Comparison of methods for the determination of organic oxygen in coals

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Coals distributed widely in rank and geographical origin have been analysed for organically-bound oxygen by several conventional and fast neutron activation analysis (FNAA) techniques. Pyrolysis of demineralized coal with measurement of evolved CO_2 by coulometry was found to be the most reliable of the conventional methods. Direct FNAA determinations of organic oxygen by analyses of demineralized coal (DMC) samples yielded data in excellent agreement with pyrolysis, as did values computed using a modified 'by difference' calculation. The convergence of data from these totally independent approaches, suggests a measure of true organic oxygen levels has been achieved. A 'difference method' based on FNAA determinations of total dry coal oxygen and inorganic oxygen in low temperature ash yielded organic oxygen data that were typically lower than pyrolysis values, possibly due to oxidation of organic sulphur in the ashing process and/or the presence of non-extractable mineral oxygen in the DMC used in the pyrolysis method. A third FNAA 'difference method' based on simultaneous determinations of both total oxygen and silicon contents of dry whole coals, followed by estimation of the inorganic oxygen contents based on the silicon contents, was found to be rapid and adaptable to on-stream analysis. However, observed mineralogy-dependent deviations from a simple inorganic oxygen–silicon relationship suggest that the latter technique would be most successful when applied to coals with similar mineralogy.

(Keywords: coal; oxygen; instrumental methods)

The occurrence of organically-bound oxygen is second only to carbon in most coals of lignite through bituminous rank. Consideration of atomic O/C ratios for such coals indicates that an oxygen atom is bound to every 3–15 carbon atoms, depending on rank. The role of oxygen in influencing the 'primary structure' of coal is therefore evident. Oxygen also possesses an electronegative characteristic that manifests itself through extensive hydrogen bonding among the various molecular units of coal (i.e., the 'secondary structure'). Oxygen thus exhibits a dual bonding role composed of intra- and inter-molecular associations that is unique in scope among the major constituents of coal.

The secondary structural effects have been implicated in the inhibition of coal-to-liquid conversion[1,2]. Various investigators have examined oxygen functional group distribution among liquefaction products[3-5], yield dependence on oxygen distribution and removal[6,7], and the dependence of low temperature solubilization reactions on oxygen content[8,9]. These studies indicate that oxygen and its compounds have an important, albeit partial, influence on the liquefaction behaviour of coals.

The presence of oxygen is also an important factor in determining the surface properties of coal. Such properties are crucial to the wet beneficiation or preparation of coal. The polar nature of oxygen controls the hydrophilic character of the coal surface, thereby affecting the wettability of the material. Reports relevant to this property are available; one deals with relationship between oxygen group content and flotation response[10], another with oxidation effects on coal hydrophobicity[11].

Oxygen has not been an element easily determined in coal, either in total or as its functional moieties. The difficulties associated with its determination have been recognized by the coal science community; the discussions of Given and co-workers have been especially enlightening[12-15]. Total oxygen in organic materials has traditionally been determined using the approaches of Schütze[16], Unterzaucher[17], or some variant of these methods[18-20]. An international standard based on these methods exists for the determination of oxygen in hard coal;[21] a similar standard is also available for other 'organic materials'[22]. Difficulties encountered when using these methods for coal have been reported to arise from coal moisture, oxygen-containing mineral constituents (carbonates, sulphates and hydration water), and the possible presence of reducible metal oxides. Other high temperature pyrolysis procedures have also been applied to coal[23], notably the work of Kinson and Belcher[24], who used an RF-heating furnace to evolve all (organic and inorganic) oxygen.

The Unterzaucher–Schütze procedures have never been widely applied to the analysis of oxygen in coal, probably due to the perception of their tedious analysis routines and the recognized need for judicious corrections[13]. Most coal scientists in the U.S. still rely on the error-prone oxygen 'by difference' procedure, a mistake that is only promulgated by the persistence of the American standard in existence[24]. Errors inherent in the use of this oxygen by difference calculation on the dry,

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aliquot. Metal concentrations were determined by fusion or acid dissolution of the sample and atomic absorption or plasma emission detection. Fluoride and chloride contents were determined using oxygen bomb combustion treatment and ion chromatographic detection.

