Tracing the maceral origin in combustion chars. The inertinite in Combustion WG of ICCP.

Report of the 1997 Round Robin microscopy exercise on a medium rank inertinite-rich coal char

ICCP

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Note: The coal to which this report refers is labelled as coal K in the CD "Tracing the maceral origin in coal chars" Borrego et al., 2008

Inertinite in Combustion WG.
Report of the Round Robin Exercise 1997 by A.G. Borrego

Introduction

A round robin was prepared to assess the combustion behaviour of inertinite following the decisions taken in the ICCP meeting hold in Heerlen in 1996. In that meeting it was agreed:

• to study pyrolysis chars rather than combustion chars in order to avoid the uncertainties derived from the different burning rates of the macerals

• to use a point-counting procedure based on the identification of the optical characteristics of the carbonaceous material rather than the identification and classification of the whole particle

• the utilisation of a relatively low rank coal yielding preferentiality isotropic vitrinite chars which should be easier to distinguish from inertinite chars

• to prepare a plate containing examples of the typical carbonaceous material to be included in each group of the proposed classification system

• to provide detailed information about the petrographic and chemical composition of the parent coal

• to use the same coal than that used for the round robin of the combustion WG so that the results of both WGs could be jointly considered and a complete picture of the combustion behaviour of that coal could be obtained.

According to this decisions a polished block containing concentrated pyrolysis chars, detailed instructions to perform the exercise and a description of the classification system was distributed to 11laboratories. 12 individual s from 8 institutions carried out the exercise (See below):

Comelia Panaitescu (University of Bucharest)
Deolinda Flores (University ofPorto)
Manuela Marques (University ofPorto)
Henrik Petersen (GEUS, Denmark)
Edward Lester (University ofNottingham)
Dave Clift (University ofNottingharn)
Krystina Kruszewska (University of Silesia)
Barbara Kwiecinska (Academy ofMining and Metalurgy, Cracow)
Ken Hall (BHP Research, Newcastle laboratories)
Diego Alvarez (INCAR-CSIC, Oviedo)
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Coal characterisation

Some of this information can appear redundant for those who carried out the exercise but it is necessary to follow the content of this report. All the analyses of the feed coal (Coal K) were carried out on the same size fraction used to produce the char (53-75 μm). The proximate and ultimate analyses of the feed coal are given in Table l. The ash content is rather low (11.69%). Volatile matter content is lower than the value expected for a coal with vitrinite reflectance Rr=O.66%. This is not surprising if it is borne in mind that the volatile content of inertinite, which is the major component of this coal, is usually lower than that of vitrinite.

Table 1. Proximate and ultimate analyses of the feed coal

	ash (%)db	V.M. (%) daf	F.R.	C	H	N (%) daf	St	Odif	H/C[a]	O/C[a]
Feed Coal	11.69	33.20	2.01	80.57	4.65	1.76	0.68	12.34	0.69	0.11

V.M.=volatile matter; F.R.=Fuel Ratio; db=dry basis; daf=dry ash free basis;[a] atomic ratio

Particles were selected for petrographic analysis as in normal maceral analysis and reflectance readings were taken on 500 points. Fig. 1 shows the histogram with the distribution of reflectances for each maceral group. The size range, smaller than that in current maceral analysis, made the identification of macerals more difficult. Some particular features may well deserve a comment: for instance the wide distribution of vitrinite reflectances with high standard deviations and the Gaussian-like distribution of the inertinite reflectances with modal values at relatively high reflectances. A close inspection of the distribution of vitrinite reflectances indicates the presence of two telovitrinite populations with mean values at 0.66% and 0.78% whereas the distribution of detrovitrinite only shows a modal value and generally lower reflectances than telovitrinite. Considering both facts together, the possibility of a blend has to be ruled out and the wide distribution of reflectances could then be attributed to paleoweathering processes though cleats or slits are only occasionally observed. Table 2 shows the distribution of reflectances within each maceral group, with special attention paid to the vitrinite sub-groups and the inertinite macerals.

