Comparison of Atomic Absorption and D.C. Plasma-Arc Spectrometry in Multi-Element Analysis of Coal

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As part of a project at The Pennsylvania State University to characterize the inorganic constituents of American coals, an analytical scheme was developed whereby most of the major and minor elements (Si, Al, Fe, Ca, Mg, Ti, Mn, Na, K) in high temperature (750°C) coal ashes were determined by atomic absorption spectrophotometry (A.A.S.) and most of the trace elements (Ba, Be, Co, Cr, Ga, Ge, La, Mo, Ni, Pb, Sc, Sn, Sr, V, Y, Yb and Zr) determined by d.c. arc emission spectrography. However, after the acquisition of a d.c. argon plasma spectrometer, a study was conducted to determine whether this instrument was capable of assuming some of the functions of the atomic absorption unit or emission spectrograph. This was done because emission spectrometry offers many advantages over A.A.S. and conventional emission spectroscopy, primarily in the area of rapid analysis of sample. Whereas in A.A.S., only one element can be determined at a time, emission spectrometry has the capability of performing simultaneous multi-element determinations (up to 18 at one time for the instrument in this study). In addition, the emission spectrometer, unlike the emission spectrograph, has a direct numerical readout which is much more amenable to efficient data handling and manipulation than the conventional photographic plates. This, in turn, coupled with a more stable excitation source, leads to greater precision among different sets of data. Additionally, the superior dispersion (between 0.61 and 2.44 A/mm in the 2000-8000 a range) of the echelle grating eliminates many of the spectral interferences common to other spectrographs. Emission spectrometry is also, unlike A.A.S., not limited by hollow cathode lamps, does not employ explosive gases, and because of the higher source temperature, has fewer chemical interferences.

Because the plasma emission spectrometer accepts only liquid samples, it was decided to initially compare the instrument with A.A.S. The emission spectrometer employed here is the Spectrametrics Incorporated (SMI) Spectraspan III in which the excitation source consists of a high temperature (up to 10,000 K, typically 6000°K in the analytical region) d.c. argon plasma. The instrument nebulizes liquid samples with argon and introduces the aerosol into the plasma at a constant rate by means of a peristaltic pump. The emitted radiation is dispersed in the spectrometer by an echelle grating, the orders separated by a quartz prism and channeled into a series of photomultiplier tubes each of which are set so as to receive the radiation at one particular wavelength characteristic of each of the various elements of interest (e.g. Cu is determined by monitoring the Cu 3274 line in the 69th order, Mn by monitoring the Mn 2576 line in the 88th order, etc.)* The capability also exists for adjusting the system so that elements other than the 18 pre-set elements can be determined. The photomultiplier tube outputs for the various elements are connected with a micro-computer which manipulates the received data according to various programs (e.g. integration over a period of time, use of an internal standard, etc.) and prints out the results on an auxiliary printer. The raw data (arbitrary units in the range 0-9999) may also be printed out if so desired.

The sample preparation for the plasma spectrometer is essentially the same as that used for A.A.S. (1). The high temperature ash (750°C) of the test coal was ground to -200 mesh (<74 μ) to ensure sample homogeneity and a 200 mg sample was mixed with 800 mg of $LiBO_2$ and fused at 1050°C for 10 minutes; the resultant molten bead is then poured directly into 80 ml of a 4% HNO_3 solution. For plasma spectrometry, 6 replica solutions were prepared from this initial solution by taking six 5.00 ml aliquots and diluting each with 35.0 ml of a solution consisting of 0.5% Li

*Analytical lines are listed in Table 1.

