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**A DATA BASE FOR THE ANALYSIS OF COMPOSITIONAL
CHARACTERISTICS OF COAL SEAMS AND MACERALS**

**Final Report. Part 8: Calculation of Calorific Values of Coals from
Ultimate Analyses: Theoretical Basis and Geochemical Implications**

**By
Peter H. Given
Diane Weldon
J. H. Zoeller
Alan Davis**

**March 1984
Date Published**

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**The Pennsylvania State University
Coal Research Section and
Department of Materials Science and Engineering
University Park, Pennsylvania**

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A DATA BASE FOR THE ANALYSIS OF COMPOSITIONAL CHARACTERISTICS OF COAL SEAMS AND MACERALS

Alan Davis, Principal Investigator

Final Report - Part 8

CALCULATION OF CALORIFIC VALUES OF COALS FROM ULTIMATE ANALYSES: THEORETICAL BASIS AND GEOCHEMICAL IMPLICATIONS

by

Peter H. Given, Diane Weldon and J.H. Zoeller

Date Published - March 1984

**Coal Research Section
The Pennsylvania State University
University Park, Pa. 16802**

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FOREWORD

The major objective of this program, "A Data Base for the Analysis of Compositional Characteristics of Coal Seams and Macerals", has been to use the Penn State Coal Data Base to gain better understanding of the systematic relationships between properties of U.S. coals. The following studies are incorporated within the program:

a) A statistical study of the interrelationships between the properties of the organic fraction of coals. The extent to which natural groupings of U.S. coals might exist are being investigated by cluster analysis. Cause for the groupings are being sought in such factors as age of coal, source material and thermal/burial history.

b) A statistical study of the interrelationships between the properties of the inorganic fraction of coals. Correlations are being sought between the major, minor, trace element and mineralogical analyses of coals in the data base.

c) Studies of the lateral and vertical variability of properties within a single coal seam in response to changes in depositional environments and post-depositional metamorphic changes. The Lower Kittanning seam has been selected because of its broad extent and the range of environments by which it is thought to have been affected. Properties which are being studied include the petrographic characteristics, mineralogy, thermoplastic characteristics and liquefaction behavior.

d) The basic physical and chemical properties of pure coal macerals. Detailed analyses of vitrinite concentrates are being made to determine what significant differences in functional group content, aromaticity, density, porosity, and optical properties arise from variation in the environmental conditions during peat deposition and in the thermal histories of coals.

This report is the eighth of a series on the research undertaken in the course of the program. It proposes a new equation for the calculation of calorific values from ultimate analyses of 992 coals in the Penn State Coal Sample Bank/Data Base.

The following are previous reports published in this series:

- DOE-30013-F1 Relationships Between Coal Constitution, Thermoplastic Properties and Liquefaction Behavior of Coals and Vitrinite Concentrates from the Lower Kittanning Seam.
--Joseph T. Senftle and Alan Davis
- DOE-30013-F2 A Multivariate Study of the Interrelationships Among Selected Variables of the Organic Fraction of Samples of United States' Coals.
--Joseph J. Gerencher, Jr.
- DOE-30013-F3 Some Procedures for the Chemical and Mineralogical Analysis of Coals.
--Norman H. Suhr and Henry Gong
- DOE-30013-F4 Characterization of the Organic Structure of the Lower Kittanning Coal Seam Using Fourier Transform Infrared Spectroscopy and Optical Properties.
--D.W. Kuehn, A. Davis and P.C. Painter
- DOE-30013-F5 Recent FT-IR and ^{13}C NMR Studies of Coal Structure.
--P.C. Painter, A. Davis, M. Starsinic, J.L. Koenig, J.R. Havens, D.W. Kuehn, R.W. Snyder, J.T. Senftle, C. Rhoads, E. Riesser and E. Squires
- DOE-30013-F6 Petrography and Depositional Environment of the Herrin (No. 6) Seam in Central, Eastern and Northwestern Illinois.
--Suzanne J. Russell
- DOE-30013-F7 Petrographic Variation Due to Depositional Setting of the Lower Kittanning Seam, Western Pennsylvania.
--Sharon D. Allshouse and Alan Davis

