

5-14-1990

Coal Mineral Analysis: A Check on Inter-Laboratory Agreement

G. S. Casuccio
R.J. Lee Group

F. A. Gruelich
Sandia National Laboratories

G. Hamburg
Netherlands Energy Research Foundation ECN

F. E. Huggins
University of Kentucky

D. A. Nissen
Sandia National Laboratories

See next page for additional authors

Follow this and additional works at: <https://digitalcommons.usu.edu/microscopy>

 Part of the [Life Sciences Commons](#)

Recommended Citation

Casuccio, G. S.; Gruelich, F. A.; Hamburg, G.; Huggins, F. E.; Nissen, D. A.; and Vleeskens, J. M. (1990) "Coal Mineral Analysis: A Check on Inter-Laboratory Agreement," *Scanning Microscopy*. Vol. 4 : No. 2 , Article 2. Available at: <https://digitalcommons.usu.edu/microscopy/vol4/iss2/2>

This Article is brought to you for free and open access by the Western Dairy Center at DigitalCommons@USU. It has been accepted for inclusion in Scanning Microscopy by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.

Coal Mineral Analysis: A Check on Inter-Laboratory Agreement

Authors

G. S. Casuccio, F. A. Grulich, G. Hamburg, F. E. Huggins, D. A. Nissen, and J. M. Vleeskens

COAL MINERAL ANALYSIS:
A CHECK ON INTER-LABORATORY AGREEMENT

G.S. Casuccio (1), F.A. Gruelich (2), G. Hamburg (3),
F.E. Huggins (4), D.A. Nissen (2) and J.M. Vleeskens* (3)

1. R.J. Lee Group, Monroeville PA, U.S.A.
2. Sandia National Laboratories, Livermore CA, U.S.A.
3. Netherlands Energy Research Foundation ECN, The Netherlands
4. University of Kentucky, Lexington KY, U.S.A.

(Received for publication February 3, 1990, and in revised form May 14, 1990)

Abstract

Four laboratories co-operated to test repeatability and reproducibility of the semi-quantitative Coal Mineral Analysis (CMA) method. CMA is an instrumented image analysis method which identifies mineral particles in coal by chemical composition (energy dispersive X-ray spectroscopy) and size (scanning electron microscopy). The repeatability of weight percent data was better than 0.2 relative standard deviation for most minerals constituting more than five percent of all coal minerals. The type of mineral had no effect on repeatability. Errors arising from counting statistics were shown to be the major source of bias at a given instrument setting.

Inter-laboratory data for the major minerals agreed to within 0.1 relative standard deviation in about 50% of the cases. For other major minerals the relative standard deviation from the inter-laboratory average varied between 0.1 and 0.3. The weight percentages of kaolinite and "mixed silicates" showed poorer reproducibility than those of quartz and illite. Differences in detector window thickness may have affected discrimination between light elements and, therefore, inter-laboratory agreement of clay minerals data. Means to compensate window thickness effects are suggested.

KEY WORDS: Scanning electron microscopy, energy dispersive X-ray spectroscopy, coal mineral analysis, repeatability, reproducibility.

*Address for correspondence:

Dr. J.M. Vleeskens, Netherlands Energy Research Foundation ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands. Phone No. (+31)2246-4949, Fax No. (+31)2246-4480.

Introduction

Minerals in coal may have a considerable effect on coal quality. Not only do they form the coal's bulk of "ash content", but it is also important to estimate the quantities of specific minerals because the process engineer may use this data in assessment of coal quality for a particular process.

Mineral behaviour is reflected in all stages of coal utilization, from mining and beneficiation to conversion. Some clay minerals are prone to swelling and may cause degradation of coals in open storage or sludge formation in cleaning plants. In gasifiers and combustion furnaces pyrite and calcite are undesirable as they cause slagging, but in liquefaction pyrite has been reported to catalyze the process. Quartz has an erosive effect on heater tubes, and release of submicron quartz particles in mining operations and stack gases may adversely affect health. Identification and quantification of minerals will thus provide relevant data for technological and environmental management (Finkelman and Gluskoter, 1981, Straszheim et al., 1986).

Bulk chemical analysis methods can not provide the type of information required. For instance, the slagging effect of pyrite is higher than that of a mixture of sulphur and iron-oxides having the same sulphur/iron ratio. Furthermore, a mixture of kaolinite and quartz may have the same Al_2O_3/SiO_2 ratio as, for example, illite, yet show different behaviour in beneficiation or combustion operations. In contrast to chemical analysis, X-ray diffraction analysis can identify mineral types, provided they are well-crystallized. Clay minerals, however, can be poorly crystalline which makes identification and, particularly, quantification by XRD difficult (Carpenter, 1988).

Instrumented image analysis, using scanning electron microscopy in conjunction with energy-dispersive X-ray analysis, is a more powerful method for semi-quantitative analysis of minerals in coal. Coal Mineral Analysis (CMA) is essentially a multi-element analysis of mineral particles in coal from the characteristic X-rays generated by the electron beam (Energy Dispersive X-Ray Spectroscopy), coupled with a size analysis of these particles (SEM). The advantage of CMA

over XRD is that CMA identifies poorly or even non-crystalline inorganic matter. An inherent weakness of CMA is that polymorphs like quartz and cristobalite are reported under a single heading. A more important drawback with the common instrumentation is that X-rays of elements lighter than sodium do not penetrate the beryllium window of the X-ray detector. For this reason different iron-oxides and iron-carbonate can not be differentiated and are all classified as siderite (FeCO_3).