Liptinite content is low and inertinite accounts for 62.6% of the organic components in the coal and it is mainly found as macrinite, semifusinite and inertodetrinite, all of them macerals indicating a moderate degree of alteration. The term macrinite is reserved in the analysis for those rounded or elongated particles with low relief. The particles smaller than 10 µm are grouped under "inertodetrinite" though part of them appear to be similar in origin and optical properties to macrinite. Massive inertinite refers to high reflecting structureless particles with high relief and more or less angular edges which cannot be easily named as any other inertinite maceral. Some particles exhibiting oxidation rims were found in the coal.

Table 2. Maceral analysis of the feed coal including mean random reflectances (R_r), maximum and minimum values, standard deviations and percentages for each component.

Component	Mean R_r (%)	Minimum R_r (%)	Maximum R_r(%)	σ	n	Vol (%)
Telovitrinite (rank)	0.66	0.58	0.71	0.038	33	6.6
Telovitrinite (H)	0.78	0.72	0.88	0.041	41	8.2
Detrovitrinite	0.64	0.45	0.89	0.079	90	18.0
Gelovitrinite	0.69	0.58	0.89	0.108	7	1.4
Fusinite	2.03	1.34	2.78	0.369	28	5.6
Semifusinite	1.58	0.64	2.39	0.331	95	19.0
Macrinite	1.52	0.75	2.41	0.408	70	14.0
Micrinite	1.25				1	0.2
Inertodetrinite	1.81	0.70	2.74	0.331	98	19.6
Massive Inertinite	1.62	1.02	3.29	0.565	21	4.2
Liptinite	0.22	0.11	0.38	0.080	16	3.2