University Park, Pennsylvania
March 1984

Alan Davis

ABSTRACT

The various formulae for calculating calorific values for coals from ultimate analyses depend essentially on a proposition due to Dulong, that the heat of combustion of an organic compound is nearly equal to the heats of combustion of the elements in it, multiplied by their percentage content in the compound in question. This proposition assumes that the enthalpy of decomposition is negligible compared with the heat of combustion. The various published formulae, such as that due to Mott and Spooner, include empirical adjustments to allow for the fact that the enthalpy of formation or decomposition of no organic compound is zero (except rarely by chance). A new equation is proposed, which excludes empirical correction terms but includes a term explicitly related to the enthalpy of decomposition. As expected from the behavior of known compounds, this enthalpy varies with rank, but it also varies at the same level of rank with the geological history of the sample: rank is not the only source of variance in coal properties.

The new equation is at least as effective in predicting calorific values for a set of 992 coals as equivalent equations derived for 6 subsets of the coals. On the whole, the distributions of differences between observed and calculated calorific values are skewed to only a small extent. About 86% of the differences lie between -300 and +300 Btu/lb ($\pm$ 700 kJ/kg).

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	iii
ABSTRACT	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
INTRODUCTION	1
THE BASIS OF CALORIFIC VALUE FORMULAE	1
REPORTING BASIS FOR THE ELEMENTARY ANALYSES	4
REVISIONS OF THE MOTT AND SPOONER FORMULAE	5
THE TESTING OF EQUATION (7)	6
STRUCTURAL AND GEOLOGICAL EFFECTS ON THE ENTHALPY OF FORMATION	10
CALCULATION OF CALORIFIC VALUES	14
REFERENCES	24

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Coefficients of O and Mean Δ Values for Various Sets of Coals	7
2	Tests of Differences in Means for Significance	9
3	Enthalpies of Formation of Some Oxygenated Derivatives	12
4	Coefficients in Regression Equations, Experimental and Calculated Calorific Values	15

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	The Dependence of Enthalpies of Formation on Aromaticity	11
2	Enthalpies of Decomposition of Coals Classified by Rank and Province	13
3	Linear Regressions of Calculated versus Experimental Calorific Values	16
4	Distribution of Differences in Calculated and Observed Calorific Values, All Samples	18
5	Distribution of ∇Q Values for Two Provinces	19
6	Distribution of ∇Q Values for Coals of Eastern Province	20
7	Distribution of Differences in Calculated and Observed Calorific Values, Using the Equations Due to Mott and Spooner	23

INTRODUCTION

The calorific value is a property of coals that has obvious practical importance. Furthermore, it is a property that is very effective in defining the rank of a coal. Many formulae have been proposed for calculating this property from the elementary analysis, to save the trouble of experimental determination or for other reasons. As a matter of routine, we make such calculations for all coals in the Penn State Coal Sample Bank and Data Base, using the formulae due to Mott and Spooner (1940). We record the difference, (experimental) - (calculated), as a test for the consistency of the analytical data, a procedure originally suggested to us by Dr. R. Neavel. Mott and Spooner claimed that their formulae "will give calculated calorific values which should agree within 100 Btu with the determined calorific value for the whole range, peat to anthracite. If the differences are greater, the analysis should be suspected and repeated". In our experience, the differences are fairly often much greater than 100 Btu/lb; is this really due always to analytical error, or is the equation too gross a simplification?

This question, and the recent appearance of a critical review of the topic by Mason and Gandhi (1980), stimulated us to make a careful examination of the basis of the formulae, to make some revisions, and to use the results to study some effects of coal rank and geological history. We report here the examination and its results.