A useful program for Coal Mineral Analysis was developed by scientists at U.S. Steel Research Laboratories (Lee and Kelly, 1980, Huggins et al., 1980, 1982) and marketed by Tracor Northern under an exclusive licence. The program does not involve the use of standards, and ZAF corrections are omitted. The lack of accuracy thus incurred is compensated by rapidity of operation as required in technological applications for which CMA is now a widely accepted method (Birk, 1989).

So far, however, no inter-laboratory check on semi-quantitative CMA-data has been published. This paper reports on a co-operative research program between four laboratories to assess the reproducibility of CMA-data and to identify possible causes for a lack of inter-laboratory agreement. Such information is required to make CMA acceptable as an ASTM-standard procedure.

Experimental

Outline of CMA-procedure

This section is a short outline of the CMA-procedure for data collection and presentation. Aspects which may have an effect on reproducibility of data are mentioned.

For a more complete description of the background and practice of the method the reader is referred to the original papers in Scanning Electron Microscopy (Huggins et al., 1980 and 1982, Lee and Kelly, 1980). A recent paper in Journal of Coal Quality (Birk, 1989) gives an overview of the historic developments of coal mineralogy and discusses factors affecting quantitative results of SEM-EDS. A general description of the CMA-program and hardware (Tracor Energy Dispersive System) has been published in Technology in Review (Hamburg, 1984).

Sample preparation

The coal sample is powdered to 0.2 - 50 μm and mixed in a slurry of 40 weight percent epoxy (Hysol) and 60 weight percent coal. After hardening, the sample block (25 mm diameter) is ground with silicon carbide, thoroughly rinsed, and finally polished with 1 μm diamond paste. Diamond is used because its low atomic number avoids interference with X-ray spectra. Before analysis the sample blocks are coated with a thin (about 10nm) carbon layer.

Scanning analysis

The SEM-beam, set at 20 kV, scans the sample block in a stepping mode using a coarse grid. Signals above an arbitrarily set threshold value correspond to particles, those below represent noise. When a particle is located the digital beam changes to a finer grid to size the

particle. The size is measured as an average length of eight pairs of diagonals, each diagonal being terminated where the signal falls below the threshold value of the back-scatter signal. The linear size data are converted to volumes, and to weights by software memory data. The centroid position of each particle is stored in the memory to prevent duplicate counting.

With the beam in the centroid position of the particle, the EDS-function is started for elemental analysis. From the relative peak intensities of selected elements in the X-ray spectrum the chemical composition of each particle is obtained and assigned to a particular "mineral" type by the CMA-software. A short list of major coal mineral categories defined in the CMA-programme is given in table 1.

The analysis is carried out at three different magnifications, equal numbers of particles being analyzed at each magnification. Counting is terminated after analysis of 200 particles in each range and 600 particles in total. This procedure must ensure that statistically adequate information is obtained on the sample as a whole and on the distribution of minerals in different size classes.

Data representation

The CMA data outputs record for each of (maximum) 27 mineral categories:

1. the weight, as a percentage of total minerals (no. of particles counted = 100%);
2. average chemical composition;
3. size distribution.

Factors affecting results

A number of factors which may affect quantitative mineralogy have been tabulated by Birk (1989). Results may be affected by factors related to coal sampling, coal preparation, equipment, and software. In the present case coal sample and preparation were identical for all data reported because all laboratories used the same blocks. Our concern is thus mainly with bias originating from differences in equipment, software and operating conditions such as magnifications, count rate, and threshold setting. A list of the experimental conditions used at the participating laboratories is given in table 2.

It may be concluded from table 2 that:

- accelerating voltage for all four laboratories was identical;
- magnifications were similar, but not identical;
- count rates were almost identical;
- counting time was almost identical for laboratories 2, 3 and 4, but longer for laboratory 1.

The instrument settings for all four laboratories are thus very similar. A factor which is not quantified is the threshold setting. It was beyond the scope of this work, however, to perform an analysis of the effect of threshold setting. The object of the round-robin has been, rather, to compare data from different laboratories using basically identical equipment.

Sample description

Polished blocks were prepared from six samples (table 3). Five of these samples were coal, and the sixth was a mixture of reference quality minerals with active carbon.

Coal Mineral Analysis

Table 1. Minerals discussed in this paper - Definition in CMA program.

name	code in figures	formula	typical EDS percentage
quartz	Q	SiO ₂	Si > 85
kaolinite	K	Al ₂ Si ₂ O ₅ (OH) ₄	Al:Si ~ 45:55
illite	I	K(Al,Fe) ₄ (Si,Al) ₈ O ₂₀ (OH) ₄	Al:Si:K ~ 30:55:10
pyrite	P	FeS ₂	S:Fe ~ 65:30
siderite	S	FeCO ₃	Fe > 80
montmorillonite		(Ca,Na)(Al,Mg) ₄ (Si,Al) ₈ O ₂₀ (OH) ₄	(Na,Ca):Al:Si ~ 5:25:65
mixed silicates	MS	various	other than kaolinite, illite and montmorillonite