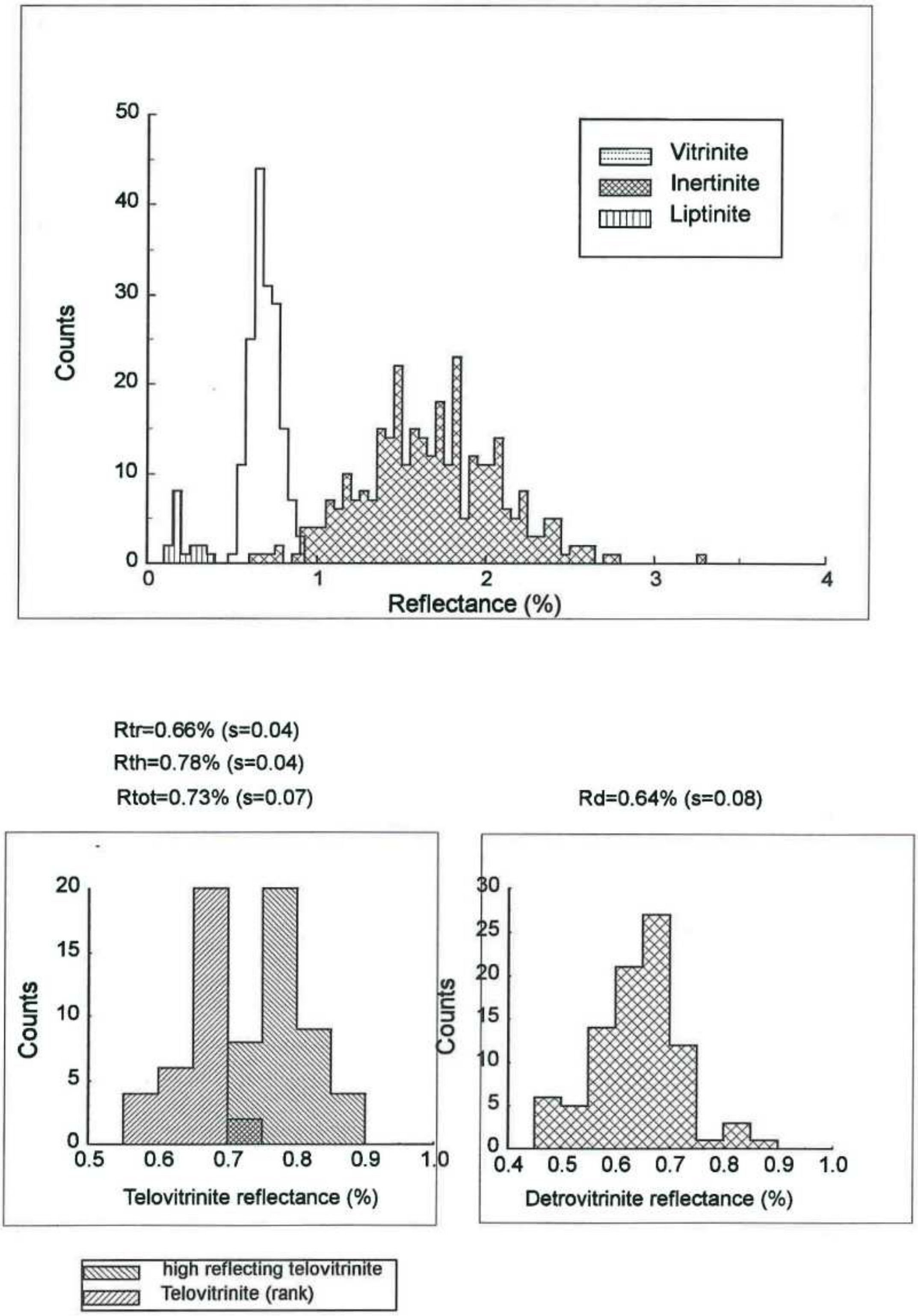


Figure 1. Histograms of reflectance of whole coal and of various vitrinite macerals

Chars were kindly prepared by Edward Lester in a Drop Tube Furnace (DTF) at 1300 ºC under Oxygen-lean atmosphere (3% oxygen) and with residence time of 100 milliseconds. Feed coal was ground and sieved to 53-75 µm.

Instructions

Blocks were prepared in a way that a minimum amount of sample was used to obtain a polished surface large enough to carry out a point-counting analysis, minimising at the same time any heterogeneity effects due to particle segregation. The arrow on the surface of the block indicates the direction in which segregation might occur (Top to bottom). Considering the small size of the particles, it should have been possible to count, at least, 250 points. Participants were invited to count the number of points they considered more appropriate given the characteristics of the material and the preparation system but they had to specify the number of total counts. It was stressed that point occurrences had to be classified, in much the same way as in a coal maceral analysis and, consequently only carbonaceous material (**NOT PORES or Mineral matter**) had to be counted. Considering that previous exercises on char were based on the classification of the whole particle, it was insisted on the fact that only the carbonaceous material with the same optical texture than that under the crosswire, **AND NOT ON THE WHOLE PARTICLE**, had to be considered when taking a decision between any of the seven groups of the classification system. It was also stressed that the classification system included all the possible occurrences of char textures but not all of them had to be necessarily present in this particular char.

Participants were asked to give some details of the equipment they used to carry out the exercise such as the magnification and the use of colour plate. In order to be able to analyse the reasons for the deviations or possible disagreements among different analysts, a "staircase" data output was proposed to report the results (Fig. 2). The diagonal line should have contained the percentage of occurrences or number of counts found in every group that the participant considered as doubtless. Any dubious identification should have been consigned in the cell whose row and column indicated the two Groups between which the participant had doubted.