Dry coal, demineralized coal (DMC) and LTA samples were stored under an inert gas atmosphere prior to analysis. Tests for sample homogeneity and the stability of the oxygen content as a function of storage time suggested that these factors did not significantly affect the comparisons presented here[37].

Three approaches to the determination of organic oxygen in coal using FNAA were evaluated and compared with conventional methods in this work. All the FNAA methods are based on the $^{16}O(n,p)^{16}N$ ($t_{1/2} = 7.1$ s) nuclear reaction induced by 14 MeV neutrons from a Raman 711 neutron generator and subsequent counting of the 6.13 and 7.11 MeV gamma rays with two 12.7 cm × 12.7 cm NaI(T1) scintillation detectors at 180°. The detectors are coupled to a Nuclear Data multi-channel analyser gated to count gamma rays above 4.5 MeV. Software normalizes the ^{16}N activity to a time increment corrected BF_3 neutron monitor count and computes oxygen content by the standard comparator method, using benzoic acid as the standard. Fluorine is the only significant interference to FNAA oxygen determinations in fossil fuels[26]. Fluorine corrections were applied to the FNAA data for the DMC samples in this study, but were generally very small (typically < 0.05 wt % equivalent oxygen).

Silicon may be determined simultaneously with oxygen *via* the $^{28}Si(n,p)^{28}Al$ ($t_{1/2} = 2.24$ m) nuclear reaction followed by counting the 1779 keV gamma rays of ^{28}Al. Typical relative standard deviations for replicate determinations are less than 1% for O and less than 2% for Si, when these elements are present at a concentration level of at least 1%. O and Si analyses were performed on National Bureau of Standards (NBS) Standard Reference Materials (SRMs) 1632, 1632a, 1633, 1633a and 1635. Although certified values for O and Si are not available for most of these SRMs, our data[37,38] are in excellent agreement with published literature values. The reliability of the Si determinations was confirmed by the method of standard additions, using high purity graphite doped with NBS SRM 91, Opal Glass. A linear correlation between observed FNAA counting rate and known Si content ($r = 0.9999$) was observed[37].

Oxygen determinations by pyrolysis of the coal or DMC, conversion of evolved CO to CO_2, and subsequent coulometric determination of the CO_2 was accomplished using the Coulometrics, Inc. Model 5060 pyrolysis furnace and CO_2 coulometer. This technique is essentially a modification of the Unterzaucher–Schütze method. Coal or demineralized coal samples were dried at 105°C for 1–2 h, cooled in a desiccator, and a sample of 5–15 mg was weighed into a high purity graphite crucible. The crucible plus sample was placed in the front of a pyrolysis tube (temperature at this point ≈ 100°C) and the tube plus contents were purged with dry, oxygen-free nitrogen for approximately 3 min. The crucible and sample were then moved to the centre of the furnace (temperature, 1130°C) adjacent to a bed of amorphous carbon, and pyrolysed. At these temperatures, the pyrolysis products consist predominantly of CO, H_2 and other minor components. The CO is quantitatively coverted to CO_2 by passing the gas stream over cupric oxide at 400°C. Acidic gases were removed by an MnO_2 filled scrubber column, and the CO_2 is absorbed in an ethanolamine solution which reacts to form a titratable acid. This acid is then titrated with a coulometrically generated base[36]. Integration of the current required to generate enough base to reach the end point allows for an absolute method of analysis (the only calibration required is the use of the well-defined Faraday's number of electrons). Blank corrections are necessary to eliminate oxygen contributions from graphitization of the quartz pyrolysis tube. Blank determinations are performed using an empty crucible and following the same procedure for actual samples. Blank corrections typically average 30 micrograms of oxygen, and are attributed to graphitization of the quartz pyrolysis tube as well as O_2 adsorption on the ladle and crucible. Graphitization produces a constant bleed of carbon dioxide and accounts for two-thirds of the blank correction. Organic standards are periodically analysed to confirm proper instrument operation. The coulometer's detection limit of approximately 0.04 mg CO_2 is adequate to allow determination of organic oxygen in coal and related materials at low levels of occurrence.