Table 2. Summary of CMA-experimental conditions

laboratory		lab 1	lab 2	lab 3	lab 4
accelerating voltage	kV	20	20	20	20
probe current	nA	1	0.7	0.7	0.6
magnifications	x ₋₁	40/120/520	20/100/500	20/100/500	50/150/450
count rate	s ⁻¹	<5000	3000	3000	3000
counting time for 1000 particles	min	240	60	60	70
SEM		JEOL-733-EM	ETEC-Autoscan*	ETEC-Autoscan*	JEOL-840
EDS		TN-2000	TN-2000*	TN-2000*	TN-2000

* laboratories 2 and 3 used the same instrument

Table 3. Sample data

sample	code	mine or stock	country	V _m wt% daf	ash wt% dry
coal	A	Commercial stock	U.S.A.	37	6
coal	B	Greenhills	B.C. Canada	29	16
coal	C	Coal Mountain	U.S.A.	34	5
coal	D	Prince, < 37 μm	N.S. Canada	ca. 34	21
coal	E	Prince, 45-63 μm	N.S. Canada	ca. 34	14
mineral	F	WARD's Nat. Sci Est. Inc.		-	~10

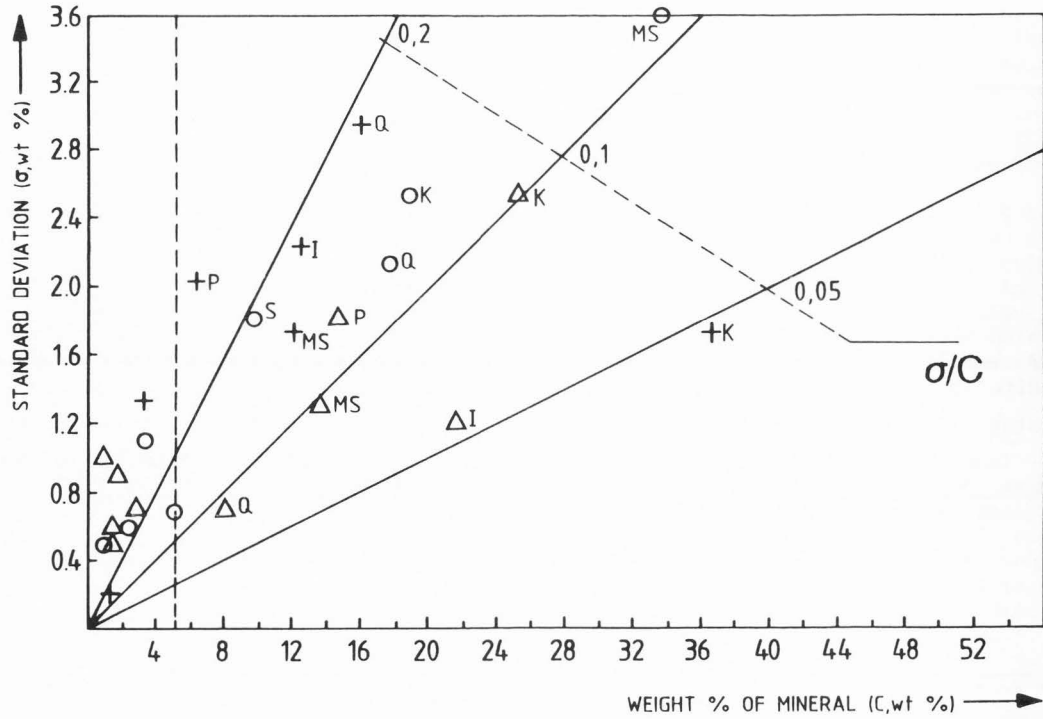


Figure 1. Repeatability. Standard deviation (σ , wt%) plotted against weight percent of mineral (C, wt%). C = average of single measurements on five blocks, laboratory 4. Samples A, B, C (+, o, Δ).

