL). The Dunn County samples were obtained by coring as part of a resource evaluation program. Dunn County and Mercer County, North Dakota are approximately 45 miles apart; both are in the Fort Union Coal Reserve (e.g., the same geological strata).

The Mercer County lignite ash samples utilized were obtained during the SASOL test. The Dunn County lignite samples were ashed and the ash analyzed using ASTM D2795-69, "Mineral Analysis of Coal and Coke Ash". Leachate tests were performed on both ash samples.

The Sasolburg Test

The chemical analyses of the Mercer County lignite reported were taken from samples obtained when 12,000 tons were gasified in the Lurgi gasifier at Sasolburg, South Africa in 1974 by Michigan-Wisconsin Gas Pipeline Company. Samples of the lignite charged to the gasifier, and the ash from the gasifier were obtained.

The coal feed rate during each test was approximately 26 tons/hr with a mass balance test lasting for about 8 hours. The following sample collection intervals were used: hourly for the coal, and each dump for the gasifier ash.

Analytical Procedures

The sample analyses were performed using the following techniques: spark source mass spectrometry (SSMS), atomic absorption (AA), flameless atomic absorption (FAA), ion-selective electrode methods (IE), colorimetric (C), standard mineral analysis (MA), and several wet chemical methods (WC). The details of the procedures and methods used are described in Appendix A. All raw data obtained from the tests and referenced in this paper may be found in Somerville et al. (1976).[1]

Leaching Study

Since it was suspected that many of the elements found in coal would probably be retained in the gasifier ash and plans called for the disposal of the ash in the mined area, an experiment was designed to study the leaching characteristics of the ash (both laboratory and SASOL). The methods selected purposefully attempted to maximize the quantity of the element leached in an attempt to predict the upper bound of the impact. The general method consisted of grinding the ash to a fine powder, and refluxing a sample for 16 to 24 hours at the boiling point of demineralized water. This is thought to yield the worst case (maximum leachate concentration) because:

1. Refluxing subjects the ash to far more water than the annual rainfall ever would. It may take many years before moisture ever reaches the buried ash.
2. The use of distilled-demineralized water subjects the ash to harsher leaching conditions than the actual groundwater (which is basic) is expected to.
3. The refluxing of the leachate at the boiling point of water greatly increases the solubility of the elements in the solvent. Groundwater temperatures are considerably lower than this.
4. The procedure used small particle size

samples, which increases the solubility rather than the ash of much larger particle size resulting from operation.

Table A-1 of Appendix A lists the element and analytical method used for determination of the concentration of that element in the particular sample. The following abbreviations were used to identify the type of analysis:

SSMS - spark source mass spectrometry
AA - atomic absorption
FAA - flameless atomic absorption with double gold amalgamation
C - colorimetric
IE - USGS method specific ion electrode
MA - ASTM-2795-69 - mineral analysis
U - ultimate analysis
G - gravimetric
NR - not reported, if present
<0.1 ppm wt gasifier ash
<0.001 μg/ml gasifier ash leach

The leaching procedure which was used consisted of the following steps:

1. The samples were crushed to 60 mesh and the 10 g of material being examined were weighed. Coal samples were weighed air dry and ash samples were weighed dry. 50 ml of deionized water was added.
2. The above mixture was refluxed for 16 to 24 h at the boiling point of water. The solution was filtered and/or decanted until clear and the laboratory examination performed on the clear solution.
3. The liquid to solid ratio (5 to 1) was maintained if a larger quantity was used for leaching.

RESULTS AND DISCUSSION

Elemental Analyses were run on the following samples:

*Mercer County lignite and its ash from the SASOL gasification test. (See Table 1)

*Mercer County lignite ash leachate from the SASOL gasification test ash. (See Table 2)

Dunn County lignite and its laboratory ash for two coal samples: 4411 and 4413. (See Table 2)

Since gasifier ash using Dunn County lignite was not available for leaching tests, laboratory ash was used in its place. Analyses were performed, on each of the samples identified above. The results of those analyses are presented in Tables 1 and 2.

The data of Table 2 can be reduced by calculating the percent leachable which is determined with the following formula:

$$\% \text{ leachable} = (CL * 5/CA) * 100$$

where

CL = concentration of element in the leachate, μg/ml
CA = concentration of the element in the ash, ppm
5 = ratio of water leach base to material weight

Table 3 presents the leachable percentages for each of the 73 elements and also reports the ratio of Mercer gasification ash percentage leachable to Dunn's laboratory ash percent leachable.

Tables 4 and 5 present the upper bounds for the estimated effluent rates from a proposed gasification facility (Somerville et al (1976)[2]) and the maximum leachate rates that can be expected. Table 4 presents the elements found to be more soluble from gasifier ash, Table 5, elements more soluble from the laboratory prepared ash. Table 6 presents the ratio of the elements for the two lignites, their ashes and ash leachates. Table 7 examines the similarity of element concentrations between the lignites, their ashes and ash leachates by reporting the cumulative probability of occurrence as a function of ratio range.

