Report on Organic Matter Concentration Working Group (OMCWG 2008)

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1. Introduction

The main objective of the Organic Matter Concentration WG was to study the effect of the isolation procedure on the organic matter optical parameters. This first exercise consisted of the analysis of two samples with terrestrial organic matter in order to minimize the difficulties for vitrinite identification. The samples studied in this exercise were of low and medium rank and the analyses performed were:

- Vitrinite reflectance of the whole-rock sample (WR);
- Vitrinite reflectance of the kerogen concentrate sample (KC);

This report includes the results obtained by sixteen participants (Table 1) of the exercise proposed in the last ICCP meeting (Victoria-Canada) in order to continue with the activities of the former Isolation WG that began in 1989 with the exercise previously convened by Andre van der Meulen and John Castaño (1995 and 1996).

The studied samples were composed by two outcrop carbonaceous shales (Type III Kerogen): one of them was from Spain (sample OMC1), Montsacro Mine, Asturias Basin (Pennsylvanian) and the other one was from Nigeria (sample OMC2), Mamu Formation (Maastrichtian), Benin-Flank Basin.

The set of studied samples comprises 4 samples numbered as follows:

Sample OMC1 (Asturias Basin - Spain):
OMC1A = whole rock and;
OMC1B = kerogen concentrate
Total Organic Carbon (TOC) about 20wt%
HI (Hydrogen Index): 151 mg HC/g TOC
T_{max}: 464°C (pointing out that this sample was thermally mature - medium rank)

Sample OMC2 (Benin-Flank Basin - Nigeria):
OMC2A = whole rock and;
OMC2B = kerogen concentrate
Total Organic Carbon (TOC) about 5wt%
HI (Hydrogen Index): 280 mg HC/g TOC
T_{max}: 427°C (pointing out that this sample was thermally immature - low rank)

Table 1 – List of Participants in the OMCWG

Participant	Affiliation	Country
Araujo, Carla V.	Petrobras R&D Center	Brazil
Borrego, Ángeles G.	INCAR-CSIC	Spain
Cook, Alan	Keiraville Konsultants Pty Ltd	Australia
Flores, Deolinda	University of Porto	Portugal
Hackley, Paul	U.S. Geological Survey	USA
Hower, Jim	University of Kentucky	USA
Kern, Marcio L.	Federal University of Rio de Janeiro	Brazil
Kommeren, Kees	Shell E&P	The Netherlands
Mendonça Filho, João G.	Federal University of Rio de Janeiro	Brazil
Mendonça, Joalice O.	Federal University of Rio de Janeiro	Brazil
Menezes, Taíssa R.	Petrobras R&D Center	Brazil
Newman, Jane	Newman Energy Research Ltd	New Zealand
Ranasinghe, Padmasiri	Keiraville Konsultants Pty. Ltd.	Australia
Souza, Igor V. A. F.	Petrobras R&D Center	Brazil
Suárez-Ruiz, Isabel	INCAR-CSIC	Spain
Ujiié, Yoshihiro	University of Hirosaki	Japan

2. Sample Preparation

2.1. Whole-Rock Preparation Procedure

The samples from Spain and Nigeria were ground to approximately 2mm size and embedded in resin. A single block was prepared for each sample.

2.2. Plug of Kerogen Concentrate Preparation Procedure

The samples from Spain and Nigeria were ground to approximately 2mm size. HCl (37%) was added to the sample for a period of 18 hrs. After this procedure the sample was washed with distilled water until the washing water was neutral. In the next step HF (40%) was added for a period of 24hrs, repeating the washing procedures, and 37% HCl was added to the sample for a period of 3 hrs to remove the fluorides. Samples were washed with water again until neutralization. After this procedure samples were floated using $ZnCl_2$ (ρ = 1.9 to 2 g/cm^3) and centrifuged to separate sulphides. The washing procedures were repeated adding some HCl (10%) drops + distilled water to eliminate the heavy liquid. The isolated kerogen was sieved (20 mm) and embedded in resin (SERIFIX-STRUERS).

2.3. Sample Polishing

The particulate blocks had their surfaces ground down using progressively finer grades of wet silicon carbide papers; the grinds used were 800, 1200 and 4000 grit wet silicon carbide paper. A single set of samples was sent to each laboratory.

3. Statistical Evaluation Criteria and Parameters

Precision and bias for the analysts: an evaluation of the suitability of the data for an accreditation program (based on Borrego *et al.* 2006 and http://www.iccop.org) was used to interpret data.

This report is based on the rules for ICCP Accreditation Program for Vitrinite Reflectance Measurements on Dispersed Organic Matter described in Borrego *et al.* (2006). According to these authors, one of the objectives of a round robin exercise is to highlight the difficulties that must be taken into account to initiate an accreditation program for vitrinite reflectance assessment on dispersed organic matter. Before initiating this task there was a need to know what the scatter of results around the calculated group means was.