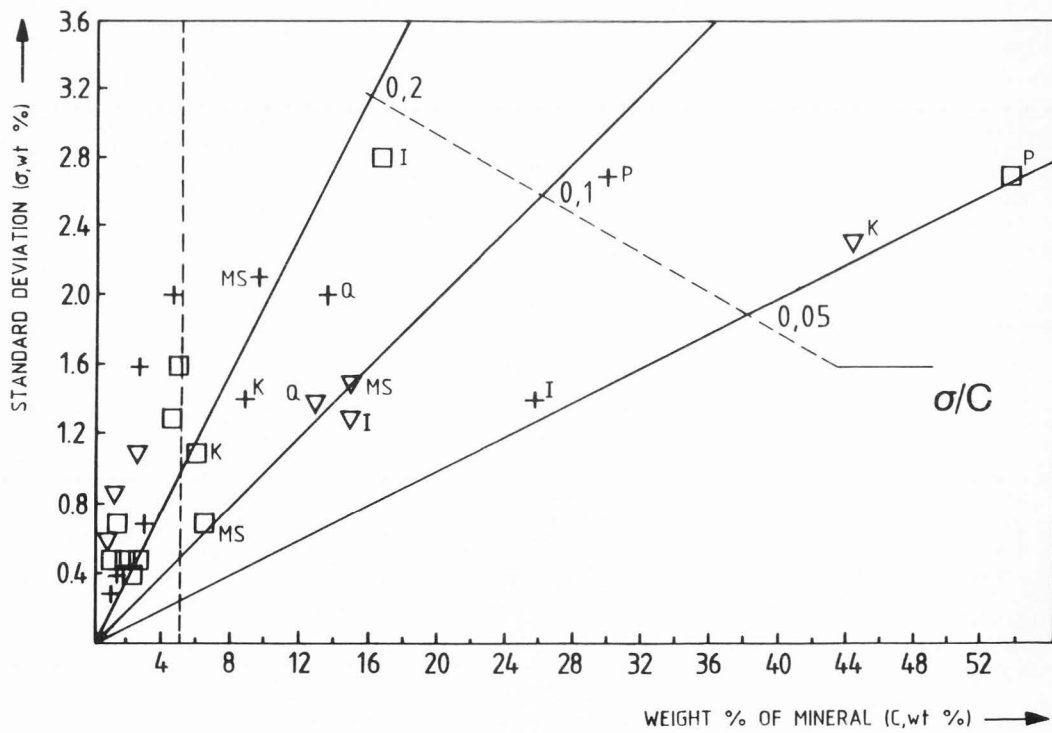


Figure 2. Repeatability. Standard deviation (σ , wt%) plotted against weight percent of mineral (C, wt%). C = average of five measurements on one block, laboratory 4. Samples D, E, F (x, \square , ∇).

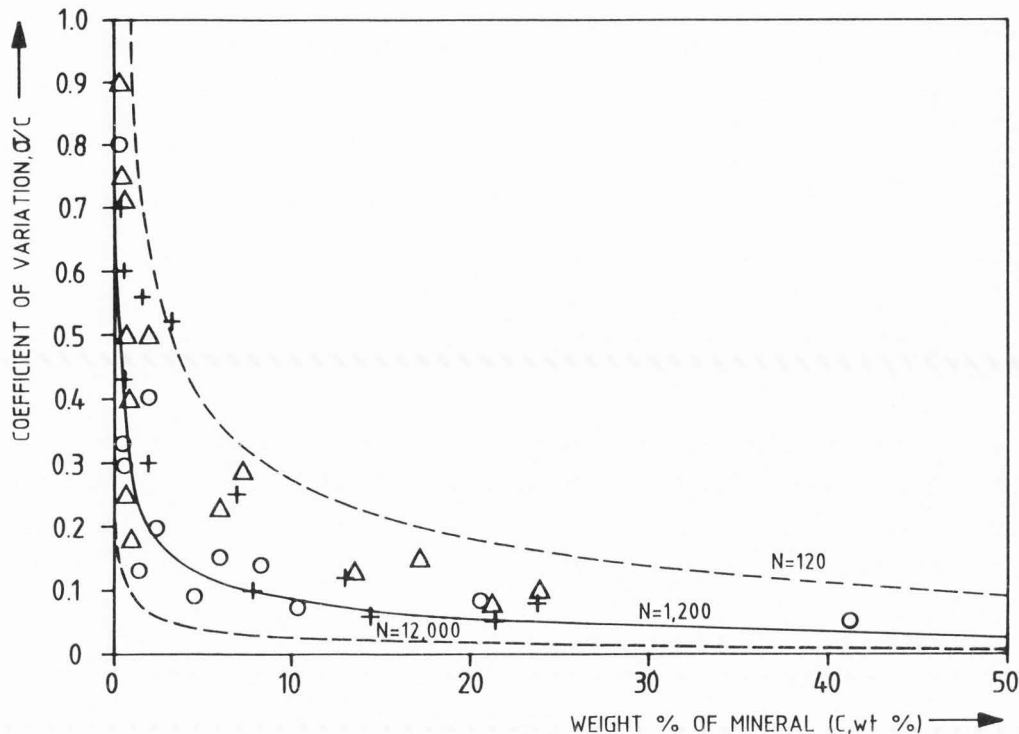


Figure 3. Repeatability. Coefficient of variation (σ/C) plotted against weight percent of mineral (C , wt%) from experimental CMA data for 5×600 particles, as determined by one laboratory. The solid and dashed curves represent the calculated variation, σ/C , for counting statistics based on different total numbers of particles, N . Samples A, B, C (+, o, Δ).

Five blocks were prepared from each of the samples A, B and C and circulated for round-robin analysis. Single blocks were prepared from samples D, E and F; these blocks were not circulated but were used to obtain additional data on repeatability.

Results and Discussion

Checks on repeatability and reproducibility of CMA were based on weight percentage data for individual minerals. The data reported below were obtained as follows. In round-robin samples A-C, 600 particles per block were analyzed on the five blocks from each sample (all laboratories). In the additional samples D-F, 600 particles were analyzed and the analysis was repeated four times on the same block (laboratory 4 only).

Repeatability

The repeatability data for samples A-C and D-F are given in figures 1 and 2 respectively. The standard deviation is plotted against the mineral concentration for major and minor minerals. Major mineral data points are marked Q (quartz), K (kaolinite), I (illite), P (pyrite), S (siderite), and MS (mixed silicates).