Acid demineralization

The acid demineralization, or more properly, the acid treatment of the project samples was carried out to remove inorganic or mineral bound oxygen. The procedure used generally followed established procedures for coal maceral or oil shale kerogen isolation[39–44] with minor modifications. Approximately 2 g of $< 75\,\mu m$ coal were extracted with 150 ml of 6 M HCl and 0.5 g of Brij-35 (a surfactant) for 1 h in an ultrasonic bath to remove carbonates and sulphates and to preclude CaF_2 formation during later stages of the procedure. The samples were then filtered and treated with 150 ml of a 1:2 mixture of concentrated HCl, 50% HF and 0.5 g Brij-35 for 18 h. The samples were then re-filtered and treated again with 150 ml of 6 M HCl to remove residual HF and other fluorides. The samples were again filtered and washed successively with distilled deionized water until the washings were neutral to pH paper. After extraction and washing, the samples were dried in an inert atmosphere at 90°C (to minimize potential oxidation) for subsequent analysis. Analyses performed on the demineralized coal (DMC) included ultimate analysis (including moisture), oxygen determination by FNAA and by pyrolysis coulometry, determination of adsorbed acid halides (F^- and Cl^-), and determination of non-extraced inorganic elements (typically Fe, Ca, Cr and Ti). Correction of the DMC weight was made for moisture adsorbed F^- and Cl^-, and unextracted inorganic species (e.g. FeS_2, CaF_2, Cr_2O_3 and TiO_2).

Low-temperature ashing

Coal mineral matter was isolated following well-documented low-temperature ashing techniques[45–47,15]. Both LFE Model 504 and IPC six-chamber low temperature ashers were utilized. Lignite samples were pretreated with 1N NH_4OAc to convert all carboxylate salts to their respective ammonium salt forms and thereby assist in the ashing procedure[15]. Sample loadings were < 50 mg cm^{-2}, plasma power levels were maintained at 50 W per chamber, and oxygen flow rates were such that chamber pressures were < 270 Pa as recommended by

Table 3 Analyses of dry demineralized PSOC coals

Sample	%C	%H	%N	%S	%O Pyrolysis	%Fe	%Cl	%F	Ca, ppm	Cr, ppm	Ti, ppm	Summation, %	% Residual Ash[a]
548	76.8	5.06	1.46	0.50	15.8	0.08	0.51	0.11	688	14.6	50	100.4	0.0
680	75.0	4.96	1.69	3.61	12.8	1.67	0.40	0.06	266	20.5	50	100.2	3.0
739	79.1	5.31	1.66	2.42	9.80	0.65	1.52	0.06	219	5.0	259	100.6	1.0
773	77.0	5.16	1.44	1.77	12.6	0.71	0.76	0.12	371	21.2	50	99.6	0.0
782	88.5	4.34	1.72	0.69	3.37	0.10	0.97	0.12	208	17.0	50	99.9	1.0
785	71.8	5.15	1.58	1.02	20.8	0.04	0.31	0.04	435	5.0	50	100.8	0.0
791	72.3	5.19	1.96	1.01	21.4	0.09	2.66	0.22	567	43.7	50	104.8	0.0
801	81.2	4.97	1.65	4.30	4.52	3.20	0.74	0.06	249	5.0	50	100.7	4.5
808	82.9	5.53	1.89	1.5	7.11	0.96	1.27	0.05	273	5.0	50	101.3	1.5
821	81.2	5.41	2.02	1.5	8.48	0.41	1.01	0.16	276	5.0	135	100.2	1.5
833	69.3	4.39	1.08	0.55	23.6	0.21	0.16	0.01	108	5.0	50	99.4	0.0
854	79.8	5.42	1.66	0.43	11.7	0.05	0.80	0.12	163	5.0	50	100.0	0.0
866	75.9	4.87	1.34	0.54	16.2	0.13	0.66	0.33	3170	5.0	50	100.3	1.5
871	93.0	2.05	1.01	0.67	1.41	0.07	1.08	0.18	100	5.0	76	99.5	0.5