A visual examination of the element concentrations of Table 1 for the Dunn and Mercer lignites reveals that they are similar. This observation is also supported by our experience with Fort Union Lignites which indicates that they are generally similar (Sondreal et al. (1968)[5]). It is not obvious that the ash element concentrations reported in Table 1 are similar. This may be due to the different environment that Mercer ash experienced during gasification as opposed to laboratory ashing environment. The difference becomes even more pronounced in the ash leachate data reported in Table 2. This difference is further amplified when the percentage of the element that is leachable is calculated and the ratio of the Mercer to Dunn percentage leachable is calculated. These

TABLE 1

COMPARISON OF TRACE ELEMENT AND MAJOR CONSTITUENTS IN MERCER COUNTY AND DUNN COUNTY NORTH DAKOTA LIGNITE AND THEIR ASHES, ppm

Element	Dry Coal[a,b]				Ash[b]		
	Mercer Co.	Dunn Co.			Mercer Co.	Dunn Co.	
		4411	4413	Avg./12 Samples		4411	4413
Ag	<0.1			<0.1	<1	<0.3	<0.3
Al	5,666[c]			6,697[d,e]	63,400[d]	94,000[f]	110,000[f]
As	8	11	9	10.13	74	36	30
Au	<0.1			<0.1			
B	56	135	39	62.95	1,680[f]	380	450
Ba	616[f]	113	81	229.82	8,270[f]	3,800[f]	10,200[f]
Be	0.27	0.8	0.3	0.31	6	0.3	0.5
Bi	<0.1			<0.1		0.3	0.3
Br	0.27	1.5	0.75	1.71	3	0.3	0.6
Ca	16,225[c]			16,108[d,e]	181,600[d]	236,000[f]	300,000[f]
Cd	<1[f]	<0.15[f]	<0.15[f]	0.21[f]	0.5[f]	<1	<1
Ce	34.6	24	11	14.06	190	37	85
Cl	26.7	92	39	46.62	67	15	62
Co	1.2	10.7	4.5	4.98	13	6	6
Cr	5.3	490	7.5	65.26	140	35	17
Cs	4	1.1	<0.15	0.26	9	0.9	0.4
Cu	10.6	73	17	22.92	27	18	27
Dy	0.67			<0.1	8	2	3
Er	<0.1			<0.1	4	0.5	1
Eu	0.4	0.3	0.3	0.26	4	0.5	0.8
F	29.3[g]	25[g]	24[g]	20.83[g]	191[g]	220[g]	250[g]
Fe	7,936[c]			7,216[d,e]	78,800[d]	Mc[h]	Mc[h]
Ga	5.3	8	3	4.58	53	12	0.5
Gd	0.8	<0.1	<0.1	0.23	5	0.9	2
Ge	0.27	3	0.9	0.60	2	4	7
Hf	<0.1			<0.1	4	0.9	0.9
Hg	0.2[i]	0.14[i]	0.11[i]	0.20[i]	0.55[i]	0.02[i]	0.04[i]
Ho	0.4			<0.1	5	0.6	0.9
I	0.13	0.15	0.3	0.39	2		
Ir	<0.1			<0.1			

TABLE 1 (Continued)

Element	Dry Coal[a,b]				Ash[b]		
	Mercer Co.	Dunn Co.			Mercer Co.	Dunn Co.	
		4411	4413	Avg./12 Samples		4411	4413
K	268[c]			462[d,e]	4,600[d]	11,200[f]	8,200[f]
La	16	9	1.5	5.83	74	16	34
Li	0.67	6	1.5	1.24	45	8	20
Lu	<0.1			<0.1	0.5	0.1	0.2
Mg	3,877[c]			5,039[d,e]	42,100[d]	Mc[h]	Mc[h]
Mn	70.7	383	38	248.90	760	Mc	210
Mo	4	43	63	22.22	12	6	10
Na	6,994[c]			2,395[d,e]	58,604[d]	114,000[f]	174,000[f]
Nb	4	11	1.5	3.86	37	10	17
Nd	2.7	0.8	0.8	0.96	18	3	8
Ni	6.7	31	15	11.55	25	30	15
Os	<0.1			<0.1			
P	236[c]			131[d,e]	3,500[d]	Mc[h]	Mc[h]
Pb	2.7	8	1.5	5.44	58	32	33
Pd	<0.1			<0.1			
Pr	1.3	1.5	0.5	0.85	8	2	4
Pt	<0.1			<0.1			
Rb	6.7	12	1.5	4.13	35	17	4
Re	<0.1			<0.1			
Rh	<0.1			<0.1			
Ru	<0.1			<0.1			
S	11,956[c]			13,000[e,j]	12,600[d]	29,300[k]	18,400[k]
Sb	0.27	0.9	0.45	0.31	4	1	2
Sc	8	9	11	7.98	33	16	15
Se	0.4	1.5	0.6	0.85	0.5	0.2	1
Si	9,114[c]			11,011[d,e]	118,100[d]	138,000[f]	128,000[f]
Sm	1.07	0.46	0.45	0.47	7	2	2
Sn	0.27	14	1.5	5.08	4	2	7
Sr	1,729[f]	918	1,050	1,029.27	12,900[f]	40,000[f]	26,000[f]
Ta				0.1	≤0.2	≤0.1	≤0.2

TABLE 1 (Continued)

Element	Dry Coal[a,b]				Ash[b]		
	Mercer Co.	Dunn Co. 4411	Dunn Co. 4413	Avg./12 Samples	Mercer Co.	Dunn Co. 4411	Dunn Co. 4413
Tb	0.67	<0.1	<0.1	0.15	3	0.6	1
Te	0.27			<0.1	≤0.3	≤0.2	≤0.2
Th	4	9	1.5	3.64	45	8	31
Ti	193[c]			301[d,e]	3,420[d]	610	Mc[h]
Tl	<0.1			<0.1	5		
Tm	<0.1			<0.1	0.5	0.2	0.2
U	4	6	1.5	3.15	7	7	8
V	21.3	61	14	21.93	150	28	20
W	<0.1	3	0.6	0.58	2	0.9	0.8
Y	13.3	54	42	23.11	320	34	48
Yb	<0.1			<0.1	4	1	2
Zn	6.7	23	23	10.87	10	70	30
Zr	85.3	184	68	68.42	520	100	94

[a] Analysis are reported on dry coal basis.

[b] Method of analysis, spark source mass spectrometry; unless noted otherwise. Detection limits for coal and gasifier ash at 0.1 ppm.

