ELECTRON MICROPROBE TECHNIQUE FOR QUANTITATIVE ANALYSIS OF COAL AND COAL MACERALS

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Electron microprobe analysis is a powerful tool for analyzing the chemical composition of component grains and whole samples when sample quantities are too small for other analytical techniques. A quantitative procedure for microanalysis of elements such as Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Sr, Ba in coal and coal macerals is highly desirable but development of quantitative techniques for microanalysis of organic materials has lagged behind progress in the material sciences. The heterogeneous character, low density, and light element composition of organic materials present special problems not accounted for in the usual microanalytical methods employing standard ZAF correction procedures applicable to mineralogy and metallurgy.

Alternative procedures developed by workers in the biological sciences, which minimize the problems specific to work with organic materials, might be better suited for analysis of coal than standard ZAF techniques. Quantitative methods have been most extensively developed for thin-sectioned specimens. Those techniques, which include Hall's (1968) peak-to-continuum and Russ's (1974) elemental ratio methods, rely on the assumption that absorption and fluorescence effects may be neglected because of the extremely short path length for exiting x-rays. For thick specimens these assumptions must be modified. Techniques include the standard ZAF correction procedures for material with light element matrices (Love and Scott, 1980) and peak-to-background methods (Miller and Corbet, 1972). Other techniques closely related to our approach are the peak-to-continuum (P/C) methods used for the analysis of particles by Statham and Pawley (1978) and Small and others (1980).

Most of the P/C methods rely on the hypothesis that, as an initial approximation, continuum and characteristic radiation are similarly affected by changes in particle-size, density, or specimen thickness. Thus the ratio of peak intensity to continuum intensity is approximately constant for a given elemental concentration. The P/C method should thus solve the major problems with microanalysis of organic materials: a dominantly light elemental composition which is not directly measurable by microprobe techniques, inhomogeneity, and variable density. Even though the analyzed elements have a low concentration in a light-element matrix the question remains as to whether the assumption of negligible absorption and fluorescence effects is valid for this method.

Methods

A set of organic reference standards has been analyzed as the first step in establishing a P/C procedure for electron microanalysis of minor and trace elemental concentrations in organic materials such as coal macerals. The one-to-one linearity of published to observed elemental concentrations is used as a test of the validity of the P/C method and its internal assumptions. Programmed correction factors relating peak intensity to concentration are obtained from best fit procedures and are then used for analysis of unknowns of similar composition.

Nine National Bureau of Standards (NBS) reference standards of selected organic materials were chosen for this evaluation of the P/C method. The standards consist of four bituminous and two subbituminous coals, citrus and tomato leaves, and pine needles. Samples were ground to a fine powder, vacuum-dried, and compressed under 10 tons pressure to form two flat pellets for each standard. The pellets were then carbon-coated for electron microprobe analysis.

Microprobe operating conditions during acquisition of chemical analyses were 15 keV accelerating voltage and 920 picoamperes beam current. The probed area was approximately one square millimeter. Fifty-three 400 second analyses were obtained during May and June 1985. Five analyses of incompletely ground and/or improperly coated samples were removed from the data set.

Between four and ten analyses were combined to obtain a single averaged spectrum for each reference standard. The region 2.00-5.00 keV was chosen for measurement of continuum intensity. A reference library of pure element and oxide standard spectra was used with the Tracor-Northern XML least squares fitting routine to generate peak-to-continuum elemental ratios for each averaged spectrum. This ratio was computed by the relationship: correction factor x (peak intensity)/(continuum intensity).

The peak-to-continuum ratio, assumed in the P/C method to be proportional to absolute elemental concentration, was plotted against reported concentration for each element of interest (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe). The amount of deviation of the best-fit line through the origin from the hypothetical one-to-one relationship between observed P/C and reported concentrations was used to change the reference library stored correction factors. The peak-to-continuum ratios were then computed with the adjusted correction factors and final plots for each element were made.