[a] Not included in summation; data were obtained using a high-temperature thermogravimetric ashing procedure

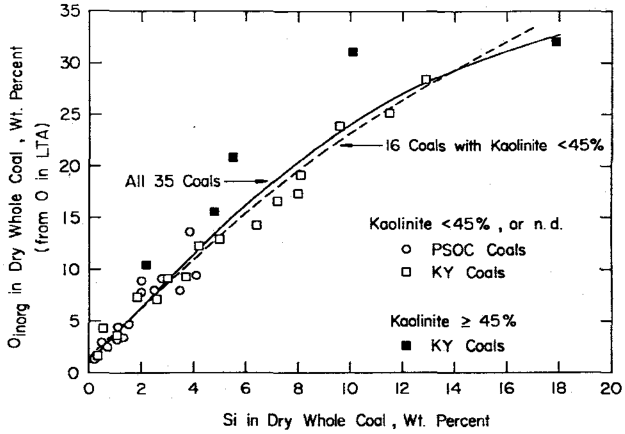

Figure 1 Relationship of silicon content to inorganic oxygen (from LTA analysis), expressed on a whole coal basis

determined by FNAA in a single step irradiation. A plot of silicon content (Si) *versus* the inorganic oxygen content (O_i) derived from analyses of LTA (*Figure 1*) gave the following quadratic best fit relationship ($r = 0.97$) for all 35 samples:

$$O_i^{WC} = (0.84 \pm 0.71) + (2.96 \pm 0.26)Si - (0.065 \pm 0.017)Si - (0.065 \pm 0.017)Si^2 \tag{7}$$

The organic oxygen content of the whole coal on dry basis can be calculated by difference between total oxygen content of the whole coal as obtained by FNAA and the inorganic oxygen content of the whole coal determined from the silicon content by the above mathematical relationship:

$$O_0^{WC} = O_T^{WC} - O^{WC} \tag{8}$$

In practice, total oxygen and silicon contents are determined simultaneously by a single FNAA irradiation of dry whole coal.

RESULTS AND DISCUSSION

Inter-method comparisons

Coal characterization data on our study samples are presented in *Table 4*. These data were determined in our laboratory and may not agree with the Penn State Coal Database information available from Pennsylvania State University (particularly some data for sulphur, ash and carbon). Consultation with Pennsylvania State University scientists involved in the Coal Sample Bank programme indicated that such discrepancies are not unusual and are attributable to sampling differences. Consequently, we relied upon the data obtained internally on our particular aliquot of the sample. Our ultimate analysis data, which are important in determining the calculated oxygen-by-difference values, were checked by comparing our empirically determined calorific values with those calculated using the Mott–Spooner formula, as recommended by Given[15]. For all samples except PSOC 833, comparison of the two calorific values yielded differences of less than 400 Btu lb^{-1}. Attempts to reconcile the exception for PSOC 833 were unsuccessful.

Analytical results for DMC are reported in *Table 3*. This demineralization effort represents as complete an attempt at analysis as we have been able to find in the literature. The primary purpose of our demineralization attempts was to obtain enough DMC to allow a complete compositional analysis. In order to accomplish this, we found it difficult to make the quantitative material recoveries necessary for mineral matter content determination by demineralization, and we accordingly relied upon the mineral matter value determined by low temperature ashing. The results on the DMC indicate effective demineralization to less than 2% ash (HTA) in all cases except two (PSOC Nos. 680 and 801). The major non-extracted mineral elements included Fe, Ca, Cr, and Ti, presumably present as FeS_2, CaF_2, Cr_2O_3, and TiO_2. Some CaF_2 was probably formed during the HF treatment process despite prior attempts to remove calcium minerals with HCl. Mahajan has postulated that some calcium minerals may be trapped in the micropores of the coal structure and thereby escape extraction during the HCl treatment[48]. The higher than theoretical F/Ca molar ratio expected for CaF_2 in the DMC data indicates that other mechanisms for F incorporation are also operative. In spite of all attempts to prevent halide adsorption, significant amounts of residual F^- and Cl^- were found, and had to be corrected for.