The system applied is the same one used in the accreditation program for vitrinite reflectance in coal. The criteria used for coal might be too strict for dispersed organic matter but there is no doubt that the precision achieved for coal vitrinite reflectance should be the goal. The parameters considered in the accreditation program are:

UMSD: refers to participant's **U**nsigned **M**ultiple of the **S**tandard **D**eviation, calculated against the group mean and standard deviation data, for each sample analysed as per the formula below:

$$UMSD = \left| \left(\frac{X_i - \overline{X}}{\sigma} \right) \right|$$

X_i = the participant vitrinite reflectance

$\overline{X}$ = the group mean vitrinite reflectance

σ = the standard deviation of the group

SMSD: refers to participant's **S**igned **M**ultiple of the **S**tandard **D**eviation, calculated against the group mean and standard deviation data, for each sample analysed.

AUMSD and **ASMSD** are the average UMSD and SMSD values respectively for each participant. The AUMSD value is a measure of the participant's **accuracy** and the ASMSD is an indicator of the participant's measurement **bias** in the techniques being assessed.

Once all these parameters are calculated depending on the figures obtained by each participant the information received is the following:

(A) AUMSD: dispersion around group mean values, that is, a measure of accuracy.

<1.5	≥1.5
Pass	Fail
Your analytical technique is acceptable	You have serious problems with your analytical technique

(B) ASMSD: bias of reported results (±), that is, indicates consistency of an analyst. A negative bias (for example, -1.3061) indicates that your results, on average, are always lower than the group mean values and a positive bias (for example, +1.3061) indicates that your results, on average, are higher than the group mean values. Where the AUMSD and ASMSD values are **exactly the same** indicates that your results are always below (negative value) or above (positive value) the established group values.

<±0.5	±0.5-<±1.0	±1.0-<±1.5	≥±1.5
Minor bias	Medium bias	Significant bias	Extreme bias
Your results are always consistent	Some improvement is required	Examine the method being used	You have serious problems with your analytical technique

The SMSD was calculated for each vitrinite population and also the averaged AUMSD and ASMSD for each participant.

It is worth mentioning that these statistical systems are being used only as a learning tool, giving information on how the participants should proceed in the vitrinite reflectance analysis on dispersed organic matter.

4. Results

The participants are being identified by alphabetic letters (from A to O) in this report. Fifteen participants provided results based on standard vitrinite reflectance, and one participant provided results based on VIRF analysis.

Table 2 shows the distribution of vitrinite reflectance for the different samples as reported by the participants. The Spanish carbonaceous shale (sample OMC1) with TOC of about 20 wt% and medium rank yielded more and high quality vitrinites. The Nigerian carbonaceous shale (sample OMC2) with TOC of about 5 wt% and low rank yielded fewer but high quality vitrinites as well. The selected samples allowed the accurate study of the effect of the isolation procedure on the organic matter optical parameters.

The average of vitrinite reflectance of whole rock and kerogen concentrate from the sample OMC1 was the same (1.15%). For sample OMC2, the result was 0.37% for whole-rock and was 0.40% for kerogen concentrate. Standard Deviation (SD) values in the two samples were very low.

Table 2 - Distribution of vitrinite reflectance as reported by the participants

Partic-ipant	Sample OMClA			Sample OMClB			Sample OMC2A			Sample OMC2B		
	Whole-Rock			Kerogen			Whole-Rock			Kerogen		
	R_r (%)	SD	n	R_r (%)	SD	n	R_r (%)	SD	n	R_r (%)	SD	n
A	1.15	0.05	50	1.14	0.04	50	0.4	0.08	50	0.41	0.02	50
B	1.06	0.09	50	1.07	0.08	50	0.39	0.05	37	0.42	0.03	50
C	1.03	0.03	72	1.03	0.02	63	0.41	0.01	50	0.41	0.01	51
D	1.17	0.04	61	1.16	0.05	52	0.35	0.03	51	0.37	0.03	50
E	1.52	0.08	50	1.41	0.08	50	0.38	0.04	22	0.38	0.04	50
F	1.01	0.19	50	1.09	0.06	50	0.34	0.09	50	0.4	0.09	50
G	1.25	0.7	50	1.22	0.05	50	0.37	0.06	50	0.38	0.06	50
H	1.22	0.05	51	1.17	0.06	43	0.35	0.05	46	0.37	0.04	40
I	1.14	0.07	50	1.24	0.09	50	0.38	0.06	8	0.43	0.05	20
J	1.14	0.08	50	1.12	0.06	50	0.3	0.04	50	0.37	0.03	50
K	1.02	0.06	50	1.02	0.05	50	0.4	0.02	50	0.41	0.02	50
L	1.04	0.03	50	1.04	0.03	50	0.42	0.03	49	0.44	0.04	49
M	1.01	0.09	50	1.09	0.05	50	0.34	0.08	50	0.39	0.05	50
N	1.12	0.1	100	1.1	0.06	100	0.34	0.04	100	0.37	0.04	100
O	1.25	0.06	50	1.24	0.06	50	0.38	0.05	50	0.39	0.05	25
P	1.27	0.05	22	1.22	0.04	22	0.39	0.05	16	0.44	0.05	16
Mean	1.15			1.15			0.37			0.4		
SD	0.13			0.1			0.03			0.02		

The graph of kerogen vs whole rock (Figure 1) allowed comparing the results of the whole rock sample and the kerogen. If the x and y axes have the same dimensions and the results were equivalent, all the points should be on the median or closer. This happens in the sample OMC1 for the reflectance. However, in sample OMC2 the reflectance tended to be higher in the kerogen concentrate, where it can be observed clearly that most of the points are above the median, showing that the results for sample OMC2B (kerogen concentrate) were higher than in the sample OMC2A (whole rock).