Results

Results are summarized in Table 1 and Figures 1 and 2. Some questions to be considered while evaluating the peak-to-continuum results include: whether the data show the linear one-to-one relationship between reported element concentration and P/C ratios that would indicate the method and its assumptions are valid for the elements examined; whether scatter in the data indicate possible additional effects on x-ray intensities or analytic or sample preparation problems; and what trends are specific to certain elements or appear to affect all elements. Examination of the data for each element of observed versus literature-reported concentrations yield the following observations:

1. Silicon, phosphorus, and chlorine were not present in both observed and reported analyses of enough standards to generate a significant number of data points. Although the three data points graphed for each of these elements appear to show the desired linearity, they are too few to permit conclusive interpretation of the results.

2. Magnesium and titanium were only present in very low concentrations, mostly as less than 0.2 wt%. The data points thus cluster near the origin. Mg does show linearity with two points at slightly higher concentrations, but the clustered data points of both elements show some scatter from the linear relationship. In part, this may be accounted for by the detectability limits of the EDS microprobe system and by the relatively higher error of 5%-10% reported in microanalysis of organic materials as compared to work in the material sciences.

3. Aluminum (Figure 1), calcium, sulfur, and potassium show a linear relationship between observed and literature values. Data points are spread over a range of concentration values of up to 7% and show a low degree of scatter. These elements appear to be behaving in conformity with the assumptions of the peak-to-continuum method and might be expected to yield valid results for unknowns.

4. Sodium, known to be subject to elemental mass loss problems during sample preparation and microprobe analysis, is only present in concentrations of <0.3 wt%. Most data points cluster near the origin but do not show as much scatter as would be expected if mass loss had occurred.

Table 1. Results of Microprobe Analysis of NBS Coal and Botanical Standards Comparing Observed and Reported Weight Percentages

	REF STD	H	C	N	O	Na RPT	Na OBS	Mg RPT	Mg OBS
1	1632	3.85	66.00	1.23	18.80	0.08	0.07	0.12	0.13
2	1635	4.07	62.60	1.26	24.60	0.24	0.19	0.10	0.10
3	2682	4.70	75.00	0.80		0.10	0.08	0.20	0.19
4	2683	5.00	79.00	1.60		0.05	0.05	0.05	0.06
5	2684	4.80	68.00	1.60		0.03	0.05	0.08	0.12
6	2685	4.60	66.00	1.10		0.08	0.11	0.10	0.16
7	1572							0.58	0.57
8	1573	5.08	37.80	4.97		0.06	0.10	0.69	0.62
9	1575	6.48	51.40	1.20		0.01		0.13	0.13

	REF STD	Al RPT	Al OBS	Si RPT	Si OBS	P RPT	P OBS	S RPT	S OBS	Cl RPT	Cl OBS
1	1632	3.01	2.79	6.01	5.65	0.03		1.58	1.46	0.08	0.08
2	1635	0.31	0.29	0.54	0.61	0.01		0.33	0.42	0.00	
3	2682	0.46	0.41		0.60			0.47	0.58		0.09
4	2683	0.86	0.75		1.27			1.85	1.93		0.19
5	2684	1.10	1.21		2.73			3.00	3.12		0.09
6	2685	1.70	1.93		3.95			4.62	4.16		0.06
7	1572	0.01	0.02		0.21	0.13	0.14	0.41	0.52		0.10
8	1573	0.09	0.09		0.55	0.34	0.28		0.62	1.07	1.07
9	1575	0.05	0.06	0.03	0.20	0.12	0.14	0.10	0.19	0.01	0.04

	REF STD	K RPT	K OBS	Ca RPT	Ca OBS	Ti RPT	Ti OBS	Fe RPT	Fe OBS
1	1632	0.42	0.45	0.24	0.23	0.17	0.11	1.12	1.04
2	1635	0.01		0.55	0.66	0.02		0.23	0.37
3	2682	0.01		1.10	1.35	0.05	0.05	0.24	0.40
4	2683	0.08	0.09	0.20	0.18	0.04	0.05	0.76	0.47
5	2684	0.20	0.27	0.44	0.33	0.06	0.06	1.50	0.90
6	2685	0.26	0.38	0.52	0.53	0.09	0.10	2.90	1.23
7	1572	1.82	1.72	3.15	2.95			0.01	0.07
8	1573	4.42	4.17	2.92	2.69	0.01		0.02	0.10
9	1575	0.37	0.37	0.42	0.43			0.02	0.10