[c] Sondreal, E.A., Wayne R. Kube, James L. Elder,[5] "Analysis of the Northern Great Plains Province Lignites and Their Ash: A Study of Variability," U.S. Dept. of Interior, Bureau of Mines, RI 7158, 1968, analytical data taken from Tables 3 and 4, p.8, average of 22 samples from Indianhead Mine, Mercer County, N.D.

[d] Method of analysis, ASTM, D 2795-69, Mineral Analysis of Coal and Coke Ash, part 19, 1974.

[e] Average of four lower bed composites, Nos. 3,4,5,6, Report of Paul Weir Co. to Natural Pipeline Co. of America, October 27, 1972.

[f] Method of analysis, atomic absorption vs. aqueous standards.

[g] Method of analysis, U.S.G.S. method, ion-selective electrode.

[h] Analysis not performed on these ashes. Composite of lower beds 3,4,5 and 6 is available and gives: iron, 64834 ppm; titanium, 2704 ppm; magnesium, 45274 ppm; and phosphorous, 1177 ppm.

[i] Method of analysis, flameless atomic absorption (double gold amalgamation).

[j] Method of analysis, ASTM D 271-68, Laboratory Sampling and Analysis of Coal and Coke, part 19, 1969.

[k] Gravimetric.

TABLE 2

ASH AND ASH LEACHATE ANALYSES, MERCER COUNTY LIGNITE AND DUNN COUNTY LIGNITE

	Mercer County Lignite		Dunn County Lignite			
	SASOL Gasification Test					
Element	Ash (ppm)	Leachate (µg/ml)	4411 Lab Ash (ppm)	Leachate (µg/ml	4413 Lab Ash (ppm)	Leachate (µg/ml)
Ag, silver	≤1		≤0.3		≤0.3	
Al, aluminum	63,400	230	94,000	8	110,000	130
As, arsenic	74	3	36	0.02	30	0.07
Au, gold						
B, boron	1,680	36.6	380	13.5	450	12.5
Ba, barium	8,270	0.01	3,800	<1	10,200	<1
Be, beryllium	6		0.3		0.5	
Bi, bismuth			0.3		0.3	
Br, bromine	3	0.3	0.3	0.01	0.6	0.01
Ca, calcium	181,600[a]	19	236,000	380	300,000	95
Cd, cadmium	0.7		<1	<0.01	<1	<0.01
Ce, cerium	190		37	0.007	85	
Cl, chlorine	67	38	15	2	62	3
Co, cobalt	13	0.02	6	≤0.009	6	≤0.03
Cr, chromium	140	0.07	35	0.2	17	0.2
Cs, cesium	9	0.02	0.9	0.06	0.4	0.04
Cu, copper	27	0.05	18	0.2	27	0.4
Dy, dysprosium	8		2		3	
Er, erbium	4		0.5		1	
Eu, europium	4		0.5		0.8	
F, fluorine			220	<1.5	250	2.8
Fe, iron	78,800[a]	0.3	MC[b]	0.5	MC[b]	1
Ga, gallium	53	1	12	0.02	0.5	0.5
Gd, gadolinium	5		0.9		2	
Ge, germanium	2	0.005	4	0.004	7	≤0.03
Hf, hafnium	4		0.9		0.9	
Hg, mercury			0.02	0.002	0.04	0.003
Ho, holmium	5		0.6		0.9	
I, iodine	2	0.2				
Ir, iridium						
K, potassium	4,600[a]	110	11,200	414	8,200	393

TABLE 2 (Continued)

	Mercer County Lignite SASOL Gasification Test		Dunn County Lignite			
Element	Ash (ppm)	Leachate (μg/ml)	4411 Lab Ash (ppm)	Leachate (μg/ml)	4413 Lab Ash (ppm)	Leachate (μg/ml)
La, lanthanum	74		16	0.006	34	
Li, lithium	45	0.002	8	≤0.07	20	≤0.07
Lu, lutetium	0.5		0.1		0.2	
Mg, magnesium	42,100^a	0.2	MC^b	1	MC^b	8
Mn, manganese	760	0.006	MC	0.04	210	0.2
Mo, molybdenum	12	1	6	1	10	2
Na, sodium	58,604^a	7,100	114,000	8,600	174,000	12,700
Nb, niobium	37		10		17	
Nd, neodymium	18		3		8	
nickel	25	0.009	30	0.06	15	0.05
Os, osmium						
P, phosphorous	3,500^a	0.9	MC^b	1	MC^b	1
Pb, lead	58	0.007	32	0.02	33	<0.02
Pd, palladium						
Pr, praseodymium	8		2	0.003	4	
Pt, platinum						
Rb, rubidium	35	1	17	1	4	0.7
Re, rhenium						
Rh, rhodium						
Ru, ruthenium						
S, sulfur	12,600^a	1,205	29,300	3,804	18,400	3,804
Sb, antimony	4	0.01	1		2	
Sc, scandium	33	≤0.003	16	≤0.01	15	≤0.03
Se, selenium	0.5	0.02	0.2	<0.009	1	≤0.09
Si, silicon	118,100^a	900	138,000	<5	128,000	<5
Sm, samarium	7		2		2	
Sn, tin	4	0.003	2		7	
, strontium	12,900	0.09	40,000	43	26,000	45
Ta, tantalum	≤0.2		≤0.1		≤0.2	
Tb, terbium	3		0.6		1	
Te, tellurium	≤0.3		≤0.2		≤0.2	

TABLE 2 (Continued)

	Mercer County Lignite SASOL Gasification Test		Dunn County Lignite			
Element	Ash (ppm)	Leachate (μg/ml)	4411 Lab Ash (ppm)	Leachate (μg/ml)	4413 Lab Ash (ppm)	Leachate (μg/ml)
Th, thorium	45		8		31	
Ti, titanium	3,420[a]	0.1	610	0.3	MC[b]	0.4
Tl, thallium	5					
Tm, thulium	0.5		0.2		0.2	
U, uranium	7		7		8	
V, vanadium	150	8	28	0.3	20	0.2
W, tungsten	2	0.04	0.9	0.03	0.8	0.05
Y, yttrium	320	≤0.02	34		48	
Yb, ytterbium	4		1		2	
Zn, zinc	10	0.02	70	0.1	30	0.4
Zr, zirconium	520		100	0.3	94	

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[a] Method of Analysis ASTM D2795-69, Mineral Analysis of Coal and Coke Ash, Part 19, 1974.