THE BASIS OF CALORIFIC VALUE FORMULAE

Several of the formulae proposed are purely empirical correlations (Mason and Gandhi, 1980; Jain and Sundararajan, 1981). For our purposes, such formulae are of little interest. We prefer the Mott and Spooner formula in that it has at least partially some theoretical

foundation, and it lends itself to revision on the basis of theoretical chemical considerations. This formula explicitly, and others implicitly, derive essentially from some propositions attributed to Dulong by Mott and Spooner, but not actually published by him: (1) The total heat produced by an element is the same whether it passes through one or more stages of oxidation, (2) the total heat produced by a compound is little different from the sum of the heats which would be produced by a separate combustion of its elements. One can readily show, for a pure compound, that the following equation is exactly true:

$$Q = \sum w_i q_i - \Delta H_f \text{ ----- (1)}$$

where Q = heat of combustion per mole or per unit weight, w_i = weight fraction of the i th element in the compound, q_i = heat of combustion of that element, and ΔH_f = enthalpy of formation of the compound from its elements (of course, $-\Delta H_f$ = enthalpy of decomposition). What Dulong's second principle is saying is that ΔH_f is negligible compared with $\sum w_i q_i$.

Mott and Spooner's expression of these principles was:

$$Q = 80.30 C + 339 H + 22.5 S + 34.7 O \text{ ----- (2)}$$

where Q is in cal/gm.

The term containing H is calculated as:

$$\frac{(\text{heat of combustion of } H_2) \times (\text{percentage of } H)}{100}$$

The term for S is calculated in the same way. If one calculates a term for C (graphite) also in the same way, one obtains 78.60 C . Mott and Spooner argued, with questionable logic, that for coals one should use a calorific value for amorphous carbon (charcoal), and they took a value

corresponding to a term 80.00 C. However, they arbitrarily increased this to 80.30 C as a token recognition that $\Delta H_f \neq 0$.

The need for a term containing O arises because if some of the H and the C are already combined in oxygen-containing functional groups, those fractions of the elements will not release their full heats of combustion. Therefore, the amounts of C and H so combined must be subtracted from the analytical data, and these are measured in terms of the amounts of oxygen involved. From a plot of oxygen released in high-temperature carbonization as H_2O , CO and CO_2 , Mott and Spooner estimated that about two-thirds of the oxygen would be released as water, and most of the remainder as CO. On this basis, and introducing the heat of combustion of CO, they computed a (negative) coefficient of O, as shown in equation (2).

With low-rank coals (defined as having $O \geq 15\%$ d.a.f.), an appreciable fraction of oxygen is released from carboxyl groups as CO_2 . To account for this, Mott and Spooner performed linear and non-linear regressions with experimental data, and produced an equation having a term in $(O)^2$, but otherwise identical to that for higher rank coals:

$$Q = 80.30 C + 339 H + 22.5 S - 36.6 O + 0.172 (O)^2 \quad (O \geq 15\%) \text{ ----- (3)}$$

Conversion of equations (2) and (3) to Btu/lb gives the most familiar form of the equations:

$$Q = 144.5 C + 610.2 H + 40.5 S - 62.5 O \text{ ----- (4)}$$

or:

$$Q = 144.5 C + 610.2 H + 40.5 S - 65.9 O - 0.310 (O)^2 \text{ ----- (5)}$$

REPORTING BASIS FOR THE ELEMENTARY ANALYSES

Originally, Mott and Spooner used the Parr formula for calculating the mineral-matter content of their coals from the ash yield. They used the result to put their elementary analyses on a dry, mineral-matter-free basis, and the analyses therefore showed no organic sulfur, so that the S term was omitted from the calorific value equation. They stated that the elementary composition could be on the dry, ash-free basis, in which case a term in S is required.