Figures 1 and 2 are divided into four ranges for the coefficient of variation, $\sigma/C < 0.05$, 0.05 to 0.10 , 0.10 to 0.20 , and > 0.20 . A comparison between figures 1 and 2 reveals a strong similarity in the spread of data. In both cases approximately 50% of the data is derived

from minerals that constitute less than 5 wt % of all minerals analyzed. The minor minerals generally show a coefficient of variation which is higher than 0.20. Most major minerals ($C > 5$ wt %) show a coefficient of variation below 0.20. The distribution of major minerals in figures 1 and 2 suggests that repeatability is not affected by mineral type but only by mineral concentration.

There is no indication that the repeatability of five-fold analyses on the same block (samples D-F) was better than that of single analyses performed on five blocks (samples A-C). The similarity of results in either approach may be illustrated by a tabular summary of the data spread. In samples A, B and C (fig. 1) and samples D, E and F (fig. 2) the data points for major minerals are distributed between σ/C -classes as follows.

σ/C	number of data (A+B+C)	number of data (D+E+F)
< 0.05	1	0
$0.05-0.10$	4	6
$0.10-0.20$	8	6
> 0.20	1	1

It may be inferred from these data that minerals in five blocks from samples A, B and C were randomly distributed.

The repeatability data for samples A, B and C from laboratory 4 are comparable (except pyrite) to those obtained by the other laboratories (table 4).

Table 4. Data obtained in inter-laboratory exercise - Major minerals.
For a data compilation report see Vleeskens and Hamburg (1987).

4.1. Sample A								
Type	Lab	Range (wt%)	C (wt %)	\bar{C}	σ	σ_{int} (wt %)	σ/C	σ_{int}/\bar{C}
Quartz	1	16.1-21.6	18.4		2.0		0.1	
	2	13.3-15.2	14.5		0.8		0.1	
	3	17.9-21.5	19.8		1.5		0.1	
	4	12.6-19.2	15.8		2.9		0.2	
	All			17.1		2.4		0.14
Kaolinite	1	23.9-27.8	26.5		2.4		0.1	
	2	19.8-22.5	21.4		1.0		0.1	
	3	14.1-21.2	17.2		2.5		0.15	
	4	34.6-38.4	36.2		1.7		0.05	
	All			25.3		8.2		0.32
Illite	1	6.4-13.1	10.6		2.8		0.3	
	2	12.0-15.7	13.0		1.6		0.1	
	3	9.9-14.6	11.3		2.0		0.2	
	4	9.8-15.5	12.3		2.2		0.2	
	All			11.8		1.1		0.09
Pyrite	1	5.3-12.6	9.3		2.7		0.3	
	2	6.9- 8.8	7.8		0.8		0.1	
	3	10.0-14.1	12.3		1.6		0.1	
	4	3.0- 7.8	6.4		2.0		0.3	
	All			8.9		2.5		0.28
Mixed silicates	1	9.4-18.5	14.5		3.3		0.2	
	2	22.3-26.9	23.8		1.8		0.1	
	3	19.3-25.9	23.4		2.5		0.1	
	4	10.3-14.0	12.0		1.6		0.15	
	All			18.4		6.1		0.33
4.2. Sample B								
Type	Lab	Range (wt%)	C (wt %)	\bar{C}	σ	σ_{int} (wt %)	σ/C	σ_{int}/\bar{C}
Quartz	1	17.0-23.7	20.0		2.4		0.1	
	2	18.7-23.2	20.7		1.7		0.1	
	3	19.7-23.6	21.6		1.6		0.1	
	4	15.0-20.5	17.5		2.1		0.1	
	All			20.0		1.75		0.09
Kaolinite	1	10.1-16.7	13.8		2.8		0.2	
	2	9.7-11.4	10.4		0.7		0.1	
	3	7.1-12.2	10.2		2.1		0.2	
	4	15.8-22.3	18.7		2.5		0.1	
	All			13.3		4.0		0.30
Siderite	1	6.4-11.3	9.1		1.8		0.2	
	2	6.6- 9.8	8.3		1.2		0.1	
	3	6.2-13.1	9.5		2.5		0.3	
	4	4.9- 9.4	6.4		1.8		0.3	
	All			8.3		1.4		0.17
Mixed silicates	1	35.2-40.5	37.7		1.9		0.05	
	2	38.4-43.7	41.2		2.0		0.1	
	3	35.3-42-4	39.2		2.8		0.1	
	4	27.4-37.4	33.1		3.6		0.1	
	All			37.8		3.4		0.09

Coal Mineral Analysis

4.3. Sample C

Type	Lab	Range (wt%)	C (wt %)	\bar{C}	σ	σ_{int} (wt %)	σ/C	σ_{int}/\bar{C}
Quartz	1	6.6-10.5	9.5		1.6		0.2	
	2	5.1-10.5	7.3		2.1		0.3	
	3	7.9- 9.8	8.9		0.7		0.1	
	4	6.9- 8.8	8.0		0.7		0.1	
	All			8.4		1.0		0.11
Kaolinite	1	17.4-22.3	19.8		1.9		0.1	
	2	13.2-19.3	17.2		2.6		0.2	
	3	8.6-11.0	10.1		1.0		0.1	
	4	21.9-28.2	25.0		2.5		0.1	
	All			18.0		6.2		0.35
Illite	1	17.7-20.7	19.4		1.2		0.05	
	2	18.2-22.9	21.2		1.8		0.1	
	3	17.2-25.5	19.8		3.4		0.2	
	4	20.2-23.1	21.4		1.2		0.05	
	All			20.5		1.0		0.05
Pyrite	1	12.4-18.8	15.8		2.6		0.15	
	2	10.9-15.3	13.6		1.7		0.1	
	3	12.7-18.3	15.8		2.3		0.15	
	4	12.9-17.1	14.4		1.8		0.1	
	All			14.9		1.1		0.07
Mixed silicates	1	19.4-24.5	21.2		2.3		0.1	
	2	21.0-26.9	23.9		2.5		0.1	
	3	23.4-29.2	26.6		2.2		0.1	
	4	11.7-15.3	13.5		1.3		0.1	
	All			21.3		5.7		0.27

Summarizing, the distribution of major minerals between five round-robin blocks is not significantly different from that within single blocks. Major mineral data are more suitable to assess inter-laboratory agreement than minor mineral data that are less precise.