[b] Analyses not performed on these ashes. Composite of lower beds 3, 4, 5, and 6 is available and gives: iron, 64834 ppm; titanium, 2704 ppm; magnesium, 45274 ppm; and phosphorous, 1177 ppm.

TABLE 3

PERCENT OF ELEMENT LEACHABLE FROM MERCER COUNTY GASIFIER ASH AND DUNN COUNTY LIGNITE LABORATORY ASH

Element	Mercer County SASOL Ash	Dunn County Lab Ash	Ratio
	% Leachable	% Leachable (Avg. of 4411, 4413)	Mercer/Dunn
Ag, silver	0.5		
Al, aluminum	1.8	0.32	5.63
As, arsenic	20.3	0.74	27.43
Au, gold			
B, boron	10.9	15.9	0.69
Ba, barium	0.0006	<0.09	>0.01
Be, beryllium			
Bi, bismuth			
Br, bromine	50	13	3.85
Ca, calcium	0.05	0.49	.102
Cd, cadmium		<5	
Ce, cerium		0.09	
Cl, chlorine	283[a]	46	
Co, cobalt	0.77	1.6	0.48
Cr, chromium	0.25	4.4	0.06
Cs, cesium	1.1	42	0.03
Cu, copper	0.93	7	0.13
Dy, dysprosium			
Er, erbium			
Eu, europium			
F, fluorine	10.2	4.5	2.27
Fe, iron	0.002	<0.4	>0.01
Ga, gallium	9.4	5.4	1.74
Gd, gadolinium			
Ge, germanium	1.3	≤1.3	≥1
Hf, hafnium			
Hg, mercury	0.91	4.4	0.21
Ho, holmium			
I, iodine	50		
Ir, iridium			
K, potassium	12	21.3	0.56
La, lanthanum		0.19	

TABLE 3 (Continued)

	Mercer County SASOL Ash	Dunn County Lab Ash	Ratio
	% Leachable	% Leachable (Avg. of 4411, 4413)	Mercer/Dunn
Li, lithium	0.02	11	0.002
Lu, lutetium			
Mg, magnesium	0.002		
Mn, manganese	0.004	≤0.25	≥0.02
Mo, molybdenum	41.7	92	0.45
Na, sodium	60.6	37.1	1.63
Nb, niobium			
Nd, neodymium			
Ni, nickel	0.18	1.4	0.13
Os, osmium			
P, phosphorous	0.13	<0.5	>0.26
Pb, lead	0.06	0.31	0.19
Pd, palladium			
Pr, praseodymium		.75	
Pt, platinum			
Rb, rubidium	14.3	59	0.24
Re, rhenium			
Rh, rhodium			
Ru, ruthenium			
S, sulfur	47.8	84	0.57
Sb, antimony	1.3		
Sc, scandium	0.05	<0.66	>0.08
Se, selenium	20	<34	>0.59
Si, silicon	3.8	<0.02	>190
Sm, samarium			
Sn, tin	0.4		
Sr, strontium	0.003	0.71	0.004
Ta, tantallum			
Tb, terbium			
Te, tellurium			
Th, thorium			
Ti, titanium	0.01	<2.3	>0.004

TABLE 3 (Continued)

Element	Mercer County SASOL Ash	Dunn County Lab Ash	Ratio
	% Leachable	% Leachable (Avg. of 4411, 4413)	Mercer/Du
Tl, thallium			
Tm, thulium			
U, uranium			
V, vanadium	26.7	5.2	5.13
W, tungsten	10	24	0.42
Y, yttrium	0.03		
Yb, ytterbium			
Zn, zinc	1	3.7	0.27
Zr, zirconium		1.5	

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[a] Irrational number, unexplained error.

TABLE 4

ESTIMATED MAXIMUM SOLUTION RATES FOR ELEMENTS MORE SOLUBLE FROM GASIFIER ASH[a]

	Ratio of to Mercer/Dunn Ash Leachate Rates	Dunn Co. Estimated Effluent[b] (lbs/day)	Laboratory Dunn County Ash, % Leachable	Estimated[b] Maximum Leachate Rate (lbs/day)
aluminum	5.63	243,600	0.32	780
arsenic	27.43	339	0.74	2.5
bromine	3.85	61	13	7.9
fluorine	2.27	513	4.5	23.1
gallium	1.74	168	5.4	9.1
germanium	>1.0	22	≤1.3	≤0.3
silicon	>190	393,200	<.02	78.6
sodium	1.63	86,000	37.1	31,906
vanadium	5.13	800	5.2	41.6

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[a] Mercer County coal processed at Sasolburg, South Africe.

[b] Based upon Somerville, et al (1976)[1]. Data is for a 250 MMSCFD Dry Ash Lurgi Gasification Plant.