Figure 2 shows the Standard Deviation graphs, which helped to see if there was more dispersion of data in the kerogen analyses than in those of whole rock. If the SD were always higher in one than in the other this would indicate a bigger difficulty to identify the population. In the case of the sample OMC1 there was a single result that was outlying (a statistical observation that was markedly different in value from the others of the sample). In the case of the sample OMC2 the SD values tend to be higher in the whole rock, which indicates a larger scatter of the readings.

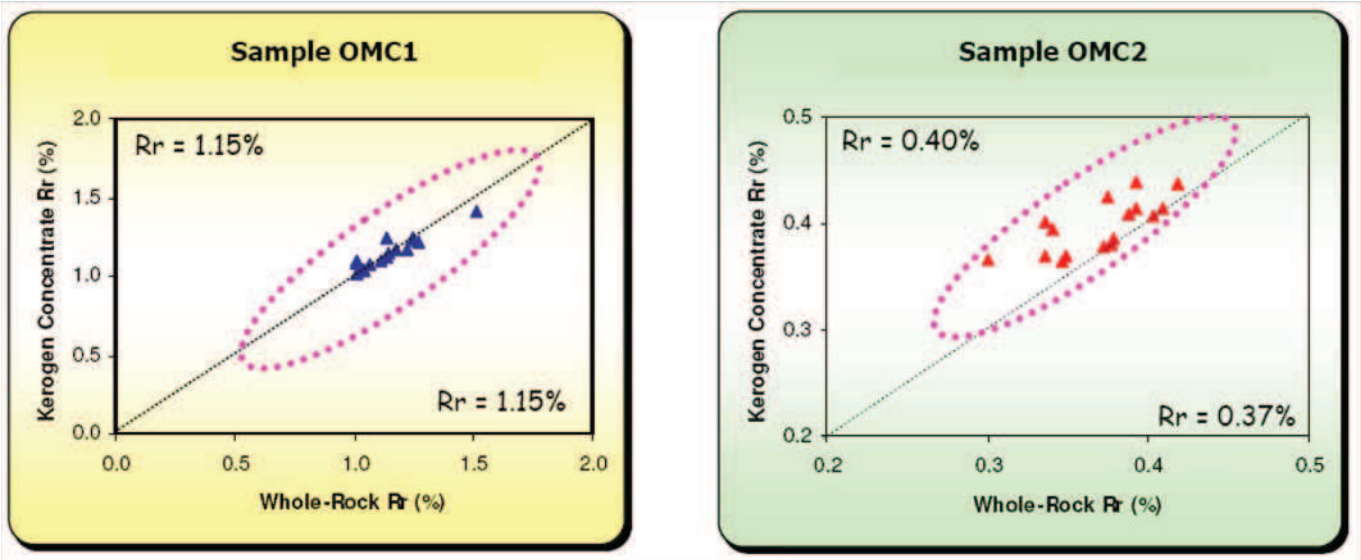

Figure 1: Comparison of mean reflectance values between WR and KC

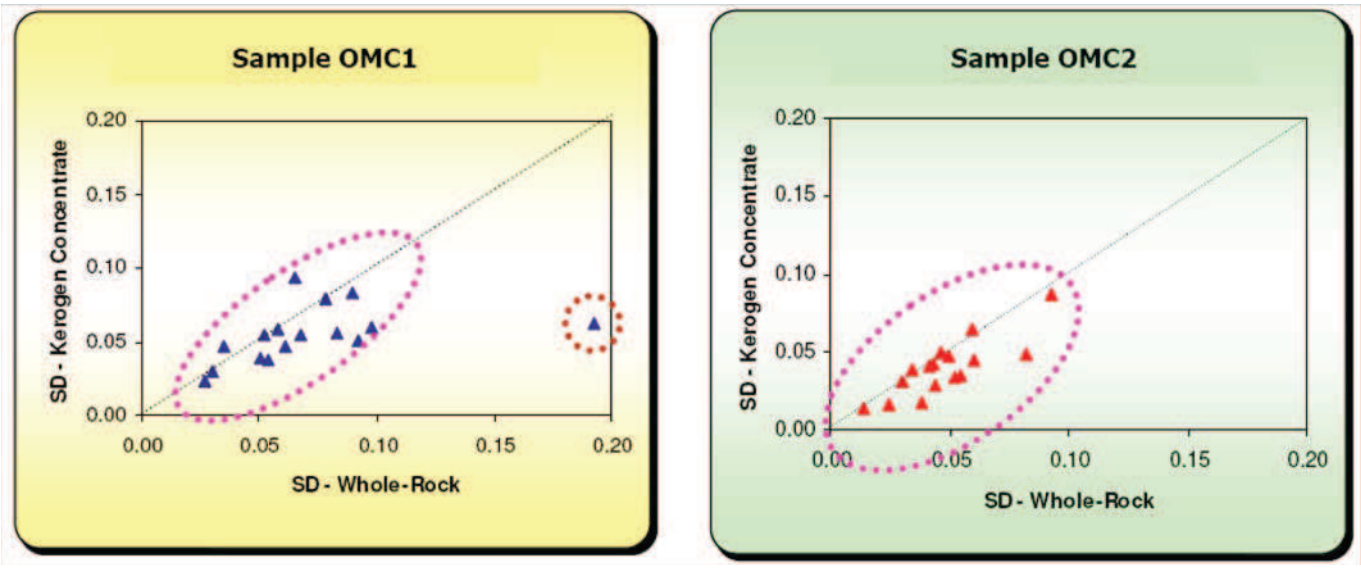

Figure 2 – Comparison of standard deviation (SD) between WR and KC - Scatter of data in the analysed samples

Figures 3 and 4 are representing the Cumulative Frequency graph, which can be grouped into various families according to the shape of the curves: curves showing a single population of vitrinite; curves showing a bimodal distribution with different proportion of the low reflecting and high reflecting population and curves showing large scatter without modal values.

Figure 3 shows the reflectance class distributions of the participants for sample OMC1A and OMC1B (Spain). The shape of the curves indicates that most of the participants identified a single vitrinite population with a rather narrow distribution of reflectance classes, excepting the Participant E who read higher values than the average in both samples (OMC1A and OMC1B), however with a rather narrow distribution as well, indicating probably some calibration problems with the microscope system. On the other hand, participants B, F and M included some readings whose values are lower than the average in the sample OMC1A (wholerock).