The basis of the equation is such that, apart from the term in O, there is no reason to restrict its applicability to coals; it should be equally valid for any organic substance. But the logic of this is that the equation is applicable to the pure substance containing no inorganic constituents, whether coals or another organic material is in question. Therefore, one should express the elementary analysis on a basis that as completely as possible eliminates the effects of mineral matter, if any, on the raw analytical data. That is, one should use the dry, mineral-matter-free basis of reporting. Thus, carbon is corrected for CO₂ from carbonates, hydrogen for water from the decomposition of clays during the analysis, only organic sulfur is included, and the mineral-matter content rather than ash yield is used to put the analysis on the pure-organic basis. In a d.a.f. analysis, the C and H are not corrected for mineral contributions, and total sulfur is included, which has a considerable effect on oxygen-by-difference if the pyrite content is high. These matters are reviewed by Given and Yarzab (1978).

In the analyses of the Penn State Coal Sample Bank and Data Base, directly determined mineral-matter contents and yields of carbonate CO₂ are available for only a minority of samples. In most cases, the

mineral-matter content is calculated by a modification of the Parr formula, and the corrections made to C and H are approximate (Given et al., 1975; Given and Yarzab, 1978). Data obtained in this way are used in the study reported below.

REVISIONS OF THE MOTT AND SPOONER FORMULAE

Mott and Spooner's use of the calorific value of charcoal seems to us highly questionable. In effect, they assumed an enthalpy of decomposition increasing linearly with rank, since they allowed for it by raising the coefficient of carbon only. Thus, their allowance was $(80.30 - 78.60) C = 1.70 C \text{ cal/gm}$, or $3.06 C \text{ Btu/lb}$. In fact, as we shall see, it does increase with rank, but it still seems to us much preferable to derive the coefficient of carbon solely from the heat of combustion of graphite, and add a term, Δ , which is, or is related to, the enthalpy of decomposition. We can then allow this enthalpy to vary with rank or other coal characteristic if this proves desirable. Thus, using modern values of the heats of combustion of the elements and CO (from JANAF tables), we obtain (in Btu/lb):

$$Q = 140.95 C + 610.2 H + 39.8 S - P \cdot O + \Delta \text{ ----- (6)}$$

P, the coefficient of O, needs further discussion. When we measured the hydroxyl contents of 53 U.S. coals of high volatile bituminous rank classes, we found that coals of the Interior province have 50-60% of their oxygen in this form, and the younger coals of the Rocky Mountain province had only 30-40% in this form, while figures for coals of the Eastern or Appalachian province were intermediate (Yarzab et al., 1979). Hydroxyl contents of coals of medium and low volatile bituminous coals, and anthracites, are very low or zero; much of the remaining oxygen is probably present as some kind of ether

(Ignasiak and Gawlak, 1977; Youtcheff and Given, 1982). Unpublished measurements on about 30 low-rank coals indicated that the carboxyl content of U.S. subbituminous coals is 1-2 meq./g., and of lignites is 3-4 meq./g. Using these data and some supplementary estimates, we employed Mott and Spooner's methods of calculation to derive coefficients for Δ separately for several groups of coals, as shown in Table 1. It is seen that the coefficients do not vary greatly, in spite of the widely differing distributions of oxygen functions used in deriving them. Moreover, the term in Δ makes a relatively small contribution to the calculated calorific value.

We have felt that this procedure, although open to objection, is preferable to the assumptions of Mott and Spooner, and it does obviate the need for the quadratic term in the equation for low-rank coals.

Thus, our preferred way of calculating calorific values is equation (6), with the coefficients for Δ as listed in Table 1. Conversion of units to kJ/kg gives:

$$Q = 327.8 C + 1419 H + 92.6 S - P' \Delta + \Delta \text{ ----- (7)}$$

Values of P' for this equation are included in Table 1.