Comparison with counting statistics

The data accumulated in this investigation can also be used to test the hypothesis that uncertainty due to counting statistics is the major source of error in the method at a given laboratory. For counting specific events, such as the number of times a particular mineral is encountered in a CMA analysis, it is well known that the precision of the determination increases as the total number of events counted, which, in the case of CMA is the total number of particles measured in the analysis. If n_i is the number of times the i -th category is counted in a total of N for all categories, it follows that:

$$C_i = 100 n_i / N \quad (1)$$

$$\sigma_i = (100/N) [n_i (N - n_i) / N]^{1/2} \quad (2)$$

$$V_i = \sigma_i / C_i = [1/n_i - 1/N]^{1/2} \quad (3)$$

where C_i , σ_i , and V_i are the measured percentage value, expected standard deviation, and expected coefficient of variation, respectively, for the i -th category. By substituting for n_i from equation 1 in equation 3, the following equation

is obtained:

$$V_i = [(100 - C_i) / N \cdot C_i]^{1/2} \quad (4)$$

From the form of equation 4 it is clear that as N increases the coefficient of variation of a determination of C_i decreases, or, equivalently, C_i becomes more precisely determined. The relationship between the coefficient of variation and C is shown by the lines in Fig. 3 for N equal to 120, 1,200 and 12,000. Superimposed on the curves in this figure, experimental values of the coefficient of variation are plotted against the weight percentage of individual minerals (5x600 particles). These coefficient of variation data define a trend that is similar to the calculated curve based on 1200 particles and indicate that much of the error in the CMA method can be attributed to errors arising from counting statistics. There are, of course, a number of other potential sources of error in the CMA method, for example particle area determination, mineral identification, etc., which is the reason why more data points plot above the calculated curve than below it. However, it is reassuring that these sources of error appear to be less significant or at least no greater than errors due to counting statistics for 1200 particles. Counting statistics for 12000 particles are, of course, better. However, to reduce the coefficient of variation to 1/3 of its former value would require an extension of analysis time from about one hour to a full day.

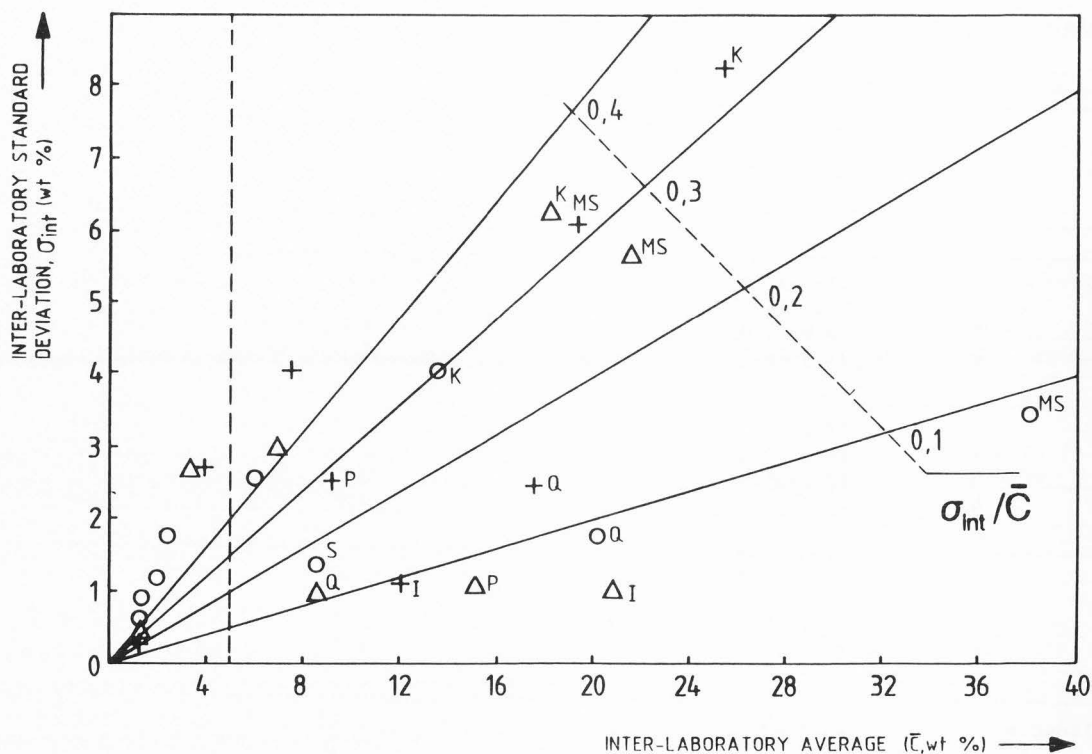


Figure 4. Inter-laboratory agreement. Standard deviation from inter-laboratory average (σ_{int} , wt%) plotted against weight percent of mineral (\bar{C} , wt%). \bar{C} = average of the C-values as determined by four laboratories. Samples A, B, C (+, o, Δ).