Figure 4 shows the reflectance class distributions of the participants for sample OMC2A and OMC2B (Nigeria). The shape of the curves indicates more vitrinite classes in the histograms, especially in those of participant F who spread the readings from R_r = 0.18% to R_r = 0.66% to sample OMC2A (whole-rock) and from R_r = 0.32% to R_r = 0.95% to sample OMC2B (kerogen concentrate), indicating the probable inclusion of readings taken on inertinites or re-worked vitrinites and liptinites in the data set.

The scatter of results is better observed in Figures 5 and 6 where it were plotted the mean reflectance reported by of each participant with the error bars corresponding to the standard deviation (SD). The scatter of the results was more reasonable and most of the values are within, according to ICCP Accreditation Criteria, 1.15 ± 1.5xSD[1] for the low and high reflecting populations.

The average of reflectance considering all the data was 1.15% for samples OMC1A (Whole-Rock) and OMC1B (Kerogen Concentrate) and the scatter of results was very low for these samples (Figure 5).

Participant E provided higher values than the mean group in both samples (OMC1A and OMC1B), although with low values of SD, indicating probably some calibration problems with the microscope system.

On the other hand, Participant F included readings whose values are lower than the mean group in the sample OMC1A (whole-rock) besides a large scatter of readings (high SD values), indicating some problems with the identification of vitrinites.

[1]1.5 x SD = represents 80% of a Gaussian distribution that gives a reasonable percentage of error

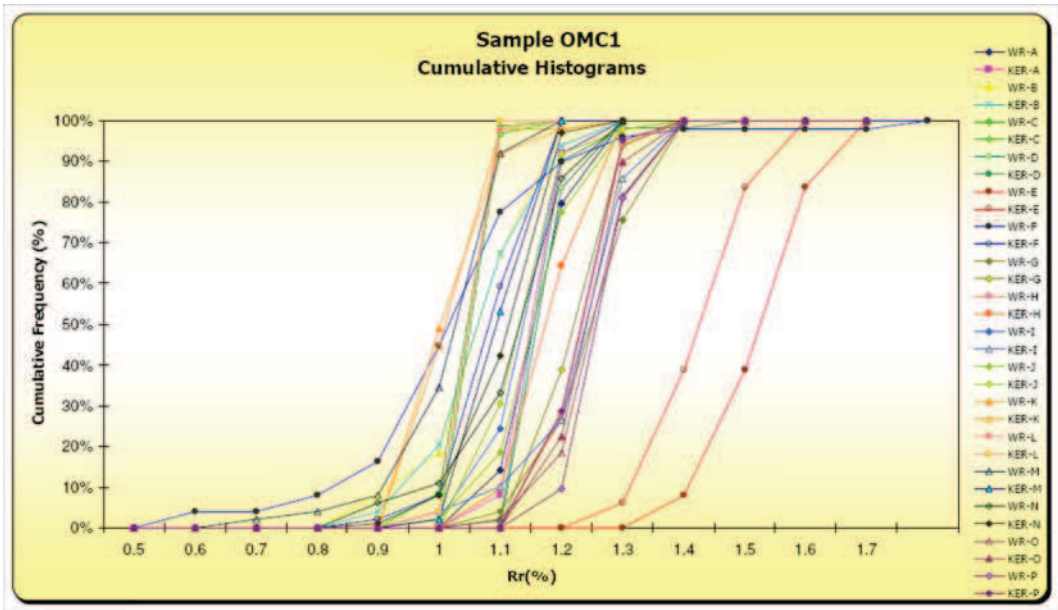

Figure 3 Graph of the Cumulative Frequency Plot (sample OMC1A and OMC1B)