5. Iron data (Figure 2) shows the least linearity and greatest scatter of the analyzed elements. Observed values of samples with the least iron are too large; measured values for samples with higher iron content are too low. There does not appear to be a consistent trend to these variations. Iron is the heaviest element analyzed in the organic standards and the assumption of negligible fluorescence and absorption effects may not be valid. However, such effects would be expected to cause data points to be consistently offset in one direction and cannot fully explain what is observed.

The peak-to-continuum method has performed well for certain elements - Al, Ca, S, K. Evaluation of standards with a greater range in concentration is required to confirm that the method works as well for elements such as Mg, Ti, and Na. Problems with evaluating Fe content might be elucidated by analysis of additional reference standards or a set of standards created using standard additions of know quantities of Fe.

Application

Initial studies using the peak-to-continuum method for microprobe analyses of organic materials (Karner and others, 1984, Karner and others, 1985) show excellent potential for obtaining valuable geochemical data for coal lithotypes and macerals. The first survey of lithotypes in lignite of the Beulah-Zap bed of the Sentinel Butte Formation (Paleocene) in North Dakota examined vitrain, fusain and attritus at several locations within the seam (Karner and others, 1984). Common inorganic elements associated with these lithotypes included Na, Mg, Al, Si, S, K, Ca, and Fe. Samples of vitrain from a single vitrain layer in the seam have quite uniform elemental compositions while vitrain from different levels in the seam have significantly different concentrations of elements particularly Mg, S, and Ca. Fusain and attritus were quite different from vitrain in chemical composition, generally containing higher Ca, Mg, and Si, and lower Al, S, and Fe.

A survey (Karner and others, 1985) of the inorganic chemistry of huminite group macerals in four low-rank coals included analyses of ulminite representative of the Beulah-Zap (BZ) and Hagel (HG) lignites, ND, the Martin Lake (ML) lignite, TX, and vitrinite of the Rosebud (RB) subbituminous coal, MT. Major differences in maceral chemistry between coals and compositionally distinct maceral types within coals are shown by characteristic analyses given in Table 2.

Table 2. Characteristic Compositions Determined by Microprobe Analyses of Huminite Group Macerals in Four United States Low-Rank Coals Given in Weight Percent.

		Na	Mg	Al	Si	S	Ca	Fe	Sr	SUM
Beulah-Zap	(BZ) Ulminite 1	0.32	0.11	0.22	0.10	0.45	0.49	0.51	0.04	2.24
Beulah-Zap	(BZ) Ulminite 2	0.54	0.38	0.18	0.12	0.43	1.54	0.79	0.06	4.04
Hagel	(HG) Ulminite 1	0.06	0.15	0.16	0.08	0.59	1.03	0.24	0.01	2.32
Hagel	(HG) Ulminite 2	0.07	0.42	0.24	0.17	0.51	2.40	0.68	-	4.49
Martin Lake	(ML) Ulminite 1	0.15	0.38	0.32	0.28	1.25	1.69	0.45	0.05	4.57
Martin Lake	(ML) Ulminite 2	0.06	0.42	0.16	0.07	1.16	1.67	0.36	0.06	3.96
Rosebud	(RB) Vitrinite 1	0.06	0.20	0.33	0.05	0.76	0.71	0.08	0.03	2.22
Rosebud	(RB) Vitrinite 2	0.12	0.32	0.18	0.11	0.73	0.86	0.06	0.04	2.42

Comparing the four coals: BZ ulminites have high Na and Fe and low S and total constituents; HG ulminites have high Ca and low Na and S; ML ulminites have low Na and high Mg, S and total constituents; while RB vitrinite has moderate to low values for all elements. Within the coals BZ and HG ulminites tend to occur as either low or high Na+Mg+Ca types; ML ulminite as a low or high Al+Si type and RB vitrinite types vary from low to high Mg/Al. The chemistry of the huminite group macerals and the bulk compositions of the four coals have striking similarities, including the

high Na and low S for BZ, high Ca and low Na and S for HG, and low Na and high S for ML. Ulminite chemical variation between coals and within seams suggests the importance of hydrogeochemical processes during diagenesis.