Table 5 presents comparative data for the organic oxygen contents of the study samples, using the seven

Table 6 Significant differences[a] between organic oxygen data sets for PSOC coals obtained by different methods

Methods compared	Mean difference $\pm\sigma_m$ (absolute %)
ASTM/BD–GIVEN/BD	1.30±0.26
ASTM/BD–PC/DMC	0.82±0.18
ASTM/BD–FNAA/DMC	0.71±0.22
ASTM/BD–FNAA/BD	1.36±0.13
ASTM/BD–FNAA/SI–O_i	1.50±0.33
PC/WC–GIVEN/BD	1.43±0.46
PC/WC–PC/DMC	0.99±0.21
PC/WC–FNAA/DMC	0.82±0.21
PC/WC–FNAA/BD	1.46±0.29
PC/WC – FNAA·SiO_i	1.46±0.25
PC/DMC – FNAA/BD	0.47±0.16
FNAA/DMC–FNAA/BD	0.64±0.17
FNAA/DMC–FNAA/Si–O_i	0.64±0.26

[a] Differences significant at the 95% confidence level

for these differences (0.47 and 0.64 wt % for the PC/DMC and FNAA/DMC, respectively) may be the oxygen fixed as sulphate during the low temperature ashing procedure caused an apparent high LTA oxygen value to be used, resulting in a lower organic oxygen value. Sulphate formation during low temperature ashing is well documented[47,48]; our ashing conditions minimized organic sulphur to sulphate conversion (as verified on other samples) but we did not correct for such oxygen fixation as the LTA had been expended for other determinations. Recent data published by Mahajan[48], in which this correction was applied, showed that the magnitude of the correction (under his LTA conditions) was less than 5% relative. A correction of this order to our data would not significantly help; it is also of interest to note that a similar comparison of FNAA/DMC and FNAA/BD data on six different coal samples by this group in 1979 gave an almost identical mean significant difference (0.66) compared to the analogous value obtained in this work (0.64).

No differences significant at the 95% confidence levels were found among the data sets for the GIVEN/BD, PC/DMC and FNAA/DMC techniques. At the 90% confidence level, however, small mean significant differences were found between the following data sets: PC/DMC–GIVEN/BD (0.48±0.27); FNAA/DMC–GIVEN/BD (0.59±0.28); and PC/DMC–FNAA/DMC (0.16±0.08). The convergence of values from these three techniques is regarded as significant, perhaps indicating that a more reliable measure of the organic oxygen content of coal is within reach.

Observations on the FNAA/Si–O_i

Our newly developed FNAA procedure for organic oxygen determination in whole dried coals based on assumption that a simple mathematical relationship exists between inorganic oxygen and silicon content (FNAA/Si–O_i) is a purely instrumental technique which could easily be adapted to on-stream analysis.

The only significant differences exhibited by this data set are lowered values compared with the ASTM/BD, PC/WC and FNAA/DMC methods. To develop such a mathematical relationship, silicon and oxygen contents in the LTA of 21 Kentucky and 14 PSOC coals were determined by FNAA (*Table 7*). Only three coals deviated appreciably from the quadratic best fit line (*Figure 1*) in spite of the coals being of varied rank, ash content, and geographical origin. The convex curve shown in *Figure 1* was expected, since $(O/Si)_{weight}$ ratios for the two major silicate minerals in ash varies from 1.89–2.57 for clays to

Table 7 Total oxygen, inorganic oxygen and total silicon in 35 selected coal samples

