

Rapid Estimation Of % Ash In Coal From % Silicon Obtained Via FNAA, XRF,
And Slurry-Injection Atomic Absorption Spectrometry Techniques

by

Donald G. Hicks, James E. O'Reilly, and David W. Koppenaar

Departments of Chemistry, Georgia State University, Atlanta, GA, 30303 and
University of Kentucky, Lexington, KY, 40506; and Institute for Mining and
Minerals Research, Kentucky Center for Energy Research, Ironworks Pike,
Lexington, Ky, 40583.

INTRODUCTION

The ash content of coals is an important classical parameter for their eventual use as fuels, as feedstocks in liquefaction and gasification processes, and in metallurgical processes. For example, it is a fairly common procedure to blend various lots of coal to obtain a more constant ash content when it is used in coal-fired boilers and power plants. Among other parameters, the relative rate of combustion as well as the maximum combustion temperature of aqueous coal suspensions were found by Isaev and Delyagin(1) to be dependent on the ash content of coals used in the study. Other workers have noted that the content of ash and certain minerals in coal can affect the yields from gasifiers and liquefiers.

The conventional method for determining the percent high-temperature ash of coal is simply to burn slowly a representative sample at elevated temperature in a muffle furnace. The method is simple, accurate, and reproducible; but requires a considerable amount of time in the laboratory.

A number of approaches, and refinements thereof, have been reported to be useful for estimating the mineral matter and ash contents of coal from the levels of the major inorganic elements present(2-7). For a variety of reasons, the use of elemental content for the estimation of ash or mineral matter in coals is considerably less exact than, for example, a somewhat similar approach for estimating BTU values(8-10).

Recently, Loska and Gorski(11) and Block and Dams(12) have shown that a reasonable correlation exists between the ash content of coal and the silicon level determined by fast instrumental neutron activation analysis (FNAA) for Silesian and Belgian coals, respectively. They reported that best results came from a logarithmic correlation, % ash = $a(\% \text{ Si})^b$ where a and b are constants. Their mean absolute error for estimation of ash content was about 1.8 % ash, or about 8 % relative error. We have recently developed a very rapid atomic absorption method for analyzing coals for many trace and minor-level elements by directly aspirating aqueous slurries of finely powdered coal into a conventional AA spectrometer(13,14). Because AA spectrometers are so common, it was our desire to see if the slurry-injection atomic absorption spectrometry (SIAAS) method would provide a suitable and fast method for estimating the ash content of some typical U.S. bituminous coals simply from measurement of their silicon concentrations. Comparisons between simple linear plots and log-log plots of data were also of particular interest to us.

This paper reports the results and statistical analyses we have obtained for the correlation of the ash content of a number of eastern Kentucky, western Kentucky(Illinois basin), and West Virginia coals with the silicon content as determined by slurry-injection atomic absorption(SIAAS), X-ray fluorescence(XRF), and fast neutron activation analysis(FNAA). In addition, results are compared with the % silicon and % ash data published by the Illinois State Geological Survey(15, 16) for a wider variety of coals.

EXPERIMENTAL

Coal samples were crushed, pulverized in a swing-mill, and sieved as previously described(13). The high temperature ash values for coals used in this work are from standard 750°C ASTM ashes(17).

The percent silicon in about 20 coals was determined by Drs R. C. Young and W. D. Ehmann of the University of Kentucky Department of Chemistry using FNAA procedures described elsewhere(18). These silicon contents from FNAA were considered to be benchmark values, and were used as standards to calibrate the signals from the XRF and AA spectrometers for determination of Si in these and other coals. The XRF and AA signals were then converted to values of % Si by XRF and % Si by slurry-AA for the various coals. Subsequently, correlations of the % ash with the % Si obtained by the several instrumental techniques were compared.

X-ray fluorescence measurements were performed using a Finnigan 900B energy-dispersive spectrometer fitted with a rhodium target tube, and operated at 14 kV and 0.30 mA. Samples were run as powders and counted for 1000 seconds. Total and net fluorescence counts were acquired for the Si K photopeak (1.74 keV). For SIAAS determinations, coal samples were further ground and sieved by procedures already reported(13). The final slurries aspirated into the burner were 1.5 % wt/vol solids in 0.5 % Triton X-100 surfactant. A 5-cm nitrous oxide/acetylene flame was used, and the analytical wavelength was 251.6 nm. The atomic absorption spectrometer employed was a Varian AA-6 whose standard tantalum nebulizer intake capillary had an inside diameter of 0.400 mm.