The results of these studies show important patterns of concentrations and variability of numerous inorganic elements. These geochemical characteristics may have great significance for development of our understanding of coal formation and utilization.

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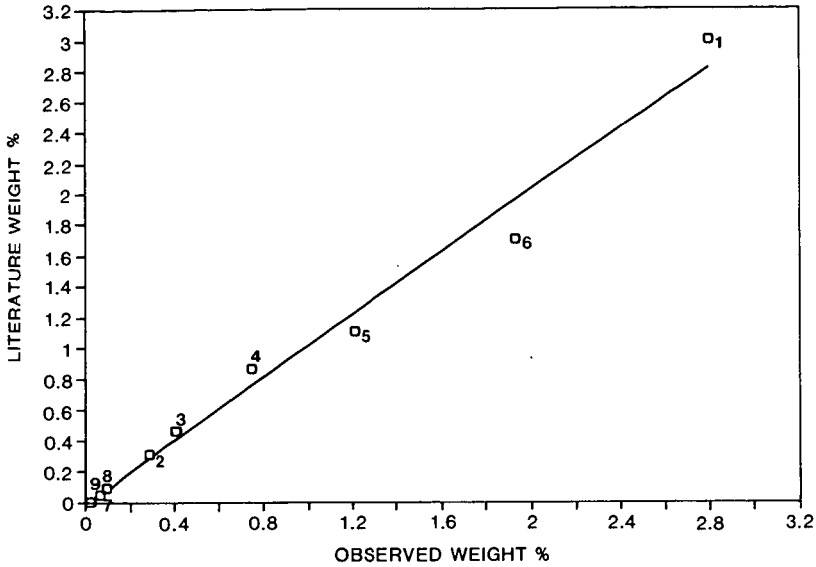

Figure 1. Aluminum calibration curve. Peak to continuum method.

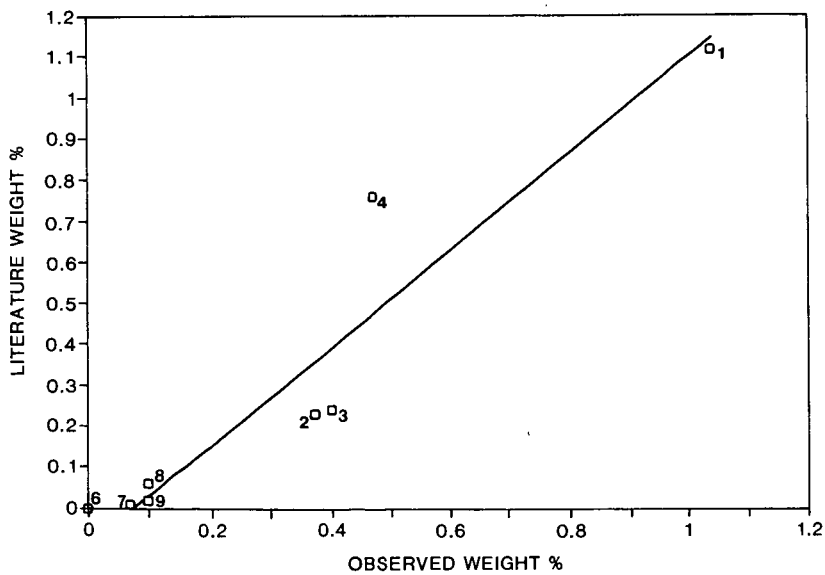

Figure 2. Iron calibration curve. Peak to continuum method.