TABLE 5

ESTIMATED MAXIMUM SOLUTION RATES FOR ELEMENTS MORE LEACHABLE FROM LABORATORY PREPARED ASH[a]

Element	Ratio of Mercer to Dunn Ash Leachate	Dunn Co. Estimated Effluent[b] (lbs/day)	% Leachable	Estimated Maximum Leachate Rate[b] (lbs/day)
boron	0.69	2,303.5	15.9	366.3
barium	>0.01	8,188.7	<0.09	7.4
calcium	.102	588,800	0.49	2,885
cobalt	0.48	178.19	1.6	2.9
chromium	0.06	2,349.5	4.4	103.4
cesium	0.03	9.48	42	4.0
copper	0.13	789.7	7	55.3
iron	>0.01	236,250.5	<0.4	<1,053.0
mercury	0.21	0.10	4.4	0.0
potassium	0.56	16,650.2	21.3	3,546.5
lithium	0.002	45.29	11	5.0
manganese	>0.02	9,098.6	≤0.25	≤22.75
molybdenum	0.45	691.9	92	636.5
nickel	0.13	397.1	1.4	5.6
phosphorous	>0.26	4,658.4	<0.5	<23.3
lead	0.19	177.01	0.31	0.5
rubidium	0.24	147.62	59	87.1
sulfur	0.57	56,048.9	84	47,081.1
scandium	>0.08	288.18	<0.66	<1.9
selenium	>0.59	4.32	<34	<1.5
strontium	0.004	37,815.9	0.71	268.5
titanium	>0.004	9,827.4	<2.3	<226.0
tungsten	0.42	21.37	24	5.1
zinc	0.27	299.3	3.7	11.1

Dunn County Coal, samples 4411 and 4413, processed in the laboratory.

[b] Based upon Somerville et al (1976)[1]. Data is for a 250 MMSCFD Dry Ash Lurgi Gasification Plant.

TABLE 6

RATIO OF ELEMENT CONCENTRATION IN MERCER COUNTY LIGNITE, ASH AND ASH LEACHATE TO THOSE OF DUNN COUNTY

Element	Lignite[a]	Ash[a]	Ash Leachate
Ag, silver	1.00[b,c]	3.00	N
Al, aluminum	0.85[c]	0.62	5.63
As, arsenic	0.80	2.24	27.43
Au, gold	1.00[c]	N	N
B, boron	0.64	4.05	0.69
Ba, barium	6.35	1.18	>0.01
Be, beryllium	0.49	15.00	N
Bi, bismuth	1.00[c]	N	N
Br, bromine	0.24	6.66	3.85
Ca, calcium	1.01[c]	0.68	.102
Cd, cadmium	6.67	0.50	N
Ce, cerium	1.98	3.11	N
Cl, chlorine	0.41	1.74	N
Co, cobalt	0.16	2.17	0.48
Cr, chromium	0.02	5.38	0.06
Cs, cesium	6.40	13.85	0.03
Cu, copper	0.24	1.20	0.13
Dy, dysprosium	6.70[c]	3.20	N
Er, erbium	1.00[c]	5.33	N
Eu, europium	1.33	6.15	N
F, fluorine	1.20	0.81	2.27
Fe, iron	1.10[c]	N	>0.01
Ga, gallium	0.96	8.48	1.74
Gd, gadolinium	8.00	3.45	N
Ge, germanium	0.14	0.36	≥1.00
Hf, hafnium	1.00[c]	4.44	N
Hg, mercury	1.60	1.83	0.21
Ho, holmium	4.00	6.67	N
I, iodine	0.58	N	N
Ir, iridium	1.00[c]	N	N
K, potassium	0.58[c]	0.47	0.56
La, lanthanum	3.05	2.96	N
Li, lithium	0.18	3.21	0.002
Lu, lutetium	1.00[c]	3.33	N
Mg, magnesium	0.77[c]	N	N

TABLE 6 (Continued)

Element	Lignite[a]	Ash[a]	Ash Leachate
Mn, manganese	0.34	3.62	≥0.02
Mo, molybdenum	0.08	1.50	0.45
Na, sodium	2.92[c]	0.41	1.63
Nb, niobium	0.64	2.74	N
Nd, neodymium	3.38	3.27	N
Ni, nickel	0.29	1.11	0.13
Os, osmium	1.00[c]	N	N
P, phosphorous	1.80[c]	N	>0.26
Pb, lead	0.57	1.78	0.19
Pd, palladium	1.00[c]	N	N
Pr, praseodymium	1.30	2.67	N
Pt, platinum	1.00[c]	N	N
Rb, rubidium	0.99	3.33	0.24
Re, rhenium	1.00[c]	N	N
Rh, rhodium	1.00[c]	N	N
Ru, ruthenium	1.00[c]	N	N
S, sulfur	0.92[c]	0.53	0.57
Sb, antimony	0.40	2.67	N
Sc, scandium	0.80	2.13	>0.08
Se, selenium	0.38	0.83	>0.59
Si, silicon	0.83[c]	0.89	>190
Sm, samarium	2.35	3.50	N
Sn, tin	0.03	0.89	N
Sr, strontium	1.76	0.39	0.004
Ta, tantallum	N	1.33	N
Tb, terbium	6.70	3.75	N
Te, tellurium	2.70[c]	1.50	N
Th, thorium	0.76	2.31	N
Ti, titanium	0.64[c]	5.61	>0.004
Tl, thallium	1.00[c]	N	N
Tm, thulium	1.00[c]	2.50	N
U, uranium	1.07	0.93	N
V, vanadium	0.57	6.25	5.13
W, tungsten	0.06	2.35	.42
Y, yttrium	0.28	7.80	N
Yb, ytterbium	1.00[c]	2.67	N

TABLE 6 (Continued)

Element	Lignite[a]	Ash[a]	Ash Leachate
Zn, zinc	0.29	0.20	0.27
Zr, zirconium	0.68	5.36	N

[N] Not calculable due to missing data.

[a] Calculated on the basis of the average of 4411 and 4413 unless otherwise noted.

[b] Number calculated on basis of a less than or greater than number. See tables 1 and 3.

[c] Calculated on the basis of an average of 12 samples instead of an average of 4411 and 4413.