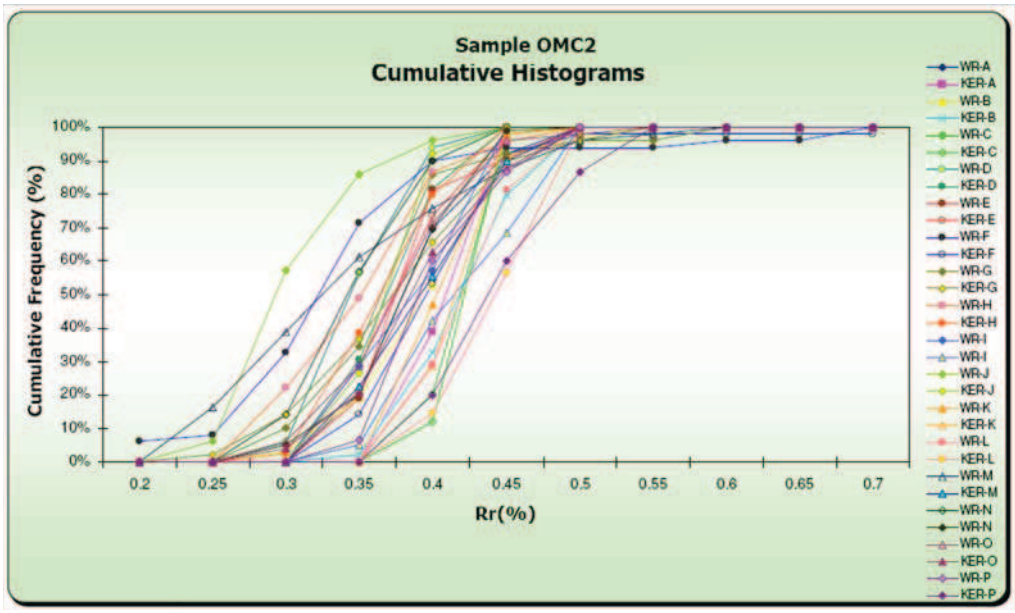

Figure 4 Graph of the Cumulative Frequency Plot (sample OMC2A and OMC2B)