Table 1. Analytical Lines Used for the Emission Spectrometric Analysis of Coal Ashes

Element	Wavelength (A)	Order
Al	3961	57
Ba	4554	50
Ca	3179	71
Cu	3247	69
Fe	2382	95
Ge*	2651	85
K	7698	29
Mg	2795	80
Mn	2576	88
Na	5895	38
Si	2516	90
Sr	4077	55
Ti	3349	67
Zn	2138	106
Zr	3601	62

*Used as internal standard.

in 2% nitric acid and containing 10 ppm Ge. The Li content of the final solution is about 4500 ppm and serves as an effective spectroscopic buffer while the Ge acts as an internal standard. Six replica solutions were also prepared for A.A.S. by diluting 5.00 ml aliquots of the initial solution with 30.0 ml of a 10,800 ppm La solution, the La acting as a releasing agent in the flame process. The appropriate sets of solutions were then ready to run on the plasma spectrometer and A.A. spectrophotometer along with sets of standards prepared in the same manner as the samples. However, the nature of the electronics on the plasma spectrometer is such that prior to the running of the solutions, it was necessary to calibrate the instrument with standards containing approximately the highest concentrations of the elements that one would expect in the solutions. Once so calibrated the instrument automatically extrapolates linearly between the calibrated maximum point and a blank to give a reading for each solution run. If, however, this calibrated upper limit should be exceeded by more than about 25% by a solution, no reading will be produced and the solution must be diluted before it can be analyzed. Although, in theory, only one standard need be run for the emission spectrometer, at least three or four were run as a check against both possible line curvature (e.g. distortion due to self-absorption) and errors in the preparation of any one standard. All of the standards used are shown in Table 2.

During the actual running of solutions in both plasma emission spectrometry and A.A.S., the standards were run first, then the six samples, then the entire set of solutions in reverse order so that two runs were performed on each solution. This was done to cancel out any instrumental drift which might occur from the first to the last sample. The results of three sets of runs; one set on the plasma spectrometer with the internal standard function off, one set with the internal standard on, and one set on the atomic absorption unit, are presented in Table 3.

Each number in Table 3 represents the mean of 6 replicas and is given ± 2 standard deviations. While the plasma spectrometer is theoretically capable of simultaneously determining all of the elements listed, in practice it was found that usually no more than 5 or 6 elements could be comfortably handled at any one time due to variations in the instrumental calibrations for each element over a long period of time (one-half hour or so). Consequently, the elements Fe, Mg, Ca, and Mn were run as a group while Si, Al, K and Na formed a second group. By A.A.S. of course, each element was determined separately. The results show that with the exception of Fe, all of the elements determined overlap each other within the 2σ significance range. Although no explanation can be given for the difference in iron values by A.A.S. and emission spectrometry, a titrimetric determination on another sample split gave a value of 4.37% Fe_2O_3 which is more in agreement with the emission spectrometric results. Table 3 also shows that the magnitude of the standard deviation tends to be significantly greater for the atomic absorption determinations than it is for either of the sets of data obtained from plasma emission spectrometry.

This is especially true for silica. Although part of the scatter may be explained by the observation that the silicon hollow cathode lamp was beginning to fail, the standard deviations obtained for silica in rocks and coal ashes by plasma emission spectrometry are nevertheless better than those obtained by A.A.S., even under optimum conditions. No attempt was made to rigidly define and compare detection limits for the various elements by emission spectrometry and atomic absorption because such limits tend to be affected by many factors which are easily altered (e.g. sample composition, gas flow and pressure, optical alignment, electronic stability, etc.). However, on the basis of observations made during this study, and ignoring the major constituents, it can generally be said that those elements that have strong emission lines or form refractory oxides are determined better at low concentrations by plasma emission spectrometry than by A.A.S.

The results in Table 3 also indicate that the standard deviations for the plasma spectrometric determinations in which an internal standard was employed tend to be somewhat better than those in which no internal standard was used, although the differences do not appear to be statistically significant.

Some studies here as to whether or not the plasma spectrometer is capable of adequately determining some trace elements currently done by conventional d.c. arc spectrography indicate that the elements Ba, Cr, Cu, Sr, V and Zr may be done on the spectrometer. In addition to the previously mentioned advantages of using the spectrometer, the initial results indicate that an improvement in precision also results. This is probably because of two factors, the first of which is the use of a more stable excitation source and second, the use of a larger sample size. A 200 mg sample is taken for the fusion technique while only 6 mg of sample is used per electrode for spectrographic analysis. The use of a greater sample size assumes added significance where trace elements tend to be concentrated in inhomogeneously distributed accessory minerals (e.g. Zr in zircon) (2).