TABLE 7

CUMULATIVE PROBABILITY OF COMMON OCCURANCE OF ELEMENTS, IN MERCER AND DUNN COUNTY LIGNITES THEIR ASHES AND ASH LEACHATES AS A FUNCTION OF CONCENTRATION RATIOS

	Lignite		Ash		Ash Leachate	
Concentration Ratio Range[a]	Number of Elements	Percent	Number of Elements	Percent	Number of Elements	Percent
0.5 through 2.0	43	58.9	17	28.8	7	21.2
0.25 through 4.0	57	78.1	44	74.6	14	42.4
0.10 through 10.0	68	93.2	57	96.6	22	66.7
Total samples	73	100.0	59	100.0	33	100.0
Total ratio range	0.02 through 8.0		0.20 through 15		0.002 through 190	

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[a] The ratio reported is the ratio of the Mercer County sample concentration in ppm to the Dunn County samples in ppm. See Table 6 for ratios for individual elements.

results, in Table 3, show wide variability with little similarity between the fraction leachable from the Mercer gasified ash and Dunn laboratory ash.

In examining Table 3, two things are apparent, neither of the samples (Dunn nor Mercer) are dominant in the leach tests *and* the variation in the ratio of the Mercer to Dunn percent leachable is large (0.002 to 190). Only five of the 33 elements common to both samples fall within plus or minus 50 percent of one another (ratio of .5 to 1.5). The variability of the results leads one to postulate, and perhaps conclude, that laboratory prepared ash is not representative of gasifier ash. This result was anticipated by the authors because of the differences in the previous chemical environments (particularly temperature) of the laboratory prepared ash and gasifier ash.

Twenty-four of the 33 elements reported in Table 3 show that Dunn County lignite laboratory prepared ash is more leachable than gasifier ash while nine were less leachable. Consequently, in the majority of cases (73%) the maximum solution rate is given by the laboratory prepared ash. These maximum solution concentrations and their rates are not to be confused with the actual field leachate concentrations and would be expected to be considerably lower than (1/10 to 1/1000 -authors' judgment) the maximum value reported. Furthermore, as time proceeds the actual leach rates and concentrations will decline due to increased compaction of the returned overburden and the progress toward chemical equilibrium between the ash and infiltrated groundwater.

In spite of the above, an estimate of the maximum initial solution rates in pounds per day has been made. The results of this analysis are shown in Tables 4 and 5. These data were generated using Table 3 (columns 1 and 3) and data from Somerville, et al. (1976)[2]. The results of the analysis have been separated into two tables (4 and 5) to show which elements were more leachable from the gasifier ash and which were more leachable from the laboratory prepared ash. The first table, 4, presents the results for the gasifier ash; the second, 5, for the laboratory ash. The results indicate that the sulfur, sodium, calcium, potassium, and iron have the highest potential to enter the groundwater system through the leaching process. The pH of the ash leachates always indicated a basic solution compatible with Fort Union Lignite. All of these elements presently exist in the groundwater of Dunn County.

The similarity of the two coals can be examined by forming the ratio of the concentrations for each element in the lignites, their ashes, and of the percentage leachable in the ashes. These ratios are reported in Table 6. A ratio value of unity means that the same concentration (dry coal basis) exists in both coals. Consequently, many ratio values close to unity imply a basic similarity between the two groups of samples. Examination of Table 6 shows that Mercer and Dunn County lignites are quite similar. This is also borne out by Table 7 which shows that 59 percent of the elements had a ratio value that fell between 0.5 and 2.0. Based upon our experience and others (See Table 10 of Gluskoter et al. (1977)[6]) this level of variability is typical of coals including western coals. On the other hand, examination of the ash and ash leachate columns indicates a general decrease in similarity. This is particularly true of the ash leachates which show only 67 percent of the elements falling within an order of magnitude of one another (ratio range of 0.1 to 10). A similar divergence from the lignite samples, although not as pronounced, can also be observed in the ash samples.

Trace Elements and Environmental Analysis of Groundwater Impact

There are several reasons, why the above data are not well suited to environmental analyses dealing with groundwater impact of mine disposed solids. Some of the principal reasons are:

*The chemistry of the element in the coal, ash, and ash leachate is completely undefined.

*A basic understanding dealing with the chemistry of trace metal components in the geochemical setting is missing.

*The physical system setting is immensely complex; it includes a short term (years), varying, ill-defined geology, particularly during post-mining conditions. Further, the geochemistry varies with depth and topography and the surface experiences a random distribution and water influx (rain).

*The potentially complex chemistry of the ash when combined with other disposed solids and sludges is not well understood. (e.g., cooling tower blowdown, biotreatment sludges (if any) and water treatment plant sludges).

*The general lack in terms of both quality and quantity of the geological field data required by the sophisticated mathematical models that possess the potential, although presently not the capability, to predict post-mining groundwater chemistry and groundwater impact.

In spite of the above, the data are somewhat useful in determining what elements are likely to not have significant impact from a quantity view point. Additionally, the analyses can narrow considerably the breadth of investigation required to assess the potential impact.

CONCLUSIONS

The data presented indicate that Mercer and Dunn County lignite are basically similar in terms of trace element constituents. Although not entirely conclusive, the same is not true of their ashes and ash leachates. Assuming that their ashes and ash leachates should show the same basic similarity, one has to conclude that the processes the two lignites and their ashes were exposed to are responsible for differences in elemental constituents. Consequently, it is probable that the laboratory ashing procedure (ASTM D 271-68) does not simulate the gasification process well enough to allow use of the laboratory data in environmental analyses.

Further, the quantity and variability of the data reported, as well as the reasons cited above, indicate that use of analytical data of this type in a mathematical model will be difficult, if not impossible. Use of "worst case" experimental biological screening analyses may be the only near term solution to this problem. It is clear that use of trace element analyses alone do not address the groundwater impact question.

RECOMMENDATIONS

The following recommendations are those of the authors and do not necessarily represent the position of either the Engineering Experiment Station or the sponsor.

1. Groundwater monitoring wells should be established in and adjacent to the mine and waste disposal areas. The wells should be sampled and samples analyzed for trace and major inorganic elements and organic compounds.