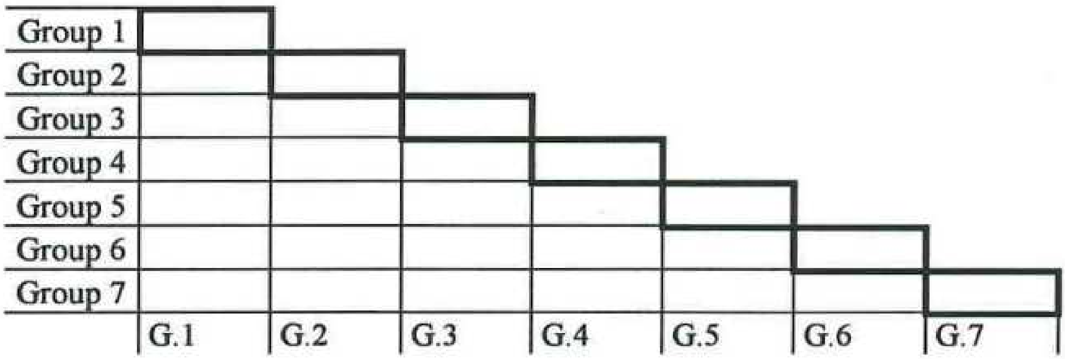


Fig. 2. Staircase to report the results. The diagonal should contain the percentage of occurrences or number of counts found in every group and regarded as doubtless. Any dubious identification should be consigned in the cell whose row and column indicate the two Groups between which you have doubted.

Classification of the carbonaceous material s in chars

The classification system was based on char texture. This is the presence/absence of degassing bubbles or holes indicating some kind of melting and the anisotropy. The description of the groups was made as follows:

Group 1 would include all kind of domains which could derive from vitrinite, and these can be isotropic or anisotropic, depending on the rank of the coal.

Group 2 would include the char materials which have been presumably formed from inertinites, but have been highly altered during pyrolysis, showing both anisotropic texture and an important porosity development.

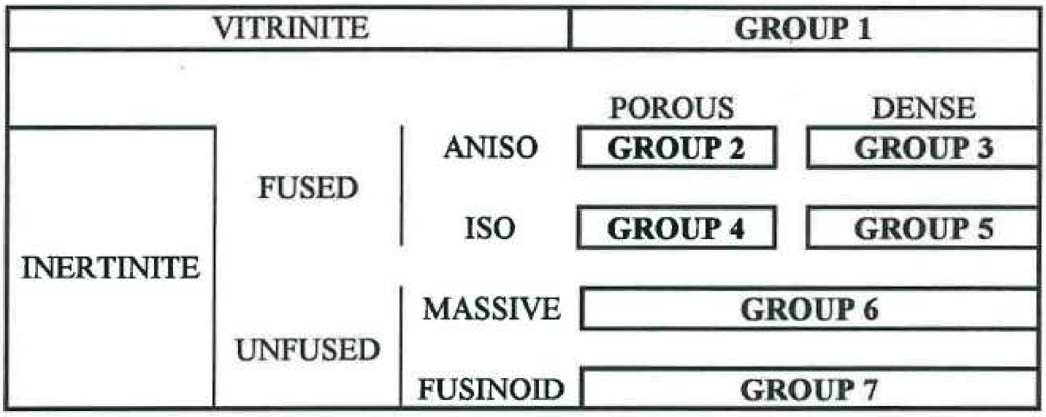
Group 3 would include those domains formed from inertinites which have developed an appreciable anisotropy without further porosity development.

Conversely, the **Group 4 m**aterials would be those which have passed though a plastic stage and generated a porous structure but do not show any signs of anisotropy.

Group 5 would include the isotropic dense domains with evidence of having fused (i.e.: srnall spherical degassing pores).

Group 6 would include the least altered inertinites, except the fusinites.

Group 7 would only include the unchanged fusinites.



Report of results

The numbers given to the participants have no relationship at all with the list at the beginning of this report. Table 3 shows some technical data of the analyses and summarises the main comments written by the participants.