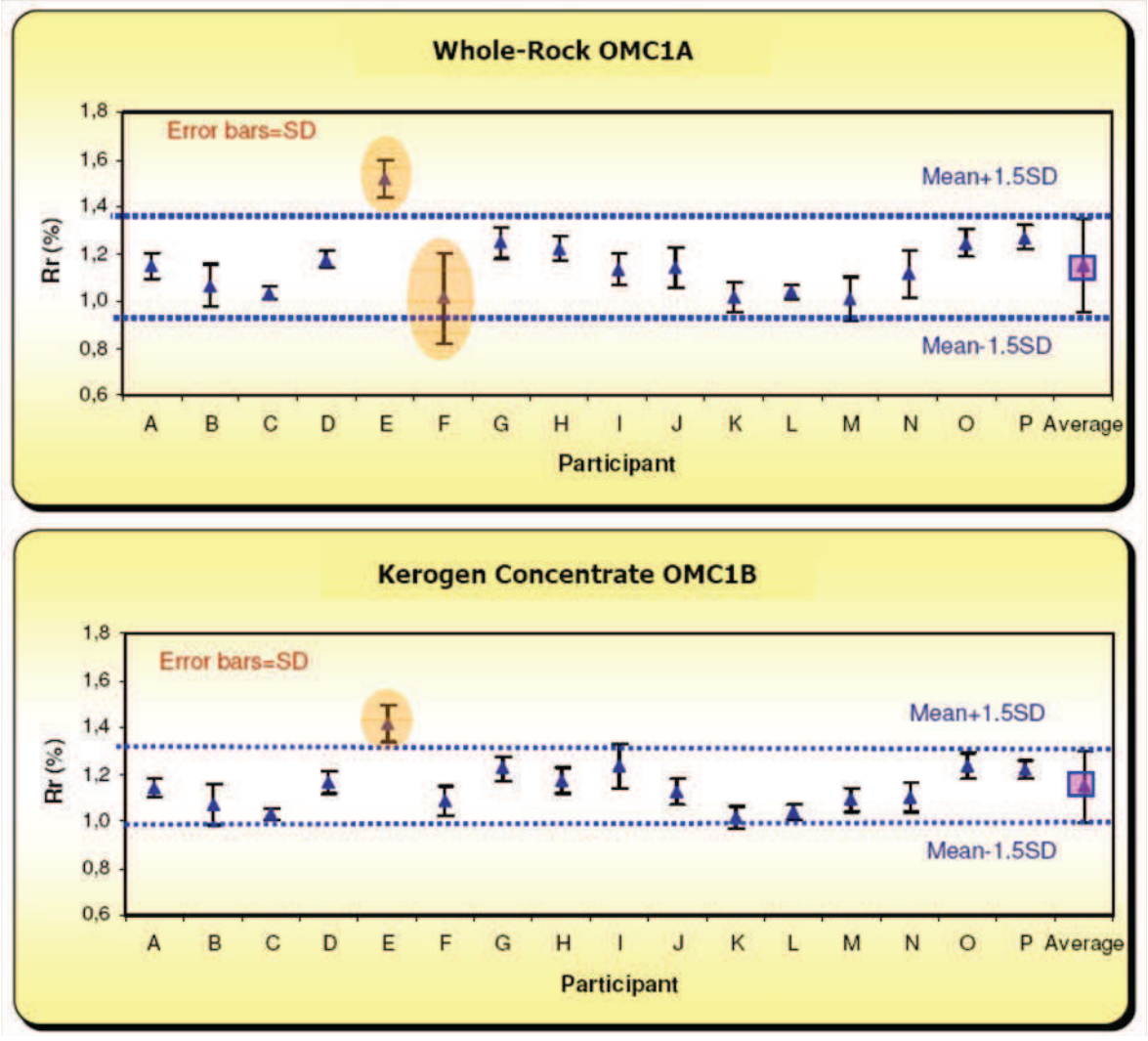

Figure 5 – Average Rr (%) values for the low and high reflecting populations in samples OMC1A (Whole-Rock) and OMC1B (Kerogen Concentrate)

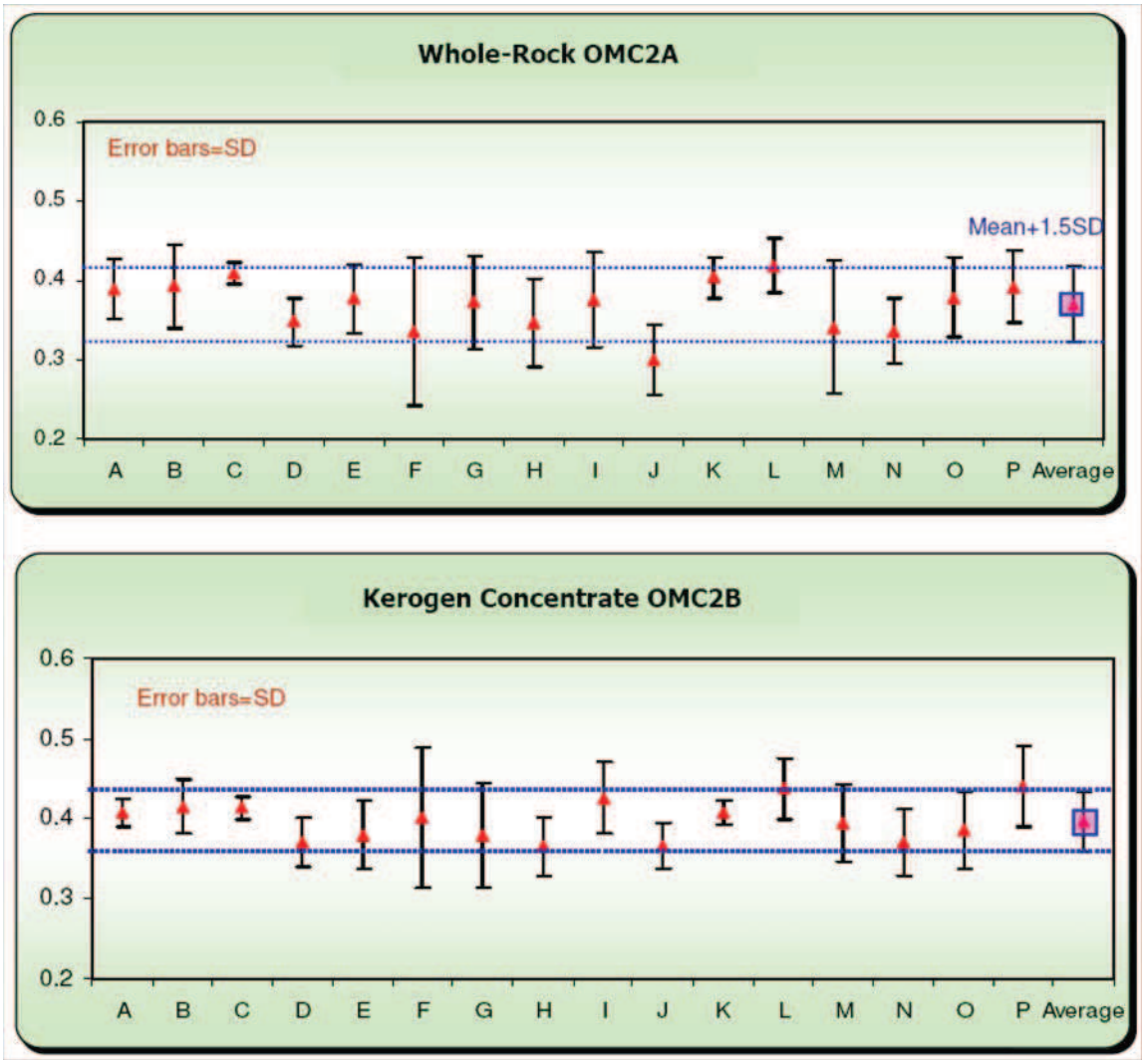

Figure 6 – Average Rr (%) values for the low and high reflecting populations in samples OMC2A (Whole-Rock) and OMC2B (Kerogen Concentrate)

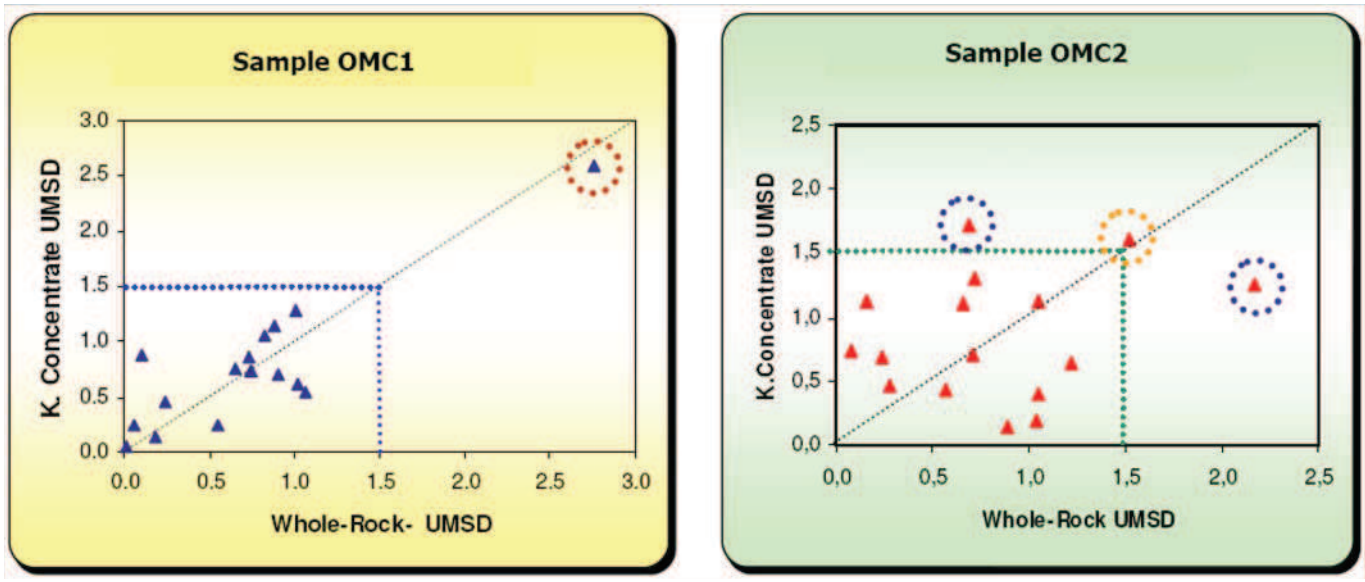

Figure 7 - UMSD (Unsigned Multiple of the Standard Deviation) (calculated against the mean group and standard deviation data)

The mean group considering all the data was 0.37% for the sample OMC2A (Whole-Rock) and 0.40% for the sample OMC2B (Kerogen Concentrate) (Figure 6).

Some participants read lower values than the mean group in samples OMC2, mainly in sample OMC2A (Whole-Rock), indicating probably inclusion of readings taken on liptinite in the data set. For this reason, the average of vitrinite reflectance for this sample decreased.

Then, it can be observed a difference in the average of reflectance between sample OMC2A (Whole-Rock) and OMC2B (Kerogen Concentrate). Some participants included readings which values are lower than the mean group mainly in the sample OMC2A (whole-rock). This is more evident mainly in the participants F, J, and M. The scatter of the readings is more pronounced in the Whole-Rock sample than in the Kerogen Concentrate sample for most participants in the low ranking samples. This is more evident mainly in the participants A, B, H, J and M.

These results could indicate that it is easier to identify the vitrinites in the Kerogen Concentrate sample than Whole-Rock sample for the low rank stage or that the vitrinite reflectance measurements are more reliable without the mineral matrix influence or the mineral matrix may affect the vitrinite surface quality due to difficulties in polishing procedure.

In Figure 7 it can be observed that in sample OMC1 only one analyst presented a result out of the mean group in both samples (OMC1A and OMC1B). In sample OMC2, there was one analyst with results closer to 1.5xSD in both samples (OMC2A and OMC2B). There were two analysts who presented good data in only one sample (one of them presented good results to the WR but high values to the KC and the other one presented good results to the KC but high values to the WR), but in general the results were dispersed reasonably around the median.

Using the criteria and parameters applied for Coal Reflectance Analysis in the existing ICCP accreditation program, www.iccop.org, (Table 3), excellent results were obtained (Table 4). Only one participant had an AUMSD value slightly over 1.5, due probably to some calibration problems with the microscope system.

Table 3 - Coal Reflectance Analysis Criteria (ICCP)

Parameters	Precision and bias for the analysts	
ASMSD	< ± 0.5	Low - Your results are always consistent
	± 0.5 < ± 1.0	Medium - Some improvement is required
	± 1.0 < ± 1.5	High - Examine the method being used
	> ± 1.5	Very High - You have serious problems with your analytical technique
AUMSD	< 1.5	Your analytical technique is acceptable
	> 1.5	You have serious problems with your analytical technique

Table 4 - Accuracy of results calculated against the mean group and standard deviation data, for each sample analyzed: SMSD (Signed Multiple of the Standard Deviation), AUMSD and ASMSD

Partic-ipant	SMSD	AUMSD	ASMSD	BIAS
A	0.93	0.26	0.23	Low
B	-0.02	0.70	-0.01	Low
C	-0.2	0.97	-0.05	Low
D	-1.44	0.52	-0.36	Low
E	4.88	1.57	1.22	High
F	-2.49	0.72	-0.62	Medium
G	0.81	0.57	0.20	Low
H	-1.23	0.71	-0.31	Low
I	2.05	0.56	0.51	Medium
J	-3.71	0.93	-0.93	Medium
K	-0.88	0.93	-0.22	Low
L	1.20	1.24	0.30	Low
M	-2.65	0.66	-0.66	Medium
N	-2.87	0.72	-0.72	Medium
O	1.38	0.58	0.35	Low
P	3.99	1.00	1.00	Medium

5. Discussion and Conclusions

Based on the proposed objectives and results obtained, it is concluded that the identification of primary vitrinite is more difficult for Whole-Rock samples than Kerogen Concentrate samples, mainly for those samples presenting lower rank.

The statistical evaluation system applied in this exercise is the same one used in the accreditation program for vitrinite reflectance in coal. However, these statistical systems are being used only as a tool to evaluate the effect of the isolation procedure on the vitrinite reflectance.

The average of reflectance considering all the data was 1.15% for samples OMC1A (Whole-Rock) and OMC1B (Kerogen Concentrate) and the mean group considering all the data was 0.37% for sample OMC2A (Whole-Rock) and 0.40% for sample OMC2B (Kerogen Concentrate). These results indicate that most of the participants identified a single vitrinite population with a rather narrow distribution of reflectance classes.

According to Mukhopadhyay (1994), in a dispersed organic matter the measurement of vitrinite reflectance in a whole rock is often extremely time consuming and show lower (0.05-0.25% R_o) values compared to the measured vitrinites in an isolated kerogen polished plug. Then, the author indicated that in an organic – or vitrinite-lean rock, the measurement of vitrinite reflectance using isolated kerogen is recommended.

Barker (1996) verified a little difference in the results of mean-random vitrinite reflectance values calculated from measurements on polished whole-rock and on concentrates of dispersed organic matter (DOM) mounts of the same samples.

Some participants included readings of vitrinite reflectance which values are lower or higher than the average, mainly in the whole-rock samples, indicating the probable inclusion of readings taken on inertinites or re-worked vitrinites and liptinites in the data set or owing to some calibration problems with the microscope system.

Senftle & Landis (1991) affirmed that the application of vitrinite reflectance in fine-grained and oil-prone rocks shown a limitation when the readings taken on whole-rock petrography, because the difficulty of locating enough acceptable vitrinite for analysis. The organic matter in sedimentary rocks frequently amounts to no more than 1-5%. Since vitrinite may be a minor element, determination may not be possible or results may be limited. On the other hand, the advantage of a whole-rock vitrinite reflectance analysis is the distinction among the vitrinite population (i.e. primary vs recycled or oxidized vitrinites) and between bitumen and inertinite macerals.

The scatter of the readings was higher in the Whole-Rock sample than in the Kerogen Concentrate sample for most participants in the low ranking samples. These results could indicate that it was easier to identify the vitrinites in the Kerogen Concentrate sample than in the Whole-Rock sample for the low rank stage or that the vitrinite reflectance measurements were more reliable without the mineral matrix influence or the mineral matrix may affect the polishing quality.

In short, following the criteria and parameters and in the statistical evaluation system (http://www.iccop.org), in general excellent results were obtained and the selected samples allowed an accurate study on the effect of the isolation procedure on the organic matter optical parameters.

6. References

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7. Acknowledgments

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