RESULTS AND DISCUSSION

To summarize, our results show that a reasonably useful linear correlation can be made between the % high-temperature ash and the % Si for typical Appalachian and Illinois Basin bituminous coals. Figure 1 illustrates a plot for such a correlation involving % Si from SIAAS data for 24 arbitrarily chosen Kentucky and West Virginia coals which range from about 4% to 28% ash. The linear least squares line fit to the data (see Table I) has a correlation coefficient of 0.890; and the standard error of estimate(SEE), the root-mean-square deviation of the y-values for the straight line fit, is 2.4 % ash. Exemplified by Figure 2, similar correlations of % Si by XRF or FNAA vs. % Ash for the same coals result in a roughly similar appearance, but the fits are significantly better as seen by the SEE values of 1.73 and 1.71 in Table I.

The visual appearance of the linear plots such as shown in Figures 1 and 2 are somewhat less satisfying than those of Loska and Gorski(11) and of Block and Dams(12). In the latter cases, however, the plots are log-log and cover a considerably wider range of % ash (about 3% to 40%)! Thus, the deviations from straight line fits appear to be less. But statistically, the fits are more or less equivalent.

Table I presents a comparison of the linear-least-squares fit for Kentucky and West Virginia coals when the % Si is determined by a number of different instrumental methods. The correlations are all roughly comparable---similar slopes, intercepts, standard errors, and correlation coefficients---except for the fact that the fit is significantly worse with the simple SIAAS method for Si determination. This is understandable in view of the facts that SIAAS is not a highly accurate method, and, is somewhat affected by the varying matrix and different particle-size distributions from one coal to another(13). Still, the median relative error in determining % Si by SIAAS is only 10 % for these coals. The larger method errors inherent in SIAAS itself, relative to XRF or FNAA,

apparently add to some degree to the natural uncertainties in the correlation, and decrease the overall fit. However, initial studies with a recently developed acid-slurry-AA method (ASIAAS) for determining silicon(19) have produced % ash-% Si correlations comparable to those obtained from XRF and FNAA data. In this ASIAAS procedure, powdered coal is slurried with a relatively dilute acid mixture (HCl-HF-Triton X-100) for a few minutes in an ultrasonic bath. Further results will be reported at a later date. Similar to previous observations(11,12), we found that relative errors of the worst individual cases seemed to be somewhat larger for coals with lower % ash.

Correlations within a Rank of Type of Coal: Included in Table I are some results for similar correlations using data published by the Illinois Geological Survey(15,16) for a greater number and wider range of coals. These were studied in order to see if significantly better correlations could be obtained within one type or rank of coal than seemed to be the case with the arbitrarily selected set of Kentucky and West Virginia coal samples we used. It was distressing at first to find the very poor correlation for coals from a single source. For example, 15 Harrisburg(No. 5) coals exhibited a correlation coefficient of only 0.417. Apparently, this is primarily a result of the restricted range of % ash values for these coals. However, it is interesting to note that the standard error of estimate (a more meaningful parameter) is actually better for these than any other set of coals. The selection of coals with more widely spaced % Si values covering a wider range of ash values results in better correlations and better appearing plots(11). This notion was tested by arbitrarily selecting one coal within each 0.1 % Si interval from the 172 coals analyzed by the ISGS(15). The correlation (labelled "arbitrary" in Table I) is about as good as any of the others.

Linear versus Logarithmic Correlations: Table II presents the results of logarithmic correlations on the same sets of coals as in Table I, and compares these with previous findings(11,12). On the whole, the logarithmic correlation coefficients for American coals were slightly worse than those from the linear correlations, and there seems to be no particular reason to prefer the former over a simple linear fit. The general conclusion from the results presented in this work is that, regardless of the source or rank of the coal or the rapid method used to measure the silicon content, the % ash of typical American bituminous coals can be estimated by simple linear correlations to within a standard absolute error of about 1.7 % ash---approximately 10 % relative error. This compares with a value of about 1.8 % ash absolute error for Silesian coals(11), and about 8.0 % relative error for Belgian coals(12).