Most of the analysts counted 250 points except one who counted 500 and one who counted 350. Some comments regarding the preparation of the block indicated that participants did not have difficulties to find particles enough to be counted. Though the direction in which segregation of particles could have occurred was marked on the block surface with an arrow, nobody commented on the existence of segregation.

Table 3. Analytical conditions and remarks

Analysts	Points	Objective	Colour Plate	Remarks
1.1	250	32x	No	Uncertainties b. G2/G4 and G3/G5)
1.2	250	32x	No	Difficulties to distinguish b. G2/G4
2	500	125x	Partially cros. Nicols	No uncertainties
3.1	250	50x		No uncertainties
3.2	250	50x		No uncertainties
4.1	250	100x	Yes	Few uncertainties (mainly G1/G2)
4.2	350	100x	Yes	Difficulties to distinguish b. G5/G7
4.3	250	100x	Yes	Few uncertainties
5	250	40x		Few uncertainties
6	250	40x	No	Few uncertainties (mainly G1/G4)
7	250	50x		Uncertainties b. G1/G2 and G5/G6)
8	250	40x	No	Few uncertainties (mainly G1/G4)

Table 4 shows the percentages reported by each analyst for each group of the classification system. The statistical data at the bottom of Table 4 have a merely informative character considering the huge dispersion of the results. Most participants did not report any doubt (5) or indicated a low amount of dubious identifications (<12%) with the exception of participant 1.1 who reported a high amount of dubious identifications due to the impossibility of distinguishing between groups G2-G4 and G3-G5. The results could have been improved a little bit if the extreme values would have been removed but this would have force to eliminate many participants, and the set of data would not have meaning anymore. For instance results from analyst 2 for G 1 appear to be significantly higher than the rest and this associate to very low amount of G2. Results of participant l.1 in groups G2, G3, G4 and G5 were zero and in G5 the analyst eliminated should have been 4.2. Therefore, 1 decided to try to understand the reasons for the spread of the results instead of removing the extreme values.

Table 4. Percentages reported by each analyst for each group of the classification system.

	G1	G2	G3	G4	G5	G6	G7	Doubts
1.1	34.4	-	-	-	-	8.4	5.2	52.0
1.2	22.0	20.4	-	30.4	3.6	17.6	6.0	-
2	57.4	3.6	1.4	1.8	2.4	9.4	24.0	-
3.1	15.2	22.4	10.0	15.6	26.8	9.6	0.4	-
3.2	13.2	26.4	9.6	16.0	25.6	8.0	1.2	-
4.1	22.4	32.4	0.8	15.6	1.6	18.4	6.8	2.0
4.2	15.2	36.9	13.1	14.3	15.1	2.3.0	3.1	-
4.3	28.0	35.2	0.8	8.8	3.6	16.0	5.2	2.4
5	20.0	27.0	10.0	15.0	6.0	14.0	2.0	6.0
6	37.2	12.8	3.2	14.4	9.6	7.6	2.0	11.2
7	40.0	10.4	1.0	4.0	15.0	17.0	2.6	10.0
8	39.0	10.2	4.1	12.3	8.4	8.1	3.0	12.6
Mean	28.8	19.9	4.5	12.4	9.8	11.4	5.1	8.1
Minimum	13.2	0.0	0.0	0.0	0.0	2.3	0.4	0.0
Maximum	57.4	36.9	13.1	30.4	26.8	18.4	24.0	52.0
Standard deviation	13.18	12.37	4.82	8.11	9.07	5.07	6.28	14.03

Table 5. Percentages of doubts reported by each analyst for each group combination

	G1-G2	G1-G3	G1-G4	G2-G3	G2-G4	G3-G4	G3-G5	G3-G6	G4-G5	G4-G6	G5-G6	G6-G7
1.1					28.4		23.6					
1.2												
2												
3.1												
3.2												
4.1			1.6						0.4			
4.2												
4.3					0.8						1.2	0.4
5	1.0	1.0	1.0	1.0				1.0	1.0			
6	2.0	0.8	4.4	1.2	1.2				2.0	0.4	1.2	
7	5.0										5.0	
8	2.3	1.0	3.6	0.8	1.4	0.4			3.0	0.6	1.8	