Sample ID	% Mois.	% LTA	% O_T	% O_{LTA}	% Si_T
PSOC 548	10.3	13.4	20.8	7.66	3.47
680	8.00	19.9	19.2	8.76	2.78
739	7.28	19.2	17.0	9.32	4.07
773	7.76	9.91	15.6	4.40	1.09
782	0.88	5.66	4.96	2.82	0.522
785	28.7	13.4	24.2	7.50	2.02
791	30.1	20.0	27.7	11.5	3.85
801	1.37	14.4	7.95	4.60	1.52
808	2.42	5.97	8.21	1.35	0.279
821	2.01	5.22	10.9	2.40	0.696
833	17.6	13.0	28.4	7.29	2.00
854	5.49	5.86	14.2	3.20	1.07
866	9.37	13.3	21.0	7.36	2.54
871	5.86	6.12	4.62	3.32	1.31
KCER 7021	2.15	5.13	32.1	28.4	12.9
7032	3.66	10.5	15.1	4.27	0.55
7047	3.61	15.8	16.6	7.13	2.61
7084	2.73	51.7	27.4	23.8	9.56
7094	4.25	18.2	18.3	9.34	3.66
7095	3.16	29.9	12.3	10.3	2.19
7098	3.68	29.8	25.1	19.1	8.09
7103	4.04	32.3	24.3	16.6	7.16
7109	3.50	28.2	20.9	14.3	6.37
7118	5.24	15.1	18.8	7.29	1.84
7430	4.34	19.8	17.8	9.08	3.04
7436	20.4	26.9	31.9	15.5	4.84
7445	7.42	3.12	18.7	1.63	0.36
7457	6.43	59.6	40.9	32.0	17.9
7464	23.8	57.0	39.3	31.3	10.5
7466	8.65	41.4	34.7	20.8	5.46
7479	1.73	34.2	14.6	12.3	4.16
7493	1.79	51.4	27.3	25.1	11.5
7516	4.85	9.41	13.9	3.49	1.09
7521	4.90	26.6	20.3	12.9	5.00
7554	4.81	37.1	24.8	17.3	8.00

% Mois. = moisture content of AR coal measured by weight loss on freeze-drying; % LTA = low temperature ash content of coal calculated on a dry whole coal basis. PSOC coal values include a small residual carbon correction. KY coal values were not corrected; % O_T = total oxygen content of the coal calculated on a dry whole coal basis; % O_{LTA} = LTA (inorganic) oxygen content of the coal calculated on a dry whole coal basis; % Si_T = total silicon content of the coal calculated on a dry whole coal basis

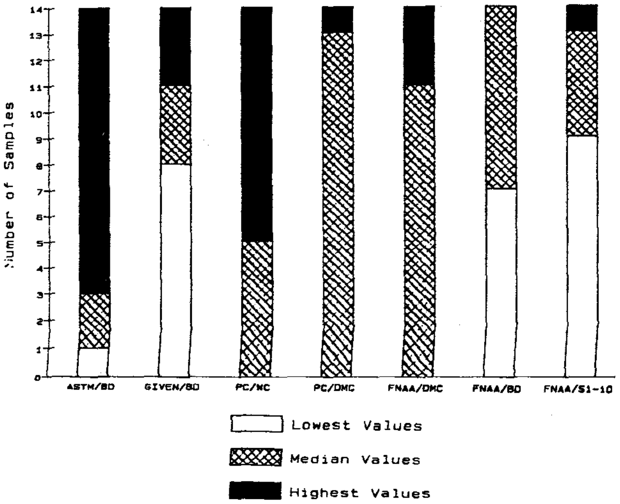

Figure 2 Comparison of relative magnitudes of organic oxygen values for each technique (see text for discussion)

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ERRATUM

A number of printers' errors which we corrected on the proofs still found their way into the final journal printing. In addition, the printers introduced one new error, a garbled equation, after we had returned the corrected proofs. The authors have registered their displeasure to the publisher. A list of the more serious corrections is given below:

p. 1563, heading-

It should have been indicated by a superscript symbol that C. E. Hamrin's affliliation was with the Department of Chemical Engineering.

p. 1565, left column, line 18-

Kaman (not Raman) neutron generator

p. 1567, Equation 7-

$$O_i^{gc} = (0.84 \pm 0.71) + (2.96 \pm 0.26)Si - (0.065 \pm 0.017)Si^2$$

(printers inserted an extra term, after we proofed)

p. 1569, Table 6-

5th line- ASTM/BD-FNAA/Si-O_i

10th line- PC/WC-FNAA/Si-O_i

p. 1570, Reference 37-

Koppenaal (not Ko''enaal)

Please make these corrections on your copy of the reprint.

The Authors
12/23/86