THE TESTING OF EQUATION (7)

The remainder of this report consists of an investigation of this equation, using data for 992 coals taken from the Penn State Coal Sample Bank and Data Base. The classification of coals used in Table 1 was based essentially on the existence of different distributions of oxygen-containing functional groups. It separates coals partly by rank, and partly by geological history, as reflected by the occurrence of coals in different provinces (Given *et al.*, 1980). It seems to have some general significance, and the characteristics of the subsets as

Table 1. Coefficients of 0 and Mean Δ Values for Various Sets of Coals

Set of Coals	P(Btu/lb)	P'(kJ/kg)	Mean Δ , kJ/kg	Standard Deviation of Δ	N*	Skew- ness
All with > 89% C	72.0	168	962	538	130	1.4
All Eastern Province $\leq$ 89%	62.1	144	798	445	324	1.9
All Interior Province < 89%	56.0	130	738	515	212	0.7
Rocky Mountain Province, bituminous	50.9	118	324	555	176	2.5
All subbituminous	55.7	130	321	573	109	-0.1
All lignites	58.2	135	343	487	41	-0.006
All coals	59.2**	138	705	529	992	0.9

* N = number of samples

**Mean value weighted according to number of samples in each set.

well as the full set are investigated in what follows. It should be noted that: (i) a few high volatile coals from the Northern Great Plains Province (Arizona, New Mexico) are added to the Rocky Mountain bituminous subset, (ii) the subbituminous subset includes coals from both the Northern Great Plains and Rocky Mountain Provinces, (iii) the lignites are from both the Northern Great Plains and Gulf Provinces, (iv) no coals from the Pacific or Alaskan Provinces are included, because of paucity or non-availability of samples.

There is no a priori means of estimating the enthalpies of decomposition of coals, and so we have treated them as empirical parameters, evaluating a figure for each coal as follows:

$$\Delta = Q_{\text{exp}} - \Sigma \text{ -----} \quad (8)$$

where Q_{exp} = experimental calorific value in kJ/kg and,

$$\Sigma = 327.8 C + 1419 H + 92.6 S - P \cdot 10.$$

Mean values of Δ for each set were then computed with results shown in Table 1, together with the standard deviations around the mean.

T tests were done to establish the significance of differences between mean values of Δ , with results shown in Table 2. The clearest observation is the marked difference between the relatively high-rank coals of Carboniferous age (Interior and Eastern provinces) and the younger coals of Cretaceous and Tertiary age (Rocky Mountain province and low-rank coals). It is also of considerable interest that values for coals of the Interior and Eastern provinces differ significantly.

Thus the data in Tables 1 and 2 suggest that the term for the enthalpy of decomposition varies with rank and geological history. This would be of interest in its own right, as showing that there are several bands of coal-rank evolution, with the implication that

Table 2. Tests of Differences in Means for Significance

Differences Compared	Conclusion, at Level of Significance Stated
> 89% C and Eastern	different at 0.005 level
Eastern and Interior	different at 0.10 level
Lignite and subbituminous	not different
Subbituminous and Rocky Mountain bituminous	not different
Lignite and Rocky Mountain bituminous	not different
Interior and Rocky Mountain bituminous	different at 0.005 level

differing geological histories affect coal structure. It might also be of practical interest to those wishing to calculate a calorific value instead of measuring it or to use the calculated value as a test of the consistency of analytical data. These two areas of interest will be discussed separately.

STRUCTURAL AND GEOLOGICAL EFFECTS ON THE ENTHALPY OF FORMATION

We have plotted in Figure 1 the enthalpies of formation, on a weight basis, for a number of hydrocarbons against their aromaticities, using literature data. It will be seen that there is a sharp, more or less linear, increase in enthalpy with aromaticity, covering a wide range of values. Introduction of oxygen functional groups tends to shift the enthalpy in the negative direction; the effect is considerably greater for phenols than for alcohols or ethers in a set of isomers, as the figures in Table 3 illustrate. Since the aromaticity of coals tends to increase, and the oxygen content to decrease, with increasing rank, and the distribution of oxygen functions varies with geological province at the same level of rank, we should not be surprised at the variations of Δ values seen in Table 1.