The distribution and amount of the dubious identifications is shown in Table 5. Those combinations of groups not reported by any participant are not included in the table 5. The percentages of doubts within each group were always less than 5% except for participant 1.1. Most of the participants who doubted did it between Gl-G2 and G1-G4. If the reasons for the doubts are analysed, they can be classified into various categories:

- **Doubts related to the coal itself**
  - Difficulties to decide if a porous anisotropic material derived from vitrinite or inertinite (GI-G2). This was particularly difficult because at the rank of this coal starts the anisotropy development of vitrinite-derived chars. In addition, the quite abundant higher reflecting vitrinites observed in the coal would have yield porous and clearly anisotropic particles whereas the low reflecting ones would have produced isotropic porous particles.
  - Difficulties to decide if a porous isotropic material derived from vitrinite or inertinite (GI-G4). Though the formulation of this doubt sounds very reasonable, the amount of dubious counts was low. The cavities generated by vitrinite of this rank should be much larger than those of inertinite since the melting ability of inertinites which remain isotropic must be quite low.
  - Difficulties to decide whether a massive unfused material belongs to a fusinoid or not (G6-G7). It was relatively common in this sample to find char particles composed of fragments of isotropic massive material. If these fragments were considered as a part of a fusinite they would have been regarded as fusinoid (G7) and if they were considered as independent unfused fragments they would have be en classified as massive (G6). The difficulties to solve this problem are evident but only one participant reported 0.4% doubts, which indicate that most of the analysts were able to take a decision when they landed on one of these particles.
- **Difficulties linked to a porosity limit**
  - Doubts between G2-G3 and G4-G5 deal with this matter but the percentages reported were generally low «3%).
- **Difficulties to distinguish some optical features**
  - Unable to distinguish anisotropy (G2-G4; G3-G5). Problem of experience?
  - Difficulties to distinguish small bubbles (G5-G6). Problem of magnification?
- **The last category groups** those doubts which have an **unclear origin** and which could be related to the size of the area to be considered for taking a decision. They include G4-G6, G3-G6, G3-G4, G1-G3 and were not relevant quantitatively <<1 %).

The results presented in this way are difficult to handle and therefore the dubious identifications were prorated in order to reduce the number of classes to look at. The way to proceed was to add to the percentage reported by each participant as non dubious identifications, the percentages resulting of prorating the dubious identifications group by group. As participant 1.1 did not report any value as surely identified in groups G2, G3, G4 and G5, the figures used to prorate these values were the mean values for each of these c1asses calculated without considering participant 1.1. Table 6 shows the percentages reported by the analysts for each group of the c1assification system after prorating for dubious identifications (italic).

Table 6. Percentages reported by each analyst for each group of the classification system after prorating for dubious identifications

	G1	G2	G3	G4	G5	G6	G7
1.1	34.4	*17.2*	*7.3*	*11.2*	*16.3*	8.4	5.2
1.2	22.0	20.4	0.0	30.4	3.6	17.6	6.0
2	57.4	3.6	1.4	1.8	2.4	9.4	24.0
3.1	15.2	22.4	10	15.6	26.8	9.6	0.4
3.2	13.2	26.4	9.6	16	25.6	8.0	1.2
4.1	*23.3*	32.4	0.8	*16.7*	1.6	18.4	6.8
4.2	15.2	36.9	13.1	14.3	15.1	2.3	3.1
4.3	28.0	35.8	0.8	*9.0*	*3.8*	16.0	5.2
5	*21.8*	*28.3*	*11.0*	*16.0*	*6.3*	*14.6*	*5.3*
6	*43.5*	*14.0*	*3.5*	*17.7*	*11.1*	*8.2*	2.0
7	*44.0*	*11.4*	1.0	4.0	*17.3*	*19.7*	2.6
8	44.4	11.9	4.5	16.5	9.6	9.6	3.5
Mean	*30.2*	*21.7*	*5.3*	*14.1*	*11.9*	*11.9*	*5.2*
Mean*	28.8	19.9	4.53	12.4	9.8	11.4	5.1
Minimum	*13.2*	*3.6*	*0.0*	*1.8*	*2.3*	*2.3*	*0.4*
Maximum	*57.4*	*36.9*	*13.1*	*30.4*	*19.7*	*19.7*	*24.0*
Standard deviation	*14.32*	*10.54*	*4.71*	*7.31*	*5.4*	*5.41*	*6.25*
Standard* deviation	13.18	12.37	4.82	8.11	9.07	5.07	6.28