Inter-laboratory agreement

Reproducibility data have been plotted in figure 4 in the same format as used in the figures 1 and 2. The abscissa, \bar{C} is the average of mineral weight percentages, C, as determined by the individual laboratories. The corresponding inter-laboratory standard deviation is indicated by σ_{int} . To calculate the average, \bar{C} , the values from four laboratories were used (see also Table 4 for data of major minerals).

Figure 4 shows all data in excess of $\bar{C} = 1$ wt %. However, in view of the repeatability results only data for major minerals (right) were used for assessing inter-laboratory agreement. The left side of figure 4 shows that for low mineral contents the inter-laboratory variation (σ_{int}/\bar{C}) is considerable, but the numbers in this area may suffer from poor counting statistics. At mineral concentrations above 5 wt % half of the data points show a coefficient of variation lower than 0.15. For the remaining data the agreement between laboratories is poor; the coefficient of variation for these data is about 0.3. From table 4 it can be observed that the inter-laboratory variation - in contrast to repeatability - is dependent on mineral type in some cases. Whereas low variation data are obtained for quartz, illite and pyrite (two of three data), a high coefficient of variation is observed for all data of kaolinite and two of the three data of mixed silicates. For this reason the individual data of kaolinite and mixed silicates were reviewed.

Table 5 shows that laboratories reporting high kaolinite consistently report low mixed silicates. In fact, both errors nearly compensate and the sum of kaolinite + mixed silicates has σ_{int}/\bar{C} values of 0.08, 0.02 and 0.05 for the three coal samples investigated (table 5). The combined silicates, therefore, would be situated in the lower segment of figure 4, together with the other minerals. Evidently, resolution between kaolinite and mixed silicates is rather sensitive to instrumental or software factors affecting element discrimination. This may result from mixed silicate Al/Si ratios being close to that of kaolinite. The discrimination between kaolinite and illite is probably good because of the presence of 10% potassium. With other clay minerals, however, the classification of a mineral could be more sensitive to its Al/Si signal ratio which may vary with window thickness or threshold setting. In principle, window thickness may vary by the manufacturing process. Also, temporary variations in effective window thickness may occur by smudging with vacuum oil. Window cleanliness may be tested by the Cu K α to La peak ratio, using a pure copper standard. In CMA practice it is advisable to take a pure Cu-spectrum to adjust the software for the sensitivity of a particular detector system towards light elements (Al, Si). Our conclusion is that the inter-laboratory agreement, although generally acceptable for major minerals, such as quartz and pyrite, should be improved for the clay mineral groups.

Coal Mineral Analysis

Table 5. Weight percent of kaolinite and mixed silicates - 4 laboratories.

sample	mineral	lab 1	lab 2	lab 3	lab 4	laboratories 1-4		
						C, wt %	\bar{C} , wt %	σ_{int} , wt %
A	kaolinite	26.5	21.4	17.2	36.2	25.3	8.2	0.32
	mixed silicates	14.5	23.8	23.4	12.0	18.4	6.1	0.33
	sum (K+MS)	41.0	45.2	40.6	48.2	43.8	3.6	0.08
B	kaolinite	13.8	10.4	10.2	18.7	13.3	4.0	0.30
	mixed silicates	37.7	41.2	39.2	33.1	37.8	3.4	0.09
	sum (K+MS)	51.5	51.6	49.4	51.8	51.1	1.1	0.02
C	kaolinite	19.8	17.2	10.0	25.0	18.0	6.2	0.35
	mixed silicates	21.2	23.9	26.6	13.5	21.3	5.7	0.27
	sum (K+MS)	41.0	41.1	36.6	38.5	39.3	2.1	0.05

A better control of experimental conditions would be required to compare clay mineral data obtained by different laboratories. It is suggested that use of a standard could eliminate bias originating from differences in window thickness and also reduce bias caused by differences in threshold setting.

Summarizing, the reproducibility of CMA-results may be improved by correction of bias in element quantification. This would involve standardization of detector systems and development of a reproducible method of threshold setting.

Conclusions

1. Repeatability of CMA does not depend on mineral type.
2. Repeatability of CMA improves with increasing mineral concentration.
3. For individual laboratories, errors can be attributed mainly to counting statistics when the procedure involves the analysis of approximately 1000 particles.
4. The coefficient of variation between five measurements is less than 0.20 for most species constituting more than 5 wt % of total mineral matter.
5. The coefficient of variation from the inter-laboratory average is less than 0.10 for 50% of the main constituents.
6. High values of deviation (> 0.10) from inter-laboratory averages were found to be due to poor resolution between kaolinite and mixed silicates.
7. The resolution between clay minerals could be improved by adjusting the software for element sensitivity of a particular detector system.
8. Using a standard detector system and a reproducible method of threshold setting could improve interchangeability of CMA-data.