We have examined the data in a more detailed manner by classifying the sample set of 992 coals as shown in Table 1 and by assigning the dmmf carbon content to one of a number of 4% ranges, that is, 72-76, 76-80, %C etc. The mean Δ for each 4% range and province was then plotted as a kind of bar graph, as shown in Figure 2. The effect of rank in the groups considered separately is confusing, inasmuch as with decreasing rank Δ tends to decrease and then increase again. This may result from the fact that with increasing rank,

Figure 1. THE DEPENDENCE OF ENTHALPIES OF FORMATION ON AROMATICITY

Table 3. Enthalpies of Formation of Some Oxygenated Derivatives.

	ΔH_f° , kcal/mole	
$C_{10}H_{12}O$		-42.42
	-53.12
$C_8H_{10}O$		-39.7
	-38.9
	-51.6
C_7H_8O		-29.83
	-39.8
	-50.24

Figure 2. ENTHALPIES OF DECOMPOSITION OF COALS CLASSIFIED BY RANK AND PROVINCE

aromaticity tends to increase at the same time as the distribution of oxygen functional group changes. The bars for Eastern and Interior Province bituminous coals vary in a parallel manner. What the Figure does show clearly is that at any given level of rank, the enthalpies of decomposition of coals from different groups tend to be very appreciably different in most cases. Thus the finding of Table 1 is amplified and made more specific. We have here further evidence that rank is not the only source of variance in coal properties, and this is perhaps the most important finding of the study.

CALCULATION OF CALORIFIC VALUES

Interesting though the variations in P and Δ are for their own sake, they are not likely to be of great importance in the calculation of calorific values, since the terms $-P.O + \Delta$ represent only 0-10% of the calorific value. Nevertheless, we have tested this in various ways.

The coefficients in a linear regression of calculated on experimental calorific values have been calculated for the subsets and the whole set of coals, with results shown in Table 4. Also, the least-squares lines are shown in Figure 3 for appropriate ranges of calorific value. It is seen that the slopes and intercepts differ appreciably in some cases, and the variance explained by the regressions is high.

However, the standard deviations around the mean values of Δ , included in Table 1, suggest that we do just as well with global mean values of P and Δ as we do when treating the sets of samples separately. Also, calorific values for individual coals have been re-computed using equation (7) and the mean values of P' and Δ in Table 1. The difference, $\nabla Q = Q_{\text{exp}} - Q_{\text{cal}}$, was evaluated for each coal; the mean values computed for each subset of coals, and for the whole

Table 4. Coefficients in Regression Equations, Experimental and Calculated Calorific Values

$$Q_{\text{exp}} = A + B Q_{\text{calc}} \text{ (Btu/lb)}$$

Group of Coals	A	B	Standard Deviation of estimate	Variance explained, R^2
All > 89% C	3860	0.776	159	0.77
Eastern < 89% C	1387	0.930	186	0.87
Interior < 89% C	1583	0.911	178	0.85
Rocky Mountain bituminous	- 732	1.06	179	0.95
All subbituminous	1589	0.886	231	0.83
All lignites	858	0.942	207	0.90
All coals	- 404	1.05	213	0.96

Figure 3. LINEAR REGRESSIONS OF CALCULATED VERSUS EXPERIMENTAL CALORIFIC VALUES

set treated as single, were essentially zero in all cases. The algebra of our manipulations is such that the standard deviations of ∇Q values are essentially the same as those shown in Table 1 for the Δ values. Values for the skewness of the distributions were included in Table 1 and are mostly not large; the group of Rocky Mountain bituminous coals has the highest value, and shows considerable tailing among positive values of ∇Q .