*Before prorating

The increase in the values obtained after prorating in those data which were modified, was below 15% of the value (Table 7), except for those of participant 1.1, indicating that prorating did not change significantly the trend.

Table 7. Increase after pro-rating (in percentage of the value) of the figures reported for each participant

	G1	G2	G3	G4	G5	G6	G7
1.1		100	100	100	100		
1.2							
2							
3.1							
3.2							
4.1	3.9			6.6			
4.2							
4.3				2.2	5.3		
5	8.3	4.6	9.1	6.3	4.8	4.1	11.7
6	14.5	9.4	8.6	15.3	13.5	7.3	
7	9	8.8			13.3	13.7	
8							

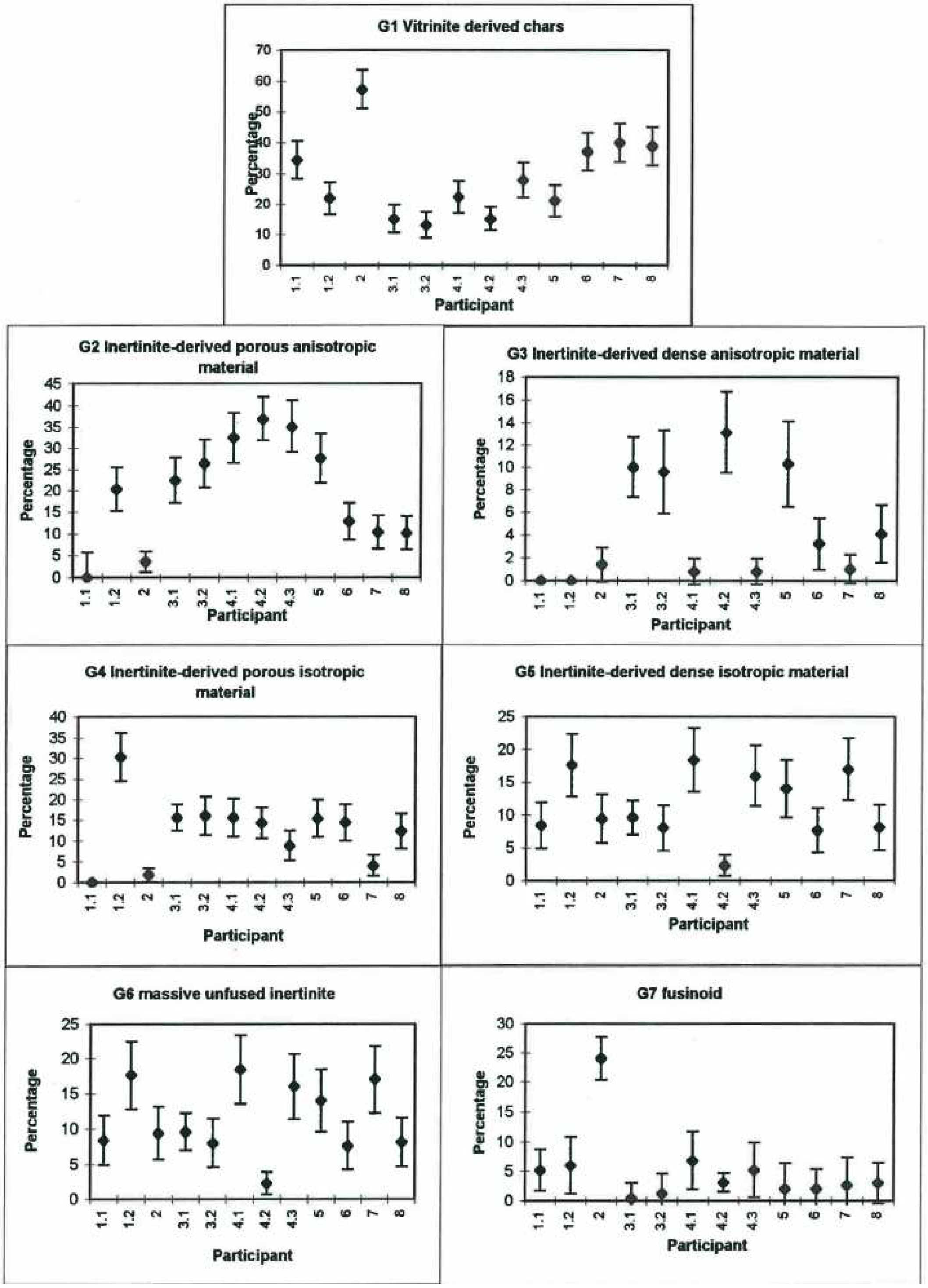


Fig.3 Plot of the different percentages reported by each participant of the various char groups.

The data did not improve significantly after prorating. The mean values increased slightly. The differences between minimum and maximum values were reduced but the standard deviations were still too high, some of them even c10se to the mean values.

Another striking feature derived from the data is that when more than one participant carried out the exercise from the same laboratory, their results were rather similar and also the similarity between participants 6, 7 and 8 though they belonged to different institutions. Fig. 3 shows the same results of Table 6 plotted for each group. It includes the error bars calculated as for coal macerals by

$$\sigma = \sqrt{\frac{p \times (100-p)}{n}}$$

Where σ is the error, p the percentages obtained and n the number of points counted

In spite of the great spread of the results shown in Fig. 3, some conclusions can be drawn about both the exercise and the inertinite behaviour.

Conclusions

- The percentages of dubious identifications were typically lower than 12% with only one participant indicating more than 50% uncertain values.