Despite the use of a greater initial sample size, however, the dilution of the sample during sample preparation is considerably greater for the spectrometer than it is for the spectrograph. Consequently, the absolute quantities of the sample excited in the spectrometer are much less than that in the spectrograph. Because of this, the conventional spectrograph is still to be preferred for trace elements which are present in minute quantities such that when diluted, would fall below the detection limits of the spectrometer. However, since detection limits, as stated above, tend to be variable in nature, it is not possible to specify the concentrations of each element below which the spectrograph is to be preferred. This must be left to the judgement of the individual operator and laboratory.

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Literature Cited

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3. "Analytical Methods for A.A.S.", (1973), Perkin-Elmer Company, Norwalk, Conn.

Table 2. Standards Used in Plasma Spectrometric and Atomic Absorption Analyses of High Temperature (750°C) Coal Ashes

Species / STD	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	TiO_2	Cu	Ba	Sr	V	Zn	Zr
G-2	69.2*%	15.1%	2.75%	2.00%	0.76%	0.034%	4.50*%	4.05*%	0.50%	-	1860ppm	477ppm	34ppm	-	300ppm
PCC-1	-	-	-	-	-	-	-	-	-	-	-	-	-	36ppm	-
W-1	52.6	15.0	11.06	10.96	6.52	0.175	0.63	2.15	1.08	110ppm	169	198	260	86	105
T-1	62.6	16.2	5.88	5.12	1.82	0.100	1.23	4.32	0.56	-	579	-	-	160*	170
BR	38.3	10.25	12.9*	13.9*	13.34*	0.205*	-	-	2.62*	72	1080	1350	240	160	-
NBS98	59.1	25.54	2.05	0.21	0.72	0.005	3.17	0.26	1.43	-	-	-	-	-	-
BR:NBS98 1:1	48.7	17.9	7.48	7.06	7.04	0.105	2.29	1.67	2.03	-	-	-	-	-	-
NBS98A	48.9	33.2*	-	-	-	-	1.04	0.082	-	-	-	-	-	-	-
NBS97	-	-	-	-	-	-	-	-	-	-	-	-	224	-	1850*
PSOC364	-	-	-	-	-	-	-	-	-	317*	2320*	5000*	400*	-	-
PSOC364:Blank 1:1	-	-	-	-	-	-	-	-	-	158	1160	2500	200	-	-
Blank+	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

*Used for high standard calibration of plasma spectrometer

+Blank is spec-pure silica

G-2 (granite), PCC-1 (peridotite), W-1 (basalt) are U.S. Geological Survey rock standards, T-1 is a tonalite rock std from Tanganyika, BR a basalt from the Centre de Recherches Petrographiques at Geochemiques, France, NBS97 and 98 are clays from the U.S. National Bureau of Standards and PSOC364 in a coal ash.

Table 3. Comparison of Atomic Absorption* and Plasma Spectrometric* Data from a Coal Ash (PSOC 361)

	d.c. Plasma Spectrometry		Atomic Absorption
	No Internal Standard	Internal Standard (Ge)	Spectrophotometry
SiO_2	61.0% ±.8	60.6% ±.5	57.5% ±5.6
Al_2O_3	27.6 ±.7	26.7 ±.5	27.1 ± .4
Fe_2O_3	4.28 ±.04	4.37 ±.04	4.54 ± .06
CaO	0.794±.008	0.798±.016	0.844± .046
MgO	0.861±.014	0.868±.010	0.875± .014
MnO	0.018±.0004	0.018±.0004	0.018± .002
K_2O	2.69 ±.036	2.65 ±.030	2.58 ± .042
Na_2O	0.767±.050	0.753±.048	0.813± .064

Each value given represents the mean of six sub-samples ± 2 standard deviations.

*Atomic Absorption unit employed was a Perkin-Elmer Model 403, instrumental parameters for A.A.S. were as stated in the Perkin-Elmer manual (3) with the exception of Ca for which a N_2O-C_2H_2 flame was used instead of the recommended air-C_2H_2. The plasma spectrometer was a Spectrametrics Spectraspan III.