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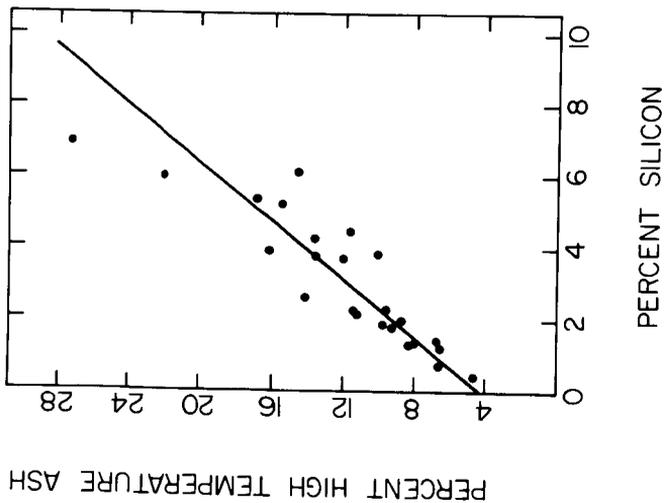


Figure 1: Plot of % high-temperature ash vs. % silicon for some Kentucky and West Virginia Coals. Si determinations by simple slurry-injection atomic absorption spectrometry (SIAAS).

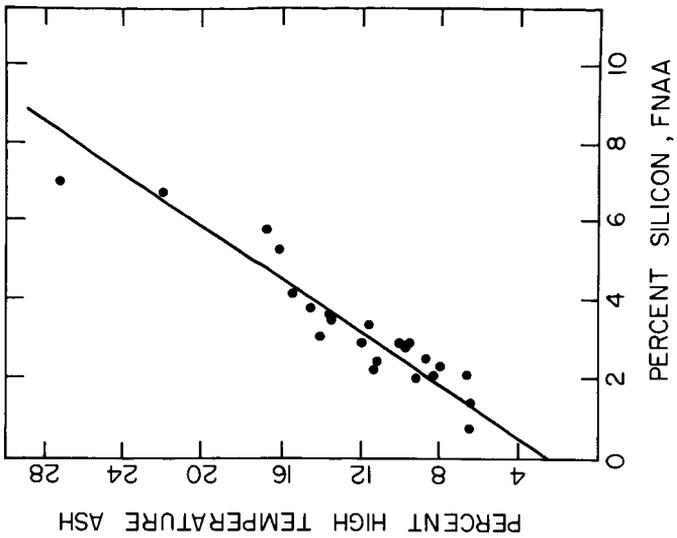


Figure 2: Plot of % high-temperature ash vs. % silicon for some Kentucky and West Virginia Coals. Si determinations by instrumental fast neutron activation analysis (FNAA).

TABLE I: Linear Least Squares Correlations Of Percent Ash vs. Percent Silicon In Some Coals

Type of Coal	Number of Samples	Range of % ash	Method of Si Determination ^a	% ash = p(% Si) + q	SEE ^b		Reference
					slope (p)	(Standard Error of Estimate) as % Ash	
KY & WV	24	4.6-27.3	SIAAS	4.33	2.41	0.890	This work
KY & WV	23	6.5-27.3	XRF	2.88	1.73	0.941	"
KY & WV	23	6.5-27.3	FNAA	2.69	1.71	0.943	"
ILL (No. 5) Harrisburg	15	10.3-14.8	XRF	7.79	1.18	0.417	15
Western	29	4.1-20.4	XRF	4.88	1.96	0.856	15
ILL Basin	80	3.3-16.0	XRF	5.70	1.65	0.659	16
Arbitrary ^c	40	4.1-25.9	XRF	4.25	1.87	0.924	15

^aSIAAS = slurry-injection atomic absorption spectrometry; XRF = X-Ray fluorescence; FNAA = instrumental fast (14 Mev) neutron activation analysis.

^bStandard error of estimate is the RMS deviation in the y-values from the straight line fit.

^cData arbitrarily selected for one coal from each 0.1 % silicon interval from the 172 coals listed.

TABLE II: Logarithmic Least-Squares Correlations of percent Ash Vs. Percent Silicon In Some Coals^a

Type of Coal	Method of Silicon Determination	% Ash = a(% Si) ^b		Correlation Coefficient
		a	b	
KY & WV	STAAS	6.82	0.525	0.917
KY & WV	XRF	5.82	0.652	0.919
KY & WV	FNAA	5.72	0.663	0.902
ILL(No.5)				
Harrisburg	XRF	8.85	0.348	0.426
Western	XRF	7.80	0.455	0.845
ILL Basin	XRF	7.20	0.507	0.699
Arbitrary	XRF	7.37	0.547	0.906
Silesian ^b	FNAA	7.63 ^d 5.27 ^e	0.634 0.89	- -
Belgian ^c	FNAA	4.78	0.930	-

^a Coals and symbols identified in Table I.
^b Reference 11; 43 coal samples.
^c Reference 12; 31 coal samples.
^d For coals with Si = 4.2 % and above.
^e For coals with Si = 4.2 % and below.