2. Trace element emissions from a gasification facility should not be regulated until their impact is well understood and adequate and inexpensive instrumentation is developed.

3. Samples of Mercer County lignite should be obtained, ashed under ASTM D 271-68 and leached. Elemental analysis of the ash and its leachate should be completed and compared with the data of this report.

4. A laboratory ashing technique that simulates the Lurgi dry ash gasification environment should be developed.

The first recommendation is obvious, and this would probably be required under existing laws. The second is justified in the authors' view by the following:

*The results of this study indicate that even under "worst case" conditions trace element impact will be minor.

*There have been only scattered instances of negative trace element impact in several decades of successful power plant operation. A gross environmental impact has not been observed.

*The measurement techniques for both trace element determinations and their impacts are still being developed and are expensive and difficult to complete.

*Monitoring of trace element emissions (gaseous, solid, or liquid) would be very difficult to carry out on a continuous basis with existing equipment.

The third recommendation would complete the baseline data missing from this paper. The fourth action is needed to allow prospective developers to make reasonable assessments of the potential impact of disposed gasification ash in the mined area.

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APPENDIX A, ANALYTICAL METHODS USED IN DETERMINING TRACE ELEMENT CONCENTRATIONS IN THE LIGNITE AND ASH SAMPLES

Analytical Methods

Several independent methods were used in the analysis of the samples resulting in some duplication for certain elements. In cases where the survey analysis, Spark Source Mass Spectrometry (SSMS) for a particular element was duplicated by a more precise analysis only the latter results are reported. The methods of analyses utilized were: spark source mass spectrometry, atomic absorption, ion-specific electrode, ultimate analysis and mineral analysis using gravimetric, volumetric, and colorimetric procedures.

SSMS has several advantages for trace element surveys and has become a commonly used analytical tool for the analysis of fossil fuels. SSMS allows the simultaneous determination of approximately 80 elements with typical detection limits for the majority of elements in the order of 50 to 100 parts per billion. An advantage of the spark source mass spectrograph is that it utilizes a small amount of sample. This fact can be a benefit when the samples are limited but is a disadvantage when tonnage quantities are to be represented by a spark source trace element scan. Sample preparation is extremely important in SSMS, but, as in any trace element analysis, large scale samples cannot be accurately represented unless great attention is paid to sample preparation.

The procedure for coal analysis includes reduction of the size of the sample particles to -200 mesh. The gasifier ash leach samples were thermally ashed at 350°C in a quartz boat in a laboratory oven. A portion of the sample was then mixed with an equal weight of high purity compactable graphite. An internal standard, indium, was added along with a few drops of redistilled ethyl alcohol. The mixture was slurried with redistilled alcohol in an agate mortar and pestle. The sample-graphite slurry was dried using infrared lamps. The procedure was then repeated, slurrying and drying, until a homogeneous electrode mixture was assured. The sample-graphite mix was then packed into holes drilled in a specially cleaned polyethylene slug. This slug was then inserted into a metal die and subjected to about 15 to 18 tons of force. The sample-graphite electrodes were then mounted in the machine for sparking.

The mass spectrum produced on the photoplate is a summation of the elemental components of the electrode. The ion intensity of a spectral line is related directly to the concentration of the components at least over a concentration range of 10^5:1. Therefore, by running a series of decreasing exposures, the relative concentration of elements from a major to a trace can be established by knowing the concentration of the internal standard added during sample preparation. Analysis by spark source mass spectrometry will not report elements with concentrations greater than 1,000 parts per million wt. Elements above this amount are reported as major components (MC).

Mineral analyses were performed by procedure listed ASTM D-2795-69, *Gaseous Fuels: Coal and Coke: Atmospheric Analysis, Analysis of Coal and Coke Ash,* part 26, November 1974. Due to the small amount of whole dry coal available for analysis, an additional source of data for the mineral analyses of coal samples from the same mine was sought. A report by the U.S. Bureau of Mines, RI 7158, containing average values from 22 sample locations in the North American Mine at Zap, North Dakota, was used to support, and in some cases supplement, values obtained for the coal sample analyzed in this study (Sondreal et al. 1968)[5]. The following elements were determined in the coal and gasifier ash from the mineral analysis: aluminum, calcium, iron, magnesium, phosphorus, potassium, silicon, sodium, sulfur, and titanium. The concentrations of 14 elements in several of the samples were determined individually by wet chemical methods.

Mercury was determined in all samples by flameless atomic absorption with a double gold amalgamation using the following procedure. The sample was burned in a quartz tube and the mercury was collected on a gold coil. The gold coil was heated and the mercury transferred to a second gold coil. The second gold coil was heated and the mercury passed through a cell in the light path of the atomic absorption spectrometer. The two transfers serve to remove hydrocarbon interferences. The equipment was standardized by injecting known amounts of mercury vapor into the system.

Fluorine was determined in all samples using the USGS method of analysis. The samples were ashed in a slurry of magnesium oxide and magnesium nitrate and then fused with sodium hydroxide. The dissolved fusion was buffered with ammonium citrate, and the fluorine was determined using a fluoride specific-ion-electrode.

Cadmium was determined in all samples via atomic absorption using the following procedure. The samples were put into solution using aqua regia and hydrofluoric acid. They were then stabilized with boric acid and analyzed via atomic absorption versus aqueous standards having the same boric acid content.

Barium and strontium were analyzed for by atomic absorption, using the procedure outlined above, in the dry coal ash and gasifier ash.

Boron was analyzed in the gasifier ash and gasifier ash leach by the following methods. The gasifier ash was washed in sodium carbonate and then fused to obtain a solution followed by a distillation to remove interferences. The solution was then analyzed via a curcumin colorimetric analysis. The gasifier ash leach was run directly with boron determined by the curcumin colorimetric method.