We have plotted in Figures 4-6 the distribution of ∇Q values for the whole set of 992 coals and for three of the subsets. It can be seen from Figure 4 that 86% of samples show ∇Q values between -300 and +300 Btu/lb (± 700 kJ/kg). In spite of the highly significant differences in Δ for the different groups of coals, it is now evident that the separate equations for each group are little or no more effective in predicting the calorific value than a single equation for all coals, using single mean values for Δ and P . This equation is:

$$(\text{Btu/lb.}) \quad Q = 140.95 C + 610.2 H + 39.8 S - 59.3 O + 302 \text{ ----- (9)}$$

$$(\text{cal./gm}) \quad = 78.34 C + 339.1 H + 22.1 S - 33.0 O + 168 \text{ ----- (10)}$$

$$\text{kJ/kg}) \quad = 328.4 C + 1422 H + 92.7 S - 138 O + 704 \text{ ----- (11)}$$

We now return to the question posed at the beginning: to what extent does the spread in ∇Q values reflect experimental error? Obviously no definite answer can be given, but we can note two points:

1. We have taken steps to account for the effect of structural differences between coals of different rank and geological history, and in fact the effect of these turns out to be fairly small.

2. The fact that we are compelled to use only approximations to true, dry, mineral-matter-free ultimate analyses must introduce some random noise into the distribution of ∇Q values.

Figure 4. DISTRIBUTION OF DIFFERENCES IN CALCULATED AND OBSERVED CALORIFIC VALUES, ALL SAMPLES

Figure 5. DISTRIBUTION OF ∇Q VALUES FOR TWO PROVINCES

Figure 6. DISTRIBUTION OF ∇Q VALUES FOR COALS OF EASTERN PROVINCE

Thus it would appear that to a considerable extent the errors in predicting calorific values do reflect experimental errors in data, including inadequate correction of ultimate analyses for interferences by mineral matter.

In their original paper, Mott and Spooner stated that calorific values calculated by means of their formula should agree with experimental values within ± 100 Btu/lb; if not, the ultimate analysis should be "suspected and repeated." R. Neavel, when first suggesting this to us as a test for the consistency of analytical data, indicated that ± 150 Btu/lb were reasonable limits. However, in a discussion of data for the Exxon standard set of 66 coals, a standard of ± 200 Btu/lb is preferred (Neavel et al., 1980). On the basis of our study, we do not feel that any precise limits of acceptability can be stated, because a considerable degree of natural variability seems to be a characteristic feature of coals. However, if calculated and observed calorific values differ by no more than 100 Btu/lb, one can be confident with all normal coals that the data are consistent. As the difference increases outside these limits, one should be increasingly suspicious of the data, which are probably wrong if ∇Q exceeds ± 250 Btu/lb, but not necessarily so for intermediate values. Analyses of coals of high mineral matter and sulfur contents, or of low rank, are the most prone to error.

We prefer to rely on the equations developed here for the calculation of calorific value because they do not require the quadratic term in oxygen content present in the Mott-Spooner version for low-rank coals, and because as a by-product they afford a means of estimating the enthalpy of formation of a coal. Also, our equations have a clearer theoretical justification than previous equations, and have received

extensive examination. However, we must admit as an empirical observation that our equations provide no better estimates of calorific values than the Mott-Spooner equations.

For the same set of 992 coals, we have computed the mean ∇Q value for use of the Mott-Spooner equations, (4) and (5). It is +30, which is quite close to zero. The standard deviation around means is 225 Btu/lb for the Mott-Spooner basis, and 227 Btu/lb for ours. The distribution of ∇Q values for the Mott-Spooner calculations is shown in Figure 7, for comparison with the distribution in Figure 4. The fraction of samples that show ∇Q values in the range ± 300 Btu/lb is again 86%.

In concluding, it is perhaps worth observing that over 50% of our sample set are from one province (Eastern), two thirds are of Carboniferous age, and roughly 60% are of high rank (arbitrarily defined as having $\%C \geq 82\%$). These characteristics might be considered biases in the sample set.

Figure 7. DISTRIBUTION OF DIFFERENCES IN CALCULATED AND OBSERVED CALORIFIC VALUES, USING THE EQUATIONS DUE TO MOTT AND SPOONER

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