- The dubious identifications reported by the participants can be grouped into three categories:
    - Analytical problems
    - Uncertainties linked to the coal itself
    - Unknown origin
- For most of the analysts, the percentage of uncertainties does not justify the spread of the results. The percentages before and after prorating were nearly equally unsatisfactory.
- The agreement, when the groups 1+2+4 (between which were particularly difficult to decide given the characteristics of this coal) were summed, was somewhat higher. Nevertheless departures from the mean were still very great.
- It appears that the background of the participants, more familiar with coke than char petrography can have played sorne role on the spread of the results.
- Data indicate that a high proportion of the material in the coal fused. The highest datum for unfused material was 34%. All other data were under 25%. This indicates that an important part of the inertinite showed plastic behaviour, in agreement with recent papers. Considering that 40% of the inertinite in the parent coal had reflectances over 1.5%, these results indicate that even part of this high reflecting inertinite exhibited some kind of plasticity.

Future work

Another Round Robin Exercise is planned within the next year activities. This coal will have a similar rank but nearly only inertinite as single maceral group. An additional pellet containing the high temperature char of a coal belonging to the same seam but with about 60% vitrinite will be also distribute so that participants will have the opportunity to check how vitrinite-derived chars look like. The exercise will have a similar design as this year one and information about the parent coal and some sentences about the existing knowledge of how inertinÍte of this kind behaves will be also provided.