Leaching Method

Since it was suspected that many of the elements found in coal would probably be retained in the gasifier ash, and plans for burial of the ash in the mine area, an experiment was designed to study the leaching characteristics of the coal ash and gasifier ash.

Ten grams of gasifier ash, ground to pass a -60 mesh screen, were slurried with 50 ml of distilled-demineralized water. The solution was refluxed for 16 to 24 h with the temperature held at the boiling point of water. At the conclusion of the refluxing the leachate was analyzed with the following tests performed.

1. Survey Analysis - Spark Source Mass Spectrometry
2. Fluorine - USGS Method Ion-Specific Electrode
3. Mercury - Flameless Atomic Absorption
4. Boron - Atomic Absorption
5. Sodium - Atomic Absorption
6. Strontium - Atomic Absorption
7. Barium - Atomic Absorption
8. Aluminum - Atomic Absorption
9. Calcium - Atomic Absorption
10. Silicon - Atomic Absorption
11. Potassium - Atomic Absorption
12. Cadmium - Atomic Absorption
13. Sulfur - Gravimetric

Table A-1 reports the method used for each of the 73 elements.

TABLE A-1

ELEMENTS CONSIDERED AND ANALYTICAL METHOD USED FOR CALCULATIONS*

Elements	Whole Coal	Gasifier Ash	Ash Leach
1. Ag, silver	NR	SSMS	SSMS
2. Al, aluminum	MA	MA	AA
3. As, arsenic	SSMS	SSMS	SSMS
4. Au, gold	NR	NR	NR
5. B, boron	SSMS	C	C
6. Ba, barium	AA	AA	AA
7. Be, beryllium	SSMS	SSMS	NR
8. Bi, bismuth	NR	NR	NR
9. Br, bromine	SSMS	SSMS	SSMS
10. Ca, calcium	MA	MA	AA
11. Cd, cadmium	AA	AA	AA
12. Ce, cerium	SSMS	SSMS	NR
13. Cl, chlorine	SSMS	SSMS	AA
14. Co, cobalt	SSMS	SSMS	SSMS
15. Cr, chromium	SSMS	SSMS	SSMS
16. Cs, cesium	SSMS	SSMS	SSMS
17. Cu, copper	SSMS	SSMS	SSMS
18. Dy, dysprosium	SSMS	SSMS	NR
19. Er, erbium	NR	SSMS	NR
20. Eu, europium	SSMS	SSMS	NR
21. F, fluorine	IE	IE	IE
22. Fe, iron	MA	MA	SSMS
23. Ga, gallium	SSMS	SSMS	SSMS
24. Gd, gadolinium	SSMS	SSMS	NR
25. Ge, germanium	SSMS	SSMS	SSMS
26. Hf, hafnium	NR	SSMS	NR
27. Hg, mercury	FAA	FAA	FAA
28. Ho, holmium	SSMS	SSMS	NR
29. I, iodine	SSMS	SSMS	SSMS
30. Ir, iridium	NR	NR	NR
31. K, potassium	MA	MA	AA
32. La, lanthanum	SSMS	SSMS	NR
33. Li, lithium	SSMS	SSMS	SSMS
34. Lu, lutetium	NR	SSMS	NR
35. Mg, magnesium	MA	MA	SSMS
36. Mn, manganese	SSMS	SSMS	SSMS
37. Mo, molybdenum	SSMS	SSMS	SSMS
38. Na, sodium	MA	MA	AA
39. Nb, niobium	SSMS	SSMS	NR
40. Nd, neodymium	SSMS	SSMS	NR
41. Ni, nickel	SSMS	SSMS	SSMS
42. Os, osmium	NR	NR	NR
43. P, phosphorus	MA	MA	SSMS
44. Pb, lead	SSMS	SSMS	SSMS
45. Pd, palladium	NR	NR	NR
46. Pr, praseodymium	SSMS	SSMS	NR
47. Pt, platinum	NR	NR	NR
48. Rb, rubidium	SSMS	SSMS	SSMS
49. Re, rhenium	NR	NR	NR

TABLE A-1 (Continued)

Elements	Whole Coal	Gasifier Ash	Ash Leach
50. Rh, rhodium	NR	NR	NR
51. Ru, ruthenium	NR	NR	NR
52. S, sulfur	WC	MA	WC
53. Sb, antimony	SSMS	SSMS	SSMS
54. sc, scandium	SSMS	SSMS	SSMS
55. Se, selenium	SSMS	SSMS	SSMS
56. Si, silicon	MA	MA	AA
57. Sm, samarium	SSMS	SSMS	NR
58. Sn, tin	SSMS	SSMS	SSMS
59. Sr, strontium	AA	AA	AA
60. Ta, tantalum	NR	SSMS	NR
61. Tb, terbium	SSMS	SSMS	NR
62. Te, tellurium	SSMS	SSMS	NR
63. Th, thorium	SSMS	SSMS	NR
64. Ti, titanium	MA	MA	SSMS
65. Tl, thallium	NR	SSMS	NR
66. Tm, thulium	NR	SSMS	NR
67. U, uranium	SSMS	SSMS	NR
68. V, vanadium	SSMS	SSMS	SSMS
69. W, tungsten	NR	SSMS	SSMS
70. Y, yttrium	SSMS	SSMS	SSMS
71. Yb, ytterbium	NR	SSMS	NR
72. Zn, zinc	SSMS	SSMS	SSMS
73. Zr, zirconium	SSMS	SSMS	NR

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* Analytical procedure used, meaning of symbols:

C - curcumin colorimetric analysis
AA - atomic absorption versus aqueous standards
IE - ion-selective electrode
MA - standard mineral analysis, ASTM D2795-69
NR - not reported
WC - wet chemical or gravimetric
FAA - flameless atomic absorption
SSMS - spark source mass spectrometry, detection limit considered <0.1 ppm