Acknowledgements

The round-robin samples were also investigated by Dr. Warren Straszheim (Ames

Laboratory) and Dr. Dieter Birk (Geofuel Research Inc., Sydney, N.S.). Due to the different mineral classification used by Dr. Straszheim, a straightforward comparison between his results and those reported here was impossible. Dr. Birk's data were not available to the authors at the time this paper was written. Mr. Jan Pinxter of Tracor Europa suggested use of a copper standard. Miss Karin van der Meer prepared the manuscript.

References

- Birk D (1989) Coal Minerals: Quantative and descriptive SEM-EDX analysis, *J. Coal Quality* 8 (2) 55-62.
- Carpenter RM (1988) Coal classification Report IEACR/12, IEA Coal Research, London, p. 23.
- Finkelman RB, Gluskoter HJ (1981) Characterization of minerals in coal: problems and promises. In: Proc. Engineering Foundation Conference, Fouling and Slagging Resulting from Impurities in Combustion Gases, Bryers RW (ed), 299-318.
- Hamburg G (1984) Description of the Tracor Northern energy-dispersive system as applied to coal minerals analysis. *Technology in Review*, Tracor Northern, Middleton WI 2 (1), 7-10.
- Huggins FE, Kosmack DA, Huffmann GP, Lee RJ (1980) Coal Mineralogies by SEM automated analysis. *Scanning Electron Microsc.*, 1980, I, 532-540.
- Huggins FE, Huffmann GP, Lee RJ (1982) Scanning electron microscope-based automated image analysis (SEM-AIA) and Mössbauer spectroscopy: Quantative characterization of coal minerals. In: *Coal and coal products: Analytical characterization techniques*, Fuller EL (ed), Am.Chem.Soc. Series No. 205, 239-258.
- Lee RJ, Kelly JF (1980) Overview of SEM-based automated image analysis, *Scanning Electron Microsc.* 1980, I, 303-310.
- Straszheim WE, Yousling JG, Markuszewski R (1986) Analysis of ash-forming mineral matter in raw and supercleaned coals by automated image

analysis, scanning electron microscopy. In: Vorres KS (ed) "Mineral Matter and Ash in Coal", Am.Chem.Soc. Washington D.C., pp. 449-461.

Vleeskens JM, Hamburg G (1989) Coal minerals analysis round-robin, data compilation, ECN-89-154 (December 1987, updated October 1989). Internal report ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands.

Discussion with Reviewers

J.F. Kelly: You give a test for the cleanliness of the X-ray detector window in terms of the ratio of the copper K α and La peaks. Considering the range in effective window thickness currently available, should not this test condition be adjusted for the individual systems?

Authors: This suggestion needs serious consideration in CMA-practice to improve interchangeability of data. Using copper as a standard may find application both to eliminate differences in window thickness used in different systems and to check for cleanliness during operation.

Upon installation of a new detector (window) the copper-spectrum may be taken to adjust the software for consequent differences in element sensitivity, particularly of the lighter elements such as aluminium and silicon. From time to time the copper spectrum may be taken again to check for variations which may be due to fouling.

G.B. Freeman: How do the results of CMA-procedure compare to standard methods quantitatively for bulk ash, bulk elemental composition and with respect to identification of mineral type distributions.

Authors: The CMA-method gives no information on total mineral content but on mineral distribution only. The important improvement of CMA over bulk elemental analysis is that it differentiates between silicon present in quartz and in several clay minerals. Some of these clays are poorly crystalline and cannot be quantitatively estimated by XRD either. A disadvantage of CMA is that results for pyrite are generally 30-50% higher than ASTM-data (Straszheim and Greer, 1990).

G.B. Freeman: You refer to particle sizing being a part of these analyses. Do you get particle sizing for each mineral type as these data are compiled? What other information "comes with" this procedure?

Authors: Particle size data are obtained for each mineral type. This is an essential step in the CMA-procedure as particle size is used to calculate particle volume, and particle mass, using the memory stored density of each mineral. This approach makes it possible to express mineral content in weight percent of all particles counted.

G.B. Freeman: What do you feel are the current limitations of the available EDS software/models which need to be modified to improve the repeatability of this procedure?

Authors: The subjective choice of threshold setting is a limitation of the CMA-method. It may not only affect comparability of data from different laboratories but, to some extent, also the comparability of data for different samples within a given laboratory. See also discussion with G. Remond.

G. Remond: The major limitation of CMA lies in the subjective selection of grey levels of the backscattered electron images. Would it be feasible to digitally measure the back-scattered electron intensity and to normalize this intensity to that of a reference compound?

Authors: With a reference compound it would be possible to subtract instrument noise for different instrument settings, for instance different magnifications. However, the noise level may also include low back-scatter intensities from finely dispersed inorganic matter. This is a coal sample specific contribution which is not related to the instrument noise as observed on a reference compound.

R.B. Finkelman: Why did not you re-check the repeatability data for five blocks on single blocks of A-C instead of D-F. You really did not accomplish what you intended.

Authors: As the repeatability data for single blocks D-F were not better than those obtained earlier for series of five blocks A-C, it did not seem necessary to repeat this test on the A-C samples.

Additional References

Straszheim WE, Greer RT (1990). Insights on pyrite sulfur in coal from automated image analysis. In: Processing and Utilization of High Sulfur Coals-III, Markuszewski R, Wheeckoek TD (eds), Elsevier, pp. 11-19.