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Influence of particle and surface quality on the vitrinite reflectance of dispersed organic matter: Comparative exercise using data from the qualifying system for reflectance analysis working group of ICCP

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Abstract

The development of a qualifying system for reflectance analysis has been the scope of a working group within the International Committee for Coal and Organic Petrology (ICCP) since 1999, when J. Koch presented a system to qualify vitrinite particles according to their size, proximity to bright components and homogeneity of the surface. After some years of work aimed at improving the classification system using photomicrographs, it was decided to run a round robin exercise on microscopy samples. The classification system tested consists of three qualifiers ranging from excellent to low quality vitrinites with an additional option for unsuitable vitrinites. This paper reports on the results obtained by 22 analysts who were asked to measure random reflectance readings on vitrinite particles assigning to each reading a qualifier. Four samples containing different organic matter types and a variety of vitrinite occurrences have been analysed. Results indicated that the reflectance of particles classified as excellent, good or poor compared to the total average reflectance did not show trends to be systematically lower or higher for the four samples analysed. The differences in reflectance between the qualifiers for any given sample were lower than the scatter of vitrinite reflectance among participants. Overall, satisfactory results were obtained in determining the reflectance of vitrinite in the four samples analysed. This was so for samples having abundant and easy to identify vitrinites (higher plant-derived organic matter) as well as for samples with scarce and difficult to identify particles (samples with dominant marine-derived organic matter). The highest discrepancies were found for the organic-rich oil shales where the selection of the vitrinite population to measure proved to be particularly difficult. Special instructions should be provided for the analysis of this sort of samples. The certainty of identification of the vitrinite associated with the vitrinite reflectance values reported has been assessed through a reliability index which takes into account the number of readings and the coefficient of variation. The same statistical approach as that followed in the ICCP vitrinite reflectance accreditation program for single seam coals has been used for data evaluation. The results indicated low to medium dispersion for 17 out of 22 participants This, combined with data from other sets of comparative analyses over a long period, is considered an encouraging result for the establishment of an accreditation program on vitrinite reflectance measurements in dispersed organic matter.

Keywords: vitrinite reflectance, dispersed organic matter, vitrinite quality, ICCP, interlaboratory exercise, reliability index

1. Introduction

Measurement of vitrinite reflectance in sedimentary rocks other than coal is commonly a difficult task due to a number of factors, amongst them: i) Vitrinite is very scarce in certain sediment types (i.e. chalk) resulting in low statistical significance of the data; ii) Particles can be too small for a reliable measurement; iii) Surrounding minerals may affect the accuracy of the reflectance determination (Bostick and Alpern, 1977); iv) Polishing may be poor and this can be linked to sample lithology (Taylor et al., 1998) and v) Particles with suppressed reflectance or reworked particles may co-exist with the first generation vitrinites (Durand et al., 1986). With this scenario, a numeric label accompanying the reflectance measurement and informing about the reliability of the mean reflectance value could be extremely useful not only for computer-based basin analysis (figures are easier to handle for computers) but also for any person having to deal with data of variable quality.

The **qualifying system for reflectance analysis working group** started its activity at the Bucharest ICCP meeting in 1999, and is aimed at discussing and testing a qualifying system for vitrinite reflectance readings, initially proposed by Joachim Koch (Koch 2000a and 2000b). This system consisted of five qualifiers ranging from q1 for the large and homogeneous vitrinite particles to q5 for small, poorly polished, or particles affected by the proximity of bright minerals. The system also contained some additional qualifiers (q6-q9) in case the vitrinite reflectance was not directly measured but estimated from bituminite reflectance or palynomorph optical properties. In order to check the applicability of the system and whether analysts could agree to classify a particle within a given qualifier a round robin exercise based on photomicrographs was performed in 2002. Participants were asked to classify 193 vitrinite particles according to the definitions. The exercise was performed by 17 participants and the results can be summarized as follows (Borrego et al., 2003):

-The number of categories in the system (five) meant that the numbers of fields reported even for the modal categories were lower than desirable for statistical analysis. Nevertheless most participants classified the particles as the modal qualifyier or as the qualifyier adjacent to the mode. Thus, although the modes may have a lower level of certainty than might be considered desirable, it is clear the level of agreement is very high once adjacent categories are taken into account. No participant was the only one to use a particular category.

-The discussion of the results of this exercise at the 2002 ICCP Meeting in Maputo-Pretoria focussed on i) the convenience of using a simplified system with only three qualifiers, ii) the significance of polishing, iii) vitrinite identification, iv) what to do with reworked, oxidised particles or particles with suppressed reflectance, v) name of the qualifiers, and vi) differences in the resolution of the screen (pixel density) used by the participants.

It was decided to run an additional exercise based on photomicrographs using improved definitions after the experience gained during the first exercise. In the modified classification system any genetic implications, such as re-worked, suppressed or oxidised were removed and sharper boundaries were established between medium (q3) and low (q4) quality surfaces. This exercise was performed in 2003 by 18 analysts. Participants were asked to classify 298 images, including 115 from the previous exercise which had been classified with a low level of agreement. The images comprised vitrinites of different maturity and rock type. The results showed a significant improvement regarding both level of agreement in the assignment of a given particle to a qualifier and certainty in the classification of particles (Borrego et al., 2004). The results were considered to be good enough that the system was ready to be tested on polished pellets.

It must be mentioned that number of categories and their definitions have changed over the years after the experience gained with the interlaboratory exercises. All the data contained in this paper are categorized according to the definitions below and are distinguished by the upper case Q. Lower case q in the text refers to previous definitions of the qualifyiers (Borrego et al., 2003 and 2004). The paper deals with the results from an exercise performed by 22 participants who were asked to measure random reflectances on vitrinite particles assigning to each reading a qualifier according to the following definitions (Figure 1).

Q1= Excellent quality: Layers, lenses, large vitrinite particles exhibiting clean surfaces (free of pores, scratches or bright minerals) under the measuring field and inside the field diaphragm.

Q2= Good quality: Layers, lenses, large vitrinite particles, distinctly thicker than the measuring field, but smaller than the field diaphragm. Clean surfaces under the measuring field but defects (pores, scratches) within the field diaphragm. Free of large pyrite particles within the field diaphragm.

Q3= Low quality: Clean particles of vitrinite about the size of the measuring field. Large particles with impurities within the measuring field (spots, granulated surface, microscratches). Large and/or bright pyrite within the field diaphragm.

Q4= Unsuitable: Suspected weathered, altered or oxidised particles. Particles of uncertain origin.

It is important to note that the exercise relates to assessments of the quality of particles of vitrinite. For some samples, diferentiation of vitrinite from inertinite or from bituminite may not be readily apparent. This study does not address this class of problems.

The main objectives of the exercise were to answer the following questions: i) Are participants identifying similar amounts of excellent, good or low quality particles in a given sample? ii) Are the mean reflectances of vitrinites assigned to a given qualifier higher or lower than the total average reflectances?. iii) Are the vitrinite reflectance results of participants reasonably close to each other?. iv) How can the system be used to provide an estimate of the reliability of vitrinite reflectance in sedimentary rocks?.

The results of this working group are expected to form a basis for a future accreditation program on vitrinite reflectance measurements of dispersed organic matter (DOM) in sedimentary rocks.

2. Provenance of samples. Preparation and analysis procedures

In order to collect the necessary data to answer the questions outlined in the introduction four samples were analysed. It was intended to include samples from different depositional environments containing a range of organic matter types in order to check the applicability of the qualifying system for a wide range of sediment types. The samples selected included three algal-rich samples of lacustrine, marine and marine-transitional depositional environments and one sample mainly containing terrestrial organic matter. Some details of the samples are presented in Table 1 and Figure 2 illustrates the aspect of the organic matter in the samples.

2.1. Samples

The carbonaceous shale (CS) corresponds to the mudstones interlayered with the economic coal seams in the Caudal-Nalon Unit of the Central Asturian Coal Basin (NW Spain). The sample consists of higher plant-derived organic matter with abundant vitrinite particles and some coaly grains containing inertinite and/or liptinite (mainly sporinite) macerals. Petrographic studies of the associated coals suggest a swamp environment with a vitrinite-rich facies, variable ash, and low sulphur contents located on a delta plain with a relatively high water table (Piedad-Sánchez et al, 2004).

The Posidonia shale (PS) was collected at Dotternhausen (SW Germany). Its organic matter is dominated by lamalginite typically found as short yellow-fluorescing lamellae under blue light excitation. Tasmanites and scarce vitrinite particles complete the organic assemblage. It is a well-known example of organic matter which accumulated under oxygen-depleted conditions in a marine depositional environment (Kauffman, 1981; Prauss et al., 1991; Rhöl et al., 2001).

The Puertollano oil shale (PT) was collected from the seam B at the mine in Puertollano (South-central Spain). It is a very rich oil shale, dominated by orange-brown fluorescing lamalginite (typically long anastomosing lamellae) with *Botryococcus* colonies dispersed in the matrix. Sporinite and common vitrinite and inertinite particles are derived from higher plants and complete the organic matter assemblage. It is considered to have been deposited in a lacustrine environment although restricted communication with the sea may have occurred (Borrego et al., 1996).

The Irati shale (IS) was collected from the lower oil shale seam of the Petrosix Quarry (São Mateus do Sul, Paraná State, Brazil). The major organic matter component is weakly fluorescing lamalginite within which mainly sporinite, vitrinite and inertinite are dispersed. The depositional environment has been described as marine-transitional based on biomarkers (Mello et al., 1993, Triguis et al., 1996) although other studies suggested a lacustrine setting (Afonso et al. 1994, Corrêa da Silva and Cornford, 1985).

2.2. Sample preparation

Samples PS, PT and IS were ground to < 3 mm size. This size, larger than the standard for coal analysis, was selected to avoid the production of excessive amounts of fines and to reduce the liberation of vitrinite particles by finer grinding. In addition, the association of vitrinite with the other organic and inorganic components of the rock facilitates the identification of particles of organic matter. The carbonaceous shale (CS) was ground to <1 mm size because in this sample vitrinite occurrences are expected to be more common and likely to be larger in size. Once ground, the sample was floated in a mixture of perchloroethylene and bromoform with a density of 1.7 g cm^{-3} in order to remove the large pure vitrinite particles. The sink residue was used to prepare the pellets ensuring that all vitrinite occurrences would be associated with minerals.

A single mount in resin was prepared for each sample with a section close to 2x2 cm. Vertical slices from this block (2-3 mm in thickness) were cut (Figure 3a) and reembedded in resin (Figure 3b) to ensure that the samples sent to the various laboratories were as homogeneous as possible. Participants were asked to follow a regular grid perpendicular to the grain segregation when analysing the sample (Figure 3c).

2.3. Sample polishing

The particulate blocks had their surfaces ground down using progressively finer grades of wet carborundum papers; the final grind used was 1200 grit wet carborundum paper. Participants had to accomplish final grinding and polishing of the blocks, using the techniques commonly used in their laboratories. After polishing, it was recommended to house the blocks in a desiccator or allowed them to equilibrate to laboratory temperature and humidity for a minimum of 8 hours before analysis. A single set of samples was sent to each laboratory. The various participants from a given laboratory were encouraged to perform the analysis on the sample within the day since oil may dissolve lipoid substances abundant in the sample so affecting the result of the measurement. Otherwise samples had to be re-polished before the second set of analyses.

2.4. Analysis Procedure

It was recommended that the readings should be spaced such that most of the particulate block surface was covered. Vitrinite abundance was known to be low in some of the samples, so analysts were requested to analyse as many vitrinite particles as possible when following a regular grid. Measurement of multiple vitrinite phytoclasts within a single grain was permitted because vitrinite clasts within a grain could have a different depositional history. No more than one reading should be taken on each vitrinite phytoclast. The microscope had to be set up to take random reflectance readings (without polarizer and analyser). The field diaphragm was to be adjusted to be three times larger than the measuring diaphragm since this helped to assign the reading to a given qualifier.

Participants were asked to record 50 vitrinite readings per sample (if enough vitrinite particles were in the sample) assigning to each reading the corresponding qualifier according to the definitions described in the introduction.

3. Results

3.1. Distribution of qualifiers in the samples

Figure 4 shows the distribution of qualifiers for the different samples as reported by the participants. A range of factors can be considered as responsible for the scatter in the relative amounts of the various qualifiers

1. Observation conditions. Magnification and size of the measuring spot were different for the various participants since they depend on the microscope setup and they cannot always be freely changed in many microscopes. As seen in the qualifier definitions the size of the vitrinite particle plays an important role in the assignment of the qualifier. The possibility that the relative amounts of the qualifiers were related to the observation conditions was also checked. A magnification factor was calculated as the ratio between actual magnification

and size of the measuring spot for each participant. As the magnification factor increases participants were able to take readings in smaller particles. The graph shown in Figure 5 shows no relationship between the magnification factor and the relative amount of low quality particles (Q3) reported for the samples.

2. Polishing quality. The homogeneity of the surface is very important in the assignment of the particle to a given qualifier. The assessment of the quality of polishing from the data is difficult because the samples may have different difficulties for polishing. A check was made to determine if any given participant was systematically reporting high amounts of low quality particles in all the samples that could be attributed to a poor quality of polishing. Again no relationship was found that could identify participants examining poorly polished samples.

In summary, no single reason was found to explain the scatter in the relative amount of excellent (Q1), good (Q2) and low (Q3) quality particles in the samples indicating that many factors may be playing a role when taking a decision, including the subjective concept behind adjectives such as clean, homogeneous, free of impurities, etc. Despite the scatter some general information can be gained about the quality of the vitrinites in the different samples. Sample CS, consisting mainly of higher plant-derived organic matter, was the sample yielding more and highest quality vitrinites. For this sample, 7 participants did not measure any low quality particles and 10 out of 22 participants reported less than one fourth of low quality (Q3) particles (Figure 6). For the marine Posidonia shale (PS), 15 participants reported more than half of the measured vitrinites as low quality and one did not find any suitable vitrinite. A similar figure was obtained for the Irati shale (IS), with 14 participants reporting more than half of the readings as taken in low quality vitrinites although in this case participants typically reported a higher number of readings. The lacustrine sample PT yielded abundant vitrinite particles and half of the participants (11) reported more than 50% of low quality particles. This indicates that the selected samples cover a wide range of situations from abundant and high quality particles to scarce and low quality that allows a test of the accuracy and utility of this method of determining the quality of vitrinite phytoclasts used for measuring vitrinite reflectance.

3.2 Differences in reflectance among the qualifiers

It could be expected that particles with imperfections at the surface would yield lower mean reflectance values than large particles with clean surfaces. Also small particles may have the reflectance affected by the darkness or lightness of the matrix. This possibility was checked by plotting the average reflectance for all the readings against the averaged reflectance of values classified with a given qualifier (Figure 7). Overall it was found that reflectances of the excellent, good and low quality particles were similar within each sample, as shown by the slopes of the regression lines and the reasonable values for most of the regression coefficients (R^2 in Figure 7). The low regression coefficient for Q1 vitrinites in sample CS is mainly due to a single value corresponding to two readings. If this value is removed the regression coefficient rises to 0.71, which is a reasonable value. The largest scatter was found for sample PS, which yielded very low regression coefficients for Q2 and Q1 vitrinites, both corresponding to rather few readings (Figure 4). No trends applicable to all the samples analysed were found for vitrinites classified with a given qualifier to yield systematically higher or lower reflectance than the total average. This indicates that the scatter of reflectance readings, typically higher for vitrinites in rocks than for vitrinites in coal, is higher than the differences in reflectance between the qualifiers. In view of these results, the assessment of the agreement for vitrinite reflectance determination among participants will be based on the total R_o values reported by participants.

3.3 Vitrinite reflectance of the samples. Agreement between participants

Two participants (numbers 12 and 13) provided R_{max} data instead of R_r. However, given the relatively low maturity of the samples R_{max} and R_r are not expected to differ significantly. The data were considered as reported without making any further transformation.

3.3.1. Carbonaceous shale

Figure 8 shows the reflectance histograms extracted from the data of the various participants for sample CS. The profiles correspond to readings with reasonably low standard deviations (0.05 to 0.08), although higher than those typically found for a coal of similar rank. Most of the histograms are placed in the same range of vitrinite classes (VR_o=0.55-0.85 %). This indicates that the participants took readings on the same type of particle. Four profiles (those of participants 9, 10, 14, 20) were shifted to lower reflectances. The group mean was $\overline{R_o}$ =0.70% and the group standard deviation 0.0456. The number of significant figures used for both the vitrinite reflectances and the standard deviations for the vitrinite reflectances are greater than recommended by ISO (ISO 7404, part5, 1994). Where subtractions and divisions using the resulting differences are involved, the potential for round-off errors is considerably increased.

The number of significant figures used are required to keep round-off errors within acceptable limits. It has to be considered that the precision and bias of the analysts is to be evaluated in this work using the accreditation procedure currently used to evaluate the data in the accreditation program for vitrinite random reflectance analysis of single seam coals of the ICCP (www.iccop.org). With the test used, 1.5 is a fail and 1.45 (3.45% relative difference) a pass, and the difference in the evaluation of an analyst precission rounding-off the standard deviation to four or two decimal places could be as high as 9.65% relative in the case of sample CS. The ISO standard was not written with this kind of use in mind and the revisions currently being made should draw attention to the need to use reporting criteria that are suited to the required use. The scatter of results is better observed in Figure 9 where the mean reflectance reported by each participant is plotted with the bars corresponding to the percentiles 25 and 75. These bars are an indication of the distribution width eliminating the effect of the most extreme values. Most of the distributions were relatively symmetrical and only those of participants number 3 and 20 were significantly wider than the others. The bars for the group mean represent 1.5 standard deviations, which approximately correspond to 80% of a normal distribution. The values within ±1.5σ are considered to have an acceptable bias according to the criterion applied by the ICCP in its accreditation program. Only two data (participants 9 and 20) fell out of these limits. The values were too low, which can be attributed to difficulties in the microscope calibration or poor polishing quality for participant 9 and to difficulties in the selection of vitrinite particles in the case of participant 20 since he reported a rather wide distribution. Data from participants measuring maximum reflectances instead of random reflectances (12 and 13), although among the highest values reported fell within the accepted limits.

3.3.2. Posidonia shale

The histograms of sample PS (Figure 10) were more complex than those of sample CS. The shape of the curves indicated more vitrinite classes in the histograms although most of them showed well-defined modal values. Profiles 10 and 11 had a small peak at higher reflectances than the mode, which probably corresponds to resedimented or altered vitrinites. Profiles 20 and 21 contain a low reflecting population and profiles 19 and 22 lack clear modal values. Participant 22 measured a population described as non-fluorescing, lenticular in shape, free of inclusions and with a surface with very fine heterogeneity. This population was classified as Q4 and therefore not included in the mean of but yielded a reflectance value of 0.45 %. The participant indicated that this population has been identified by authors working in the sample area either as heterogeneous vitrinite or bitumen. The data reported by participants apparently indicate that most of them considered these particles as vitrinite. The bars of Figure 11 show a variety of distribution widths from very low (participants 2, 6, 7, 13, 15, 17), which correspond to unimodal distributions, to rather high (participants 11, 19, 20 and 22). It must be remembered that the histograms are based on relatively few values since vitrinite was scarce and further treatment of the data to reduce the scatter will also reduce the significance of the results. The standard deviations for the individual distributions were higher than in sample CS but still under 0.08 for 70% of participants. The group mean for the sample was $\overline{R_o}$ =0.37 % and the standard deviation was higher than in sample CS (σ=0.0658). The higher standard deviation of the group and the differences in the values and distribution shapes between participants indicate a higher complexity of PS compared to CS. Only participant 9 reporting a histogram with a mode at rather low reflectance and participant 22 with a rather high R_o fell out of the limit of ±1.5σ.

3.3.3. Puertollano oil shale

The histograms of PT are shown in Figure 12. The curves show a large scatter of vitrinite classes, which range from 0.1 to 1.0 %. The presence of a low reflecting population is clear in 15 out of 22 histograms whereas a large scatter of vitrinite classes is observed for high reflectances. The result of averaging the individual mean reflectances yields a reflectance value of low significance because it is not associated to high frequency reflectances. The mean reflectances and the bars corresponding to the percentiles 25 and 75 are shown in Figure 13. Some outstanding features of figures 12 and 13 are:

i) some of the distributions were very narrow and they typically yielded the lowest mean reflectances (participants 3, 5, 8, 12, 13, 18, 19 and 21). This indicates that 8 out of 22 participants mainly measured the low reflectance population.

ii) Participant 6 also reported a narrow distribution but of significantly higher reflectance.

iii) The very high means reported by participants 11, 15 and 16 and the fact that there is nearly no superposition between the range of their readings and the range of the readings from the other participants apparently indicate that they were measuring a different type of particle.

iv) Participants 1, 2, 4, 7, 9, 10, 14, 17, 20 and 22 having wider reflectance distributions also had bimodal distributions (Figure 12), although the high reflecting population had a generally poorly defined mode.

The study of the reflectance distributions shown in Figure 12 indicates that if the group mean is calculated by just averaging the reflectance values of Figure 13 different types of particles are included in the results and the group mean ($\overline{R_o}$ =0.40 %, σ=0.1452) could be of low significance for determining the maturity of the sample. In addition the fact that nearly half of the participants identified two vitrinite populations with different weight in their respective distributions was no doubt contributing to the scatter of the results. A similar scatter of results was found in a ICCP interlaboratory exercise performed in 1983 on a sample from the same locality (Table 2) and also in this case some of the participants reported reflectance values for two populations.

An attempt was made to separate the readings corresponding to both populations selecting as threshold the minimum between the two modes if present in each distribution. These results are shown in Figure 14. The group mean ($\overline{R_o}$) for the low reflecting population was 0.27 % and the standard deviation 0.0402 (Figure 14a). Overall the bars indicate reasonably narrow distributions and this is so even for participants 20 and 21 reporting significantly lower reflectances. In addition the low superposition of reflectance readings between these two participants and all the others apparently indicates that either they were recording the reflectance of a lower reflecting component (i.e. lamalginite) or had some calibration problems with the microscope. Both were out of the limits marked by ±1.5σ.

For the high reflecting population a larger variety of distributions was found with a group mean of 0.53 % and a standard deviation of 0.0945 (Figure 14b). The bars corresponding to the percentiles 25 and 75 indicate that the participants reporting wider distributions were also those reporting higher reflectance values, which can be attributed to the inclusion of inertinite reflectances in the mean. As the scatter of results is larger in the high reflecting population, the limits marked by $\pm 1.5\sigma$ are also wider and only one participant was out of these boundaries.

The existence of more than one vitrinite population in sample PT is one of the reasons for the large scatter of data in Figure 13 as shown by the relationship between the percentage of high reflecting particles and the total average mean reflectance prior to the split of the readings into two populations (Figure 15). The results indicate very clearly the presence of an indigenous low reflecting population in sample PT and also the existence of higher reflecting vitrinite particles that do not conform a well-defined population.

The reasons for the scatter in the high reflecting readings can be identified as:

i) The common occurrence of small carbonate crystals often having an appearance similar to vitrinite.

ii) The weak fluorescence of the lamalginite and its orange to reddish colour might have lead to some participants to reject the low reflecting readings in an effort to record those better reflecting the maturity of the sample. This might be the reason for participants 11, 15 and 16 taking only readings higher than R_o=0.3 %.

The actual maturity of the sample can be considered as being close to R_o=0.65%, which is the reflectance of the overlying coals. This indicates a strong suppression of vitrinite reflectance, a common situation in oil shales (Hutton and Cook, 1980; Kalkreuth, 1982; Price and Baker, 1985).

3.3.4. Irati shale

A similar situation to that described for PT was observed for the Irati shale (IS). Rather different reflectance profiles were provided by participants indicating also the presence of more than one vitrinite population and rather different criteria between participants to select the appropriated vitrinites for taking the readings (Figure 16). As a consequence the scatter of the individual reflectances was very high (Figure 17). The R_o values determined by the participants ranged between 0.20 and 0.90 % and therefore the standard deviation of the group was too large (0.1993) to provide a reliable value for the vitrinite reflectance of the sample. The scatter of results was similar to the one observed for MOD 28 (Irati lower seam) and MOD 29 (Irati upper seam) in a 1983 ICCP Round Robin exercise (Table 2).

The histograms in Figure 16 can be grouped in various families according to the shape of the curves:

i) Curves showing a single population of vitrinite (participants 1, 4, 5, 6, 7, 8, 14, 18, 19, 21). Except for participant 6 the profiles were very similar indicating that participant 6 measured a homogeneous but higher reflectance population.

ii) Curves showing a bimodal distribution with different proportion of the low reflecting and high reflecting population (participants 10, 12, 13, 22). Although bimodal the curves were rather different, particularly regarding the high reflectance readings.

iii) Curves showing large scatter without modal values (participants 2, 3, 9, 11, 15, 16, 17, 20).

A single reflectance value was extracted from histograms with unimodal distributions, although sometimes the tail of the histograms fell in the interval of the other population. The histograms without modal values typically corresponded to high reflectance readings and they were considered as representatives of the high reflectance population. Those histograms having a clear bimodal distribution were split to provide a low and a high reflectance value and the threshold selected was the minimum between the two modes. In multimodal histograms (3, 15, 16, 20 and 22) the low reflecting population corresponding to the first modal value was separated and the remaining values were considered together as part of the high reflecting population.

Figure 18 shows the scatter of reflectances for the low and high reflecting populations in sample IS. Although still large the range of reflectance was narrower than considering all the readings. The group mean for the low reflecting population identified by 17 out of 22 analysts was 0.28% with a group standard deviation of 0.0352. Only 13 participants recorded readings for the high reflectance population, and two of them (participants 9 and 11) included readings as high as R_o=1.49 and R_o=1.69%, respectively, which were probably taken on inertinite or reworked vitrinites. The group mean for the high reflecting population was 0.64 % with a standard deviation of 0.1259, which reflects the large scatter of results. Some of the reasons for the difficulties to select a common vitrinite population to take the readings can be found:

i) Some participants identified the low reflecting population as bitumen and therefore did not include the values in the readings.

ii) The lamalginite showed very weak fluorescence intensity with brownish colour, which might have suggested a relatively high maturity level to some participants, who consequently ignored the low reflecting readings.

iii) Both inertinite and vitrinite particles were relatively common, which might have created some confusion between some of the relatively structureless inertinite and vitrinite.

The plot of Figure 5 shows that no significant differences were found between the reflectance of the various qualifiers. The possibility that the trend would change after splitting the vitrinite populations of Puertollano and Irati shale was also checked (Figure 19). Although the scatter was larger and the regression coefficients lower than those of Figure 5, the trends did not change significantly (Figure 19). The results shown up to this point indicate that the scatter of the reflectance values reported by participants are more related to the difficulties in identifying the vitrinite population where readings should be taken than with the quality of the vitrinite surfaces. Despite this it appears useful to provide a figure indicating the reliability.

3.4. Reliability of reflectance measurements

There is no doubt that the reliability of the results will depend on the number of readings and the dispersion of the values. The system originally proposed by Koch considered a matrix in which the number of particles, coefficient of variation (CV) and the quality of the surface were considered (Table 3). The procedure was based on five categories for qualifiers and the highest reliability was 1 and the lowest 5.

According to the results shown in Figures 7 and 19 and considering that the differences in reflectance between the qualifiers did not follow a defined trend a simplified reliability assessment could be used. A reliability index (RI) has been defined as the ratio between the number of readings and the coefficient of variation (RI=N/CV), where CV is defined as:

$$CV = 100 * \left(\frac{\sigma}{R_o} \right)$$

being R_o the mean reflectance of the readings and σ the standard deviation.

The highest RI values will be achieved for the samples with a high number of readings and the most homogeneous vitrinite populations (low CV). Table 4 shows the individual reliability indices calculated for the samples. Overall the highest reliability in the reflectance determination corresponded to sample CS since all participants recorded high number of readings ($\geq$ 50) and low CV (typically below 10), resulting in high reliability indices. The other samples did not have an equivalent dataset since either the participants did not find appropriate particles to measure or did not measure a given population, therefore a correction factor (number of data for the vitrinite population/number of participants) was applied to calculate an average reliability for the sample. The lowest reliability was that of the high reflecting vitrinite population of the Irati shale since only half of the participants reported readings for this population and also the RI values were rather low. The certainty in the measurement of the low reflecting population was higher than that of the high reflecting population in both PT and IS samples. It should also be noted that the RI factor does not completely cover the difficulty of separating vitrinite and inertinite populations. The samples cover a range of difficulties for this task. The study indicates that separation of these maceral groups is the easiest for the CS sample and the most difficult for the IS sample. The study does not, however, provide a method for improving recognition of these maceral groups.

3.5. Precision and bias for the analysts-an evaluation of the suitability of the data for an accreditation program

One of the objectives of the present round robin exercise was to highlight the difficulties to be taken into account to initiate an accreditation program for vitrinite reflectance assessment on dispersed organic matter. The following paragraphs evaluate the participants accuracy and bias referred to the group mean. The tools applied are the same as those currently used in the coal accreditation program for vitrinite reflectance determination (www.iccop.org). Two sets of comparative data are calculated for each analyst, for each vitrinite population analysed. The first set comprises the signed multiple of the standard deviation (SMSD) calculated against the group mean and the standard deviation data, for each sample analysed as per the formula below:

$$SMSD = \frac{\left(R_{oi} - \overline{R_o}\right)}{\sigma}$$

where R_{oi} is the participant vitrinite reflectance, $\overline{R_o}$ the group mean vitrinite reflectance and σ the standard deviation of the group; and the averaged signed multiples of the standard deviation (ASMSD), that is the sum of the signed multiples divided by the number of samples analysed. It is a measure of the bias about the group means and indicates the consistency of an analyst. The other set of data comprises the unsigned multiple of the standard deviation (UMSD), which is the absolute value of SMSD and the corresponding averaged unsigned multiple of the standard deviation (AUMSD), which is the sum of the unsigned multiples divided by the number of samples analysed. It is an indicator of dispersion about the group means and a measure of the accuracy of the analyst. If the dispersion around mean values (AUMSD) is below 1.5 the results are considered acceptable. A value of 1.5 for the cut-off was chosen to be consistent with the existing Accreditation Program for ICCP. The value of 1.5 was in turn chosen to be consistent with some other tests although it must be recalled that these other tests tend to test only bias and not precision (Cook et al., 1997). In practice it may be desirable to alter the cut-off value depending on the nature of the total data set being evaluated.

The SMSD was calculated for each vitrinite population and also the averaged AUMSD and ASMSD for each participant. It must be pointed out that the results are not totally comparable since not all participants have the same number of data but still might be useful to evaluate the results. The results shown in Table 5 indicate that only one participant had a AUMSD value over 1.5 and the ASMSD values indicate a low to medium bias for the majority of the group. The nature of the AUMSD and SMSD calculations is such that it represents a test that automatically compensates for some of the effects of the level of difficulty. However, the form of the distrubution of AUMSD values over 22 analysts suggests that the data form a consistent base for assessing the quality of the analyses. It is also noteworthy that some of the group standard deviations are similar to those obtained for many of the coals within the Accreditation Program and even the higher standard deviations for the dispersed organic matter are only marginally above those for some suites of analyses on coals.

4. Conclusions

- A system has been applied to label the quality of vitrinite particles in which reflectance readings were taken during the course of a microscope analysis of dispersed organic matter. The system was essentially based on the size of the particles and surface homogeneity. The reflectance of particles classified as excellent, good or low quality compared to the total average reflectance did not show well-defined trends in any of the samples analysed. The differences in reflectance between the qualifiers for any given sample were lower than the scatter of reflectances among participants. This apparently indicates that there is no benefit in weighting vitrinite reflectance readings as a function of the quality of vitrinite particles as defined here.

- Overall satisfactory results were obtained in determining the reflectance of vitrinite in the four samples analysed. This was so for samples having abundant and easy to identify vitrinites (higher plant-derived organic matter) as well as for samples with scarce and difficult to identify particles (samples with dominant marine-derived organic matter). A larger scatter of results was found for the two oil shales both very rich in organic matter and yielding relatively abundant particles to measure. The existence of more than one vitrinite population was derived from the results reported by participants for both oil shales. The peculiar optical properties of vitrinite in oil shales (often exhibiting severely suppressed reflectance) and the low fluorescing intensity of the lamalginite in both samples (which can lead to select higher reflecting particles to reflect the maturity of the sample) can be regarded as the main reasons conditioning the selection of the vitrinite particles in samples PT and IS. The scatter of results considerably decreased when the reflectance readings were separated into two populations. Special instructions are needed to accomplish the analysis of such samples.

- The reliability of the mean vitrinite reflectances reported varied between the samples analysed. Some of the values resulted from averaging a high number of readings with low standard deviations whereas some others were the result of few counts with high standard deviation. A reliability index has been defined to account for these differences. The highest reliability was that of the carbonaceous shale yielding abundant vitrinite particles with rather narrow reflectance distributions. The mean vitrinite reflectance of the marine shale was determined with significantly lower reliability since it was based on few measurements and the distributions were typically wider. In the two oil shales two vitrinite populations were found and the reflectance of the low reflecting population was determined with higher reliability.

- Using the criteria applied for coal reflectance analysis in the existing ICCP accreditation program (www.iccop.org) encouraging results were obtained with only one participant having an AUMSD value slightly over 1.5.

Acknowledgments

The samples were provided by Isabel Suárez-Ruíz (Carboniferous shale), Bertrand Ligouis (Posidonia shale), Carla Araujo (Irati shale) and Angeles G. Borrego (Puertollano shale). The effort of Jose Ramón Montes at INCAR, CSIC for sample preparation is gratefully acknowledged. Werner Hiltmann provided the data from previous ICCP MOD exercises (1983). Bertrand Ligouis wishes to express his gratitude to the Institute for Geosciences of the University of Tübingen, in particular to the Center for Applied Geoscience and the Department of Micropaleontology for use of the facilities.

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Table 1
Information about the samples (CS=Carbonaceous shale, PS=Posidonia shale, PT=Puertollano shale and IS=Irati shale)

Sample	Basin	Country	Age	Origin
CS	Central Asturian Coal	Spain	Pennsylvanian	Terrestrial
PS	South Western German	Germany	Jurassic	Marine
PT	Puertollano	Spain	Pennsylvanian	Lacustrine
IS	Paraná	Brazil	Permian	Marine-transitional

Table 2
Results of the ICCP exercise performed in 1983. Participants: Baskin, Castaño, Correia da Silva, Heroux, Hiltmann, Jacob, Kalkreuth, Mukhopadhyay, O'Connor/Dow, Ottenjann, Pittion, Robert, Siskov, Somers

Participant	Puertollano (MOD 27) R_o (%)	Irati Lower Seam (MOD 28) R_o (%)	Irati Upper Seam (MOD 29) R_o (%)
A	0.42	0.6*	> 0.55/~0.6*
B	0.53	0.62	0.61
C	0.8-1.2	< 0.7	< 0.7
D	0.37	0.56	0.49
E	0.45		
F	0.55	0.53	0.52
G	0.33	0.33	0.43
H	0.61	0.59	0.59
I	0.31	0.35	0.34
J	0.45	0.35-1.00	0.21
K	0.36	0.26 / 0.73	0.27/ 0.69
L	0.27/ 0.43	0.5	~ 0.4
M	0.29 /0.37	0.52	0.35/0.55
N	0.25	0.18	0.17

* estimated from sporinite fluorescence after Ottenjann et al., 1974

Table 3
Reliability system proposed by Koch in the 1999 ICCP Meeting. N = number of readings, CV= Coefficient of variation, q1-5=qualifyiers as defined in his system

N CV	≥30 ≤10	≥30 >10	29-10 ≤10	29-10 >10	9-5	4-1
q1	1	1	1	2	3	3
q2	1	2	2	3	3	4
q3	2	3	3	4	4	5
q4	3	4	4	5	5	5
q5	5	5	5	0	0	0

Table 4
Reliability Index calculated for the data as the ratio between number of readings and coefficient of variation

Participant	CS	PS	PT Low[a]	PT High[b]	IS Low[a]	IS High[b]
1	7.0	1.7	1.6	2.1	5.4	
2	6.4	1.0	0.9	2.4		1.5
3	9.1	2.4	5.4	2.1	3.2	3.4
4	6.5	1.6	3.9	1.4	3.2	
5	7.6	3.7	3.7		4.6	
6	5.8	5.2		6.0		7.0
7	6.7	3.2	3.4	2.3	2.7	
8	6.4	0.9	3.0		2.3	
9	4.4	0.5	0.9	2.1		1.0
10	4.3	0.3	1.5	1.2	3.2	1.1
11	5.5	1.3		1.7		1.2
12	6.1	1.6	3.5	0.9	2.7	0.5
13	6.7	2.2	3.0		1.6	0.3
14	4.0		2.2	0.9	1.7	
15	6.1	2.0		2.3	1.3	1.1
16	4.3	1.2		2.0	1.1	1.0
17	9.2	1.6	2.3	2.1		0.5
18	6.8	1.2	2.9	0.1	3.9	
19	6.6	0.2	2.8	0.5	0.5	
20	3.4	0.2	0.4	0.6	0.4	0.5
21	6.4	1.0	1.8		1.5	
22	5.9	0.6	1.7	1.0	2.7	0.8
RI Sample	6.1	1.5	2.0	1.4	1.9	0.9

[a]Low reflecting population, [b]High reflecting population

Table 5
Accuracy and bias of results calculated against the group mean and standard deviation

Participant	SMSD						AUMSD	ASMSD	Bias
	CS	PS	PT Low[a]	PT High[b]	IS Low[a]	IS High[b]			
1	0.4	-0.2	0.3	-0.2	-0.3		0.3	0.0	Low
2	0.1	-0.6	0.2	-0.3		-0.5	0.3	-0.2	Low
3	0.8	0.4	0.5	-0.9	0.7	-0.7	0.7	0.1	Low
4	0.1	-0.7	-0.1	-0.5	0.3		0.3	-0.2	Low
5	0.5	0.3	-0.1		-0.4		0.4	0.1	Low
6	0.4	0.8		-0.1		0.6	0.5	0.4	Low
7	-0.1	0.7	0.8	-0.5	0.3		0.5	0.2	Low
8	0.7	-0.3	1.4		0.6		0.7	0.6	Medium
9	-3.1	-1.8	1.0	0.0		2.4	1.7	-0.3	Low
10	-1.3	-1.0	-0.3	-0.3	1.5	-0.8	0.9	-0.4	Low
11	-0.1	0.4		2.7		1.5	1.2	1.1	High
12	0.8	0.6	0.5	-1.0	0.2	-1.3	0.7	0.0	Low
13	1.2	0.8	1.6	-0.1	2.1	-0.8	1.1	0.8	Medium
14	-1.3		0.3	-0.6	-0.3		0.6	-0.4	Low
15	-0.2	0.7		1.4	0.0	-0.1	0.5	0.4	Low
16	0.4	0.0		1.3	0.5	-0.2	0.5	0.4	Low
17	0.5	1.0	-0.1	-0.6		0.2	0.5	0.2	Low
18	-0.2	-1.3	-0.8	0.6	-1.3		0.8	-0.6	Medium
19	0.1	-0.1	-0.8	-1.3	-1.6		0.8	-0.7	Medium
20	-1.6	-1.3	-2.1	-0.7	-1.9	-0.4	1.3	-1.3	High
21	0.6	-1.3	-2.0		0.1		1.0	-0.6	Medium
22	0.8	2.4	-0.1	1.1	-0.2	0.2	0.8	0.7	Medium

[a]Low reflecting population, [b]High reflecting population

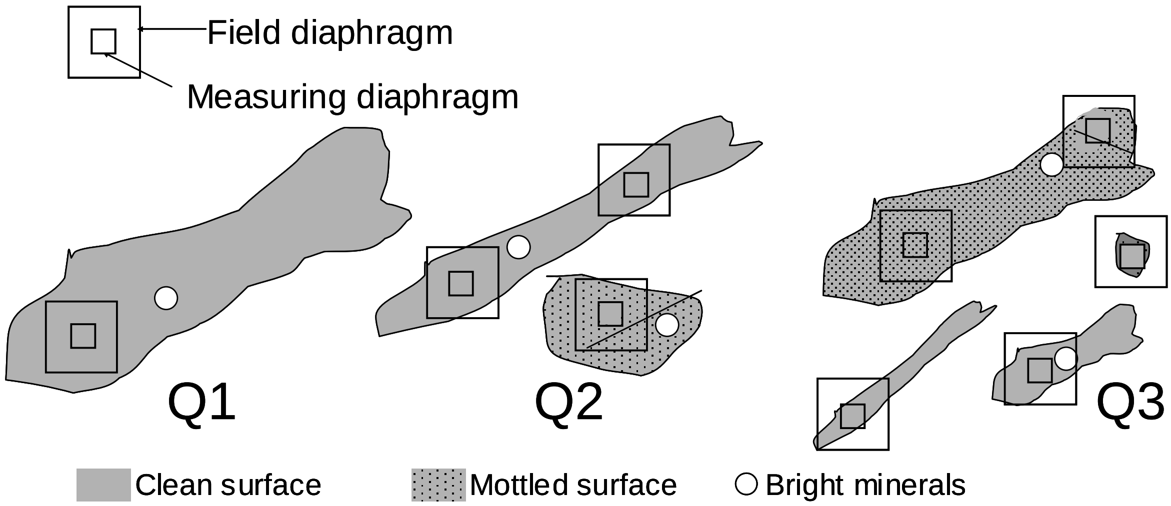

Fig. 1. Examples of the evaluation scheme.

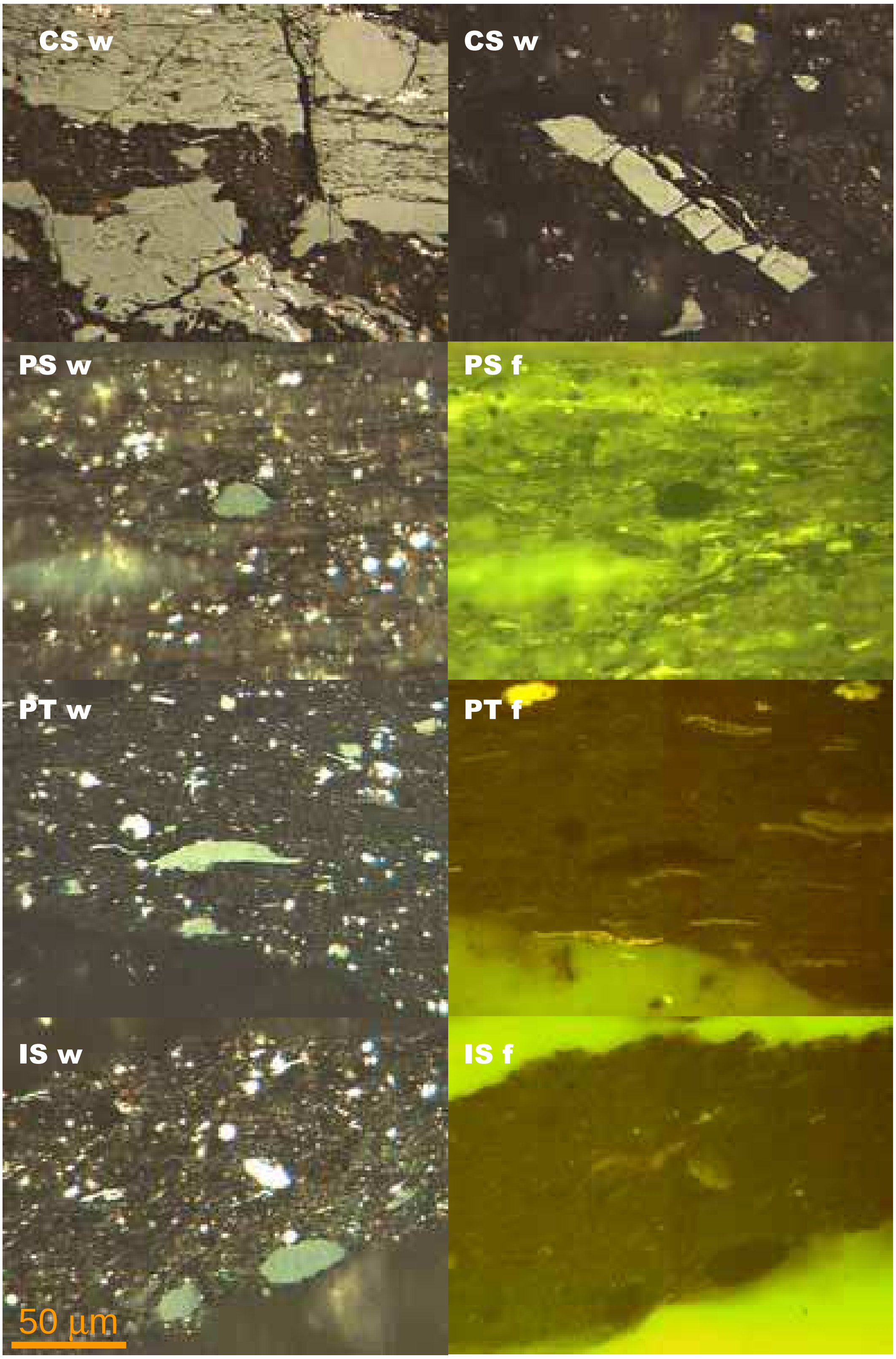

Fig. 2. Examples of the organic matter in the samples. CS=Carbonaceous shale, PS= Posidonian shale, PT=Puertollano shale, IS=Irati shale. w= white light, f=fluorescence.

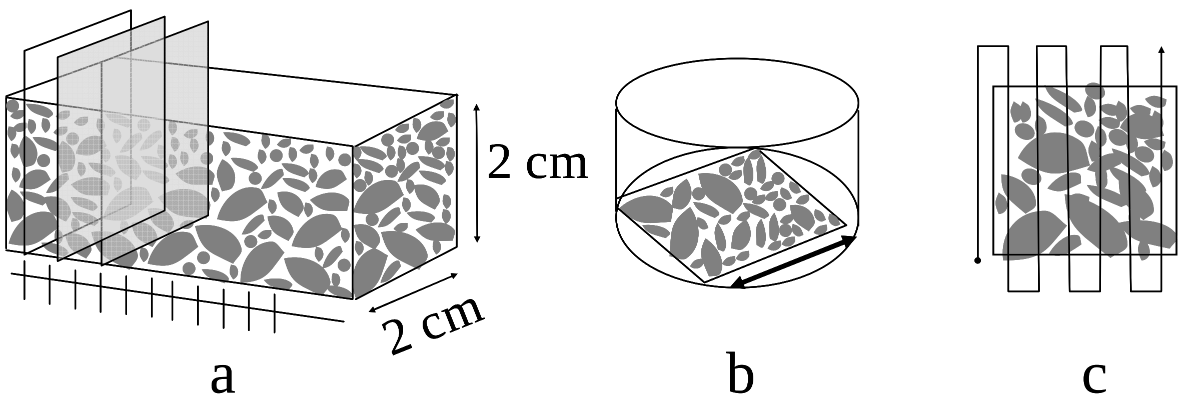

Fig. 3. Scheme of sample preparation

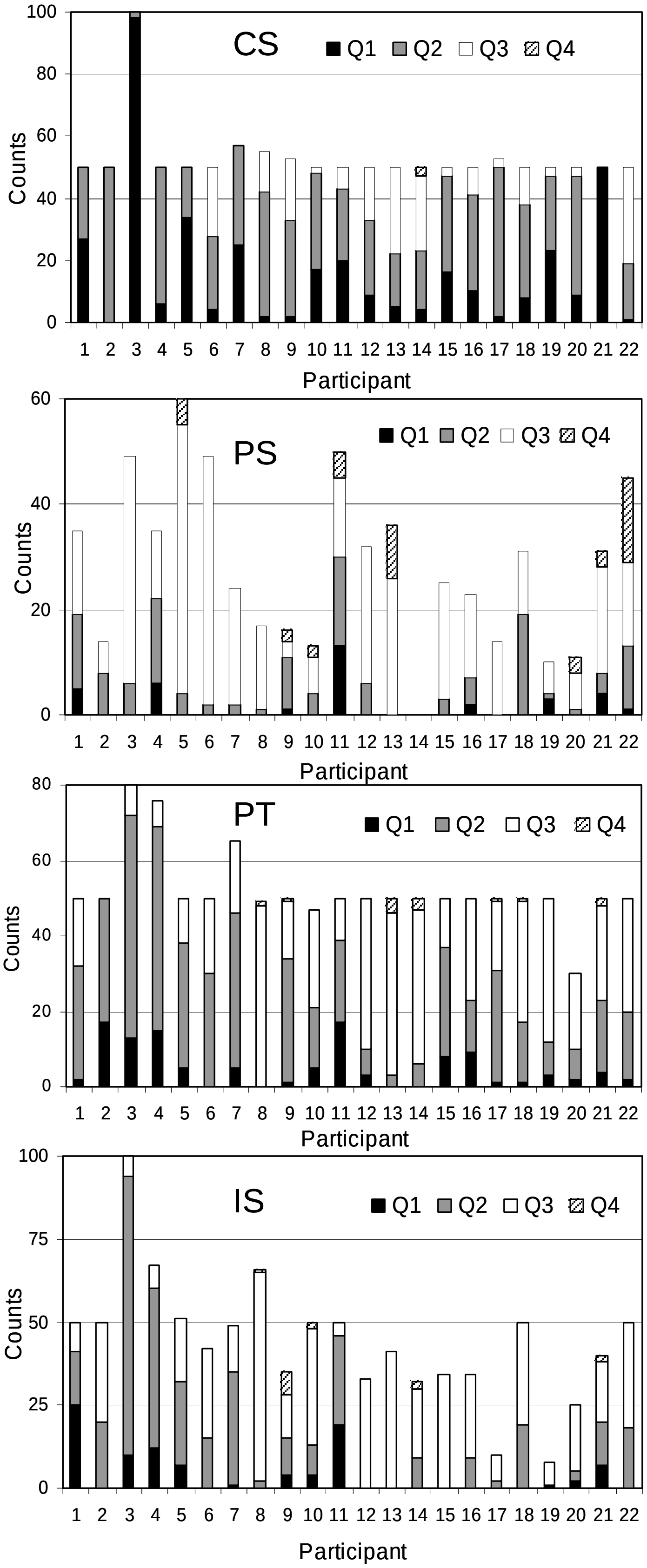

Fig. 4. Distribution of qualifiers in the samples

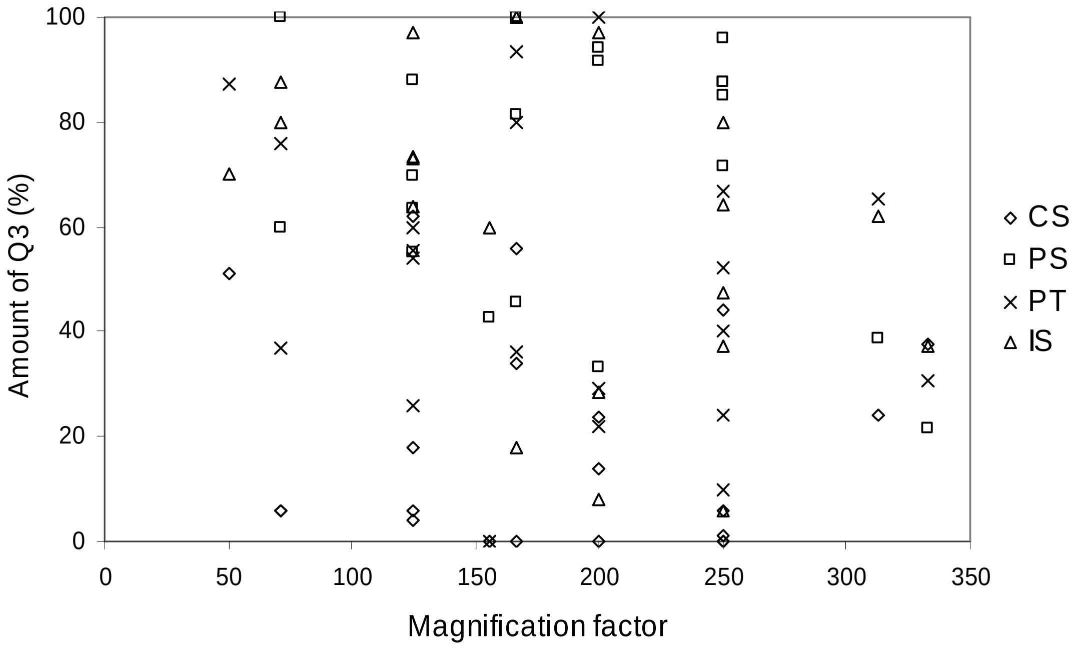

Fig. 5. Relationship of magnification factor (Magnification/size of measuring spot) and relative amount of low quality particles (Q3) for the samples.

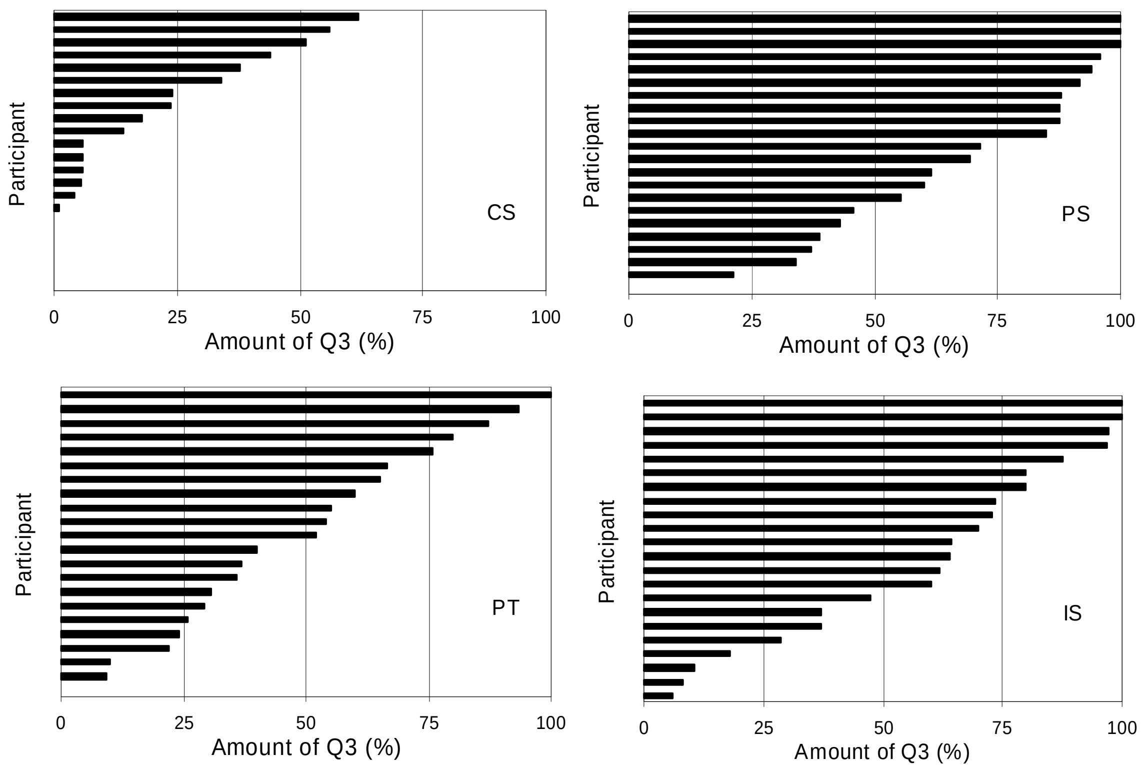

Fig. 6. Relative amount of low quality particles for the samples analysed

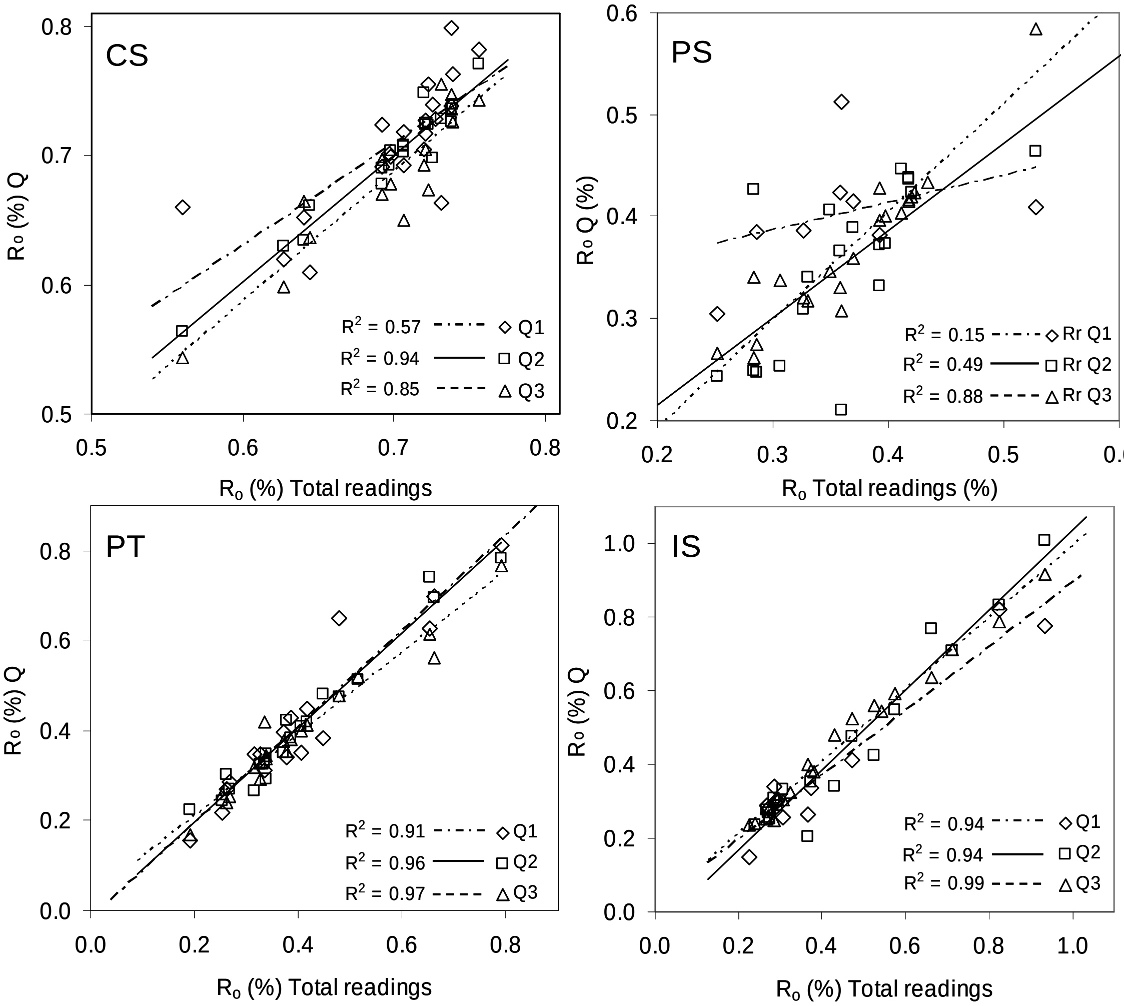

Fig. 7. Total averaged reflectances vs. averaged reflectances of particles classified with a given qualifier for the four samples.

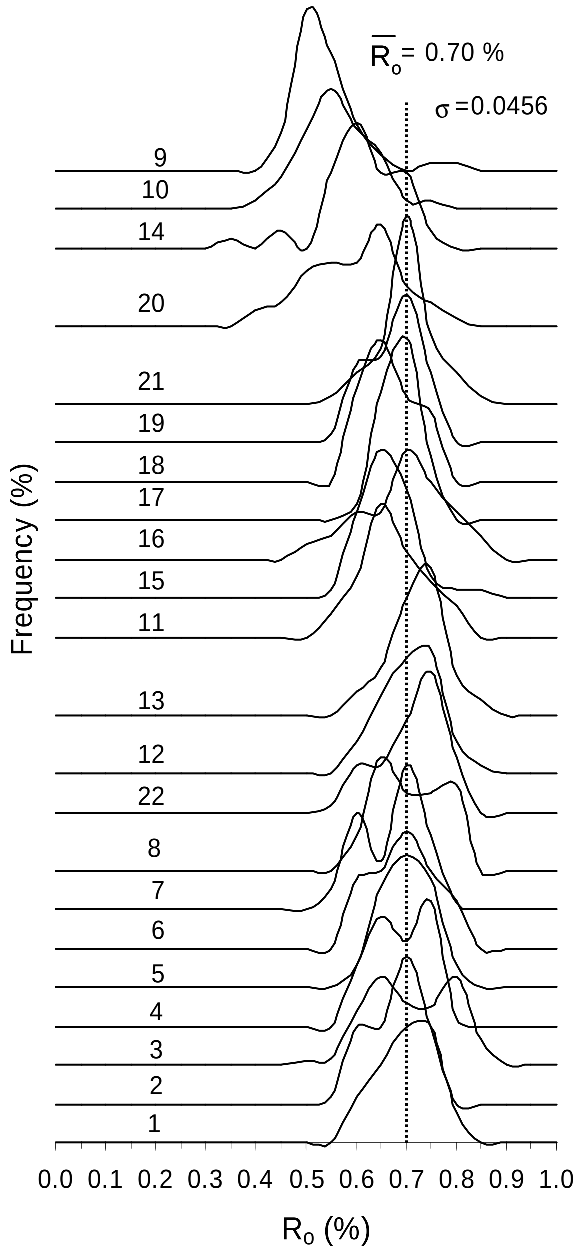

Fig. 8. Histograms of CS (the dotted line corresponds to the group mean reflectance ($\overline{R_o}$) and σ is the standard deviation of the group)

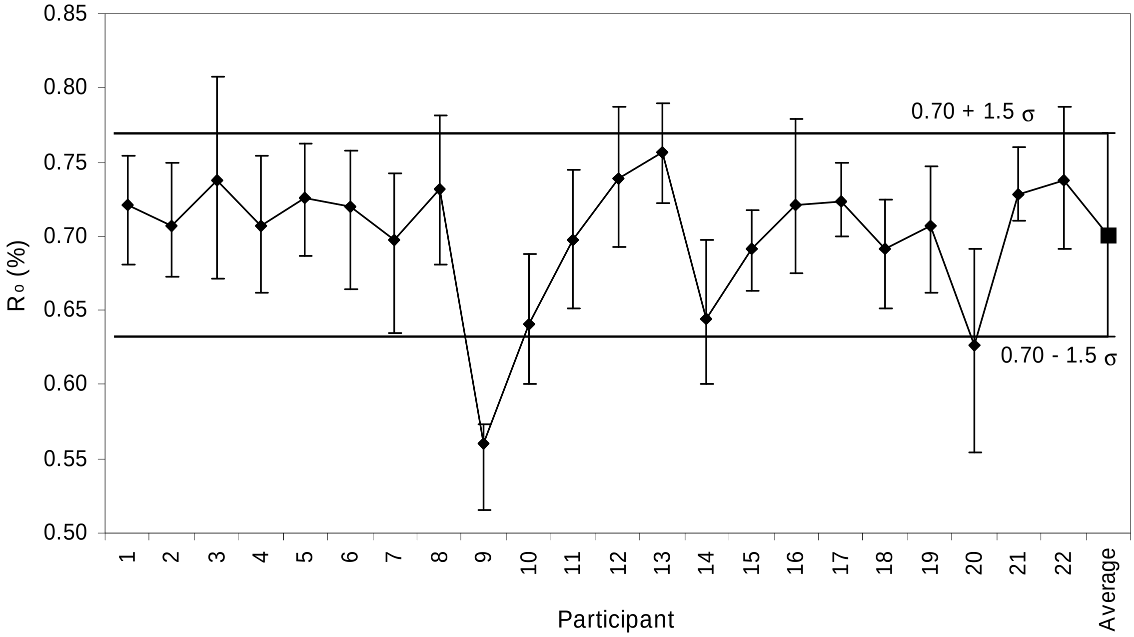

Fig. 9. Scatter of R_o reported by participants for sample CS

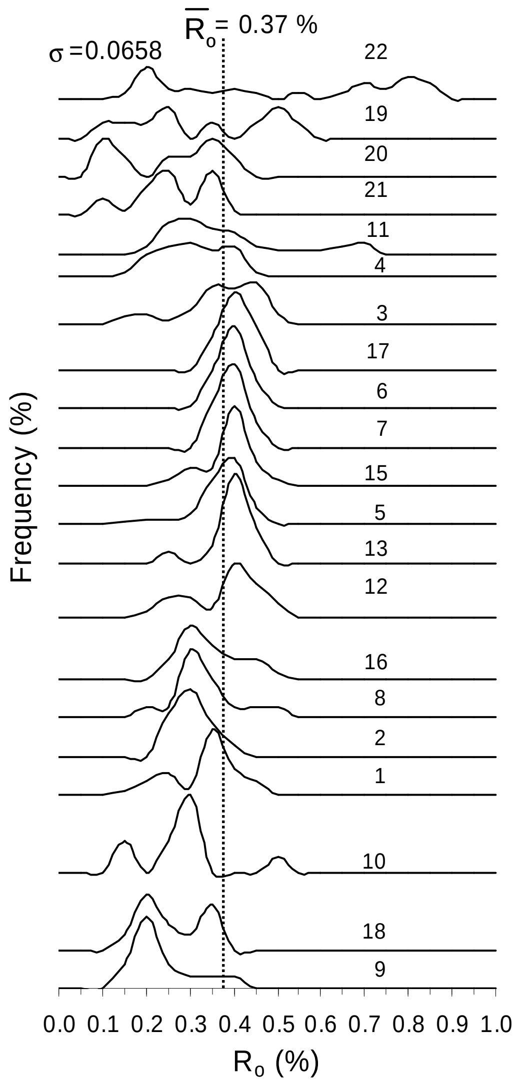

Fig. 10. Histograms of PS (the dotted line corresponds to the group mean reflectance ($\overline{R_o}$) and σ is the standard deviation of the group)

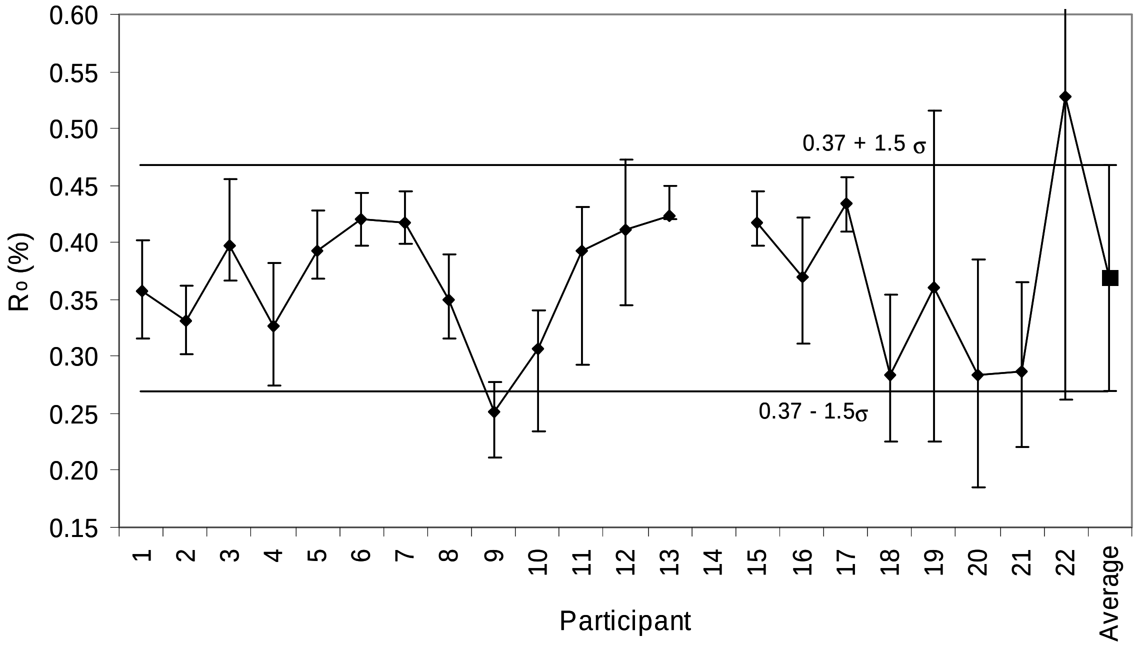

Fig. 11. Scatter of R_o reported by participants for sample PS

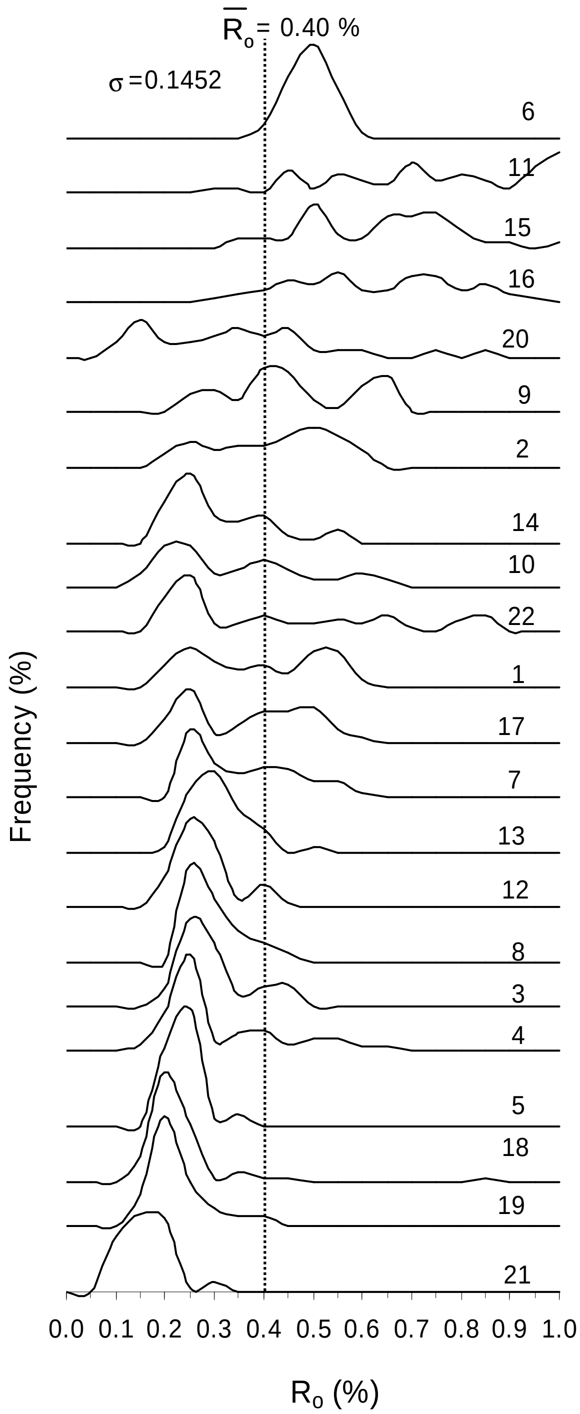

Fig. 12. Histograms of PT (the dotted line corresponds to the group mean reflectance ($\overline{R_o}$) and σ is the standard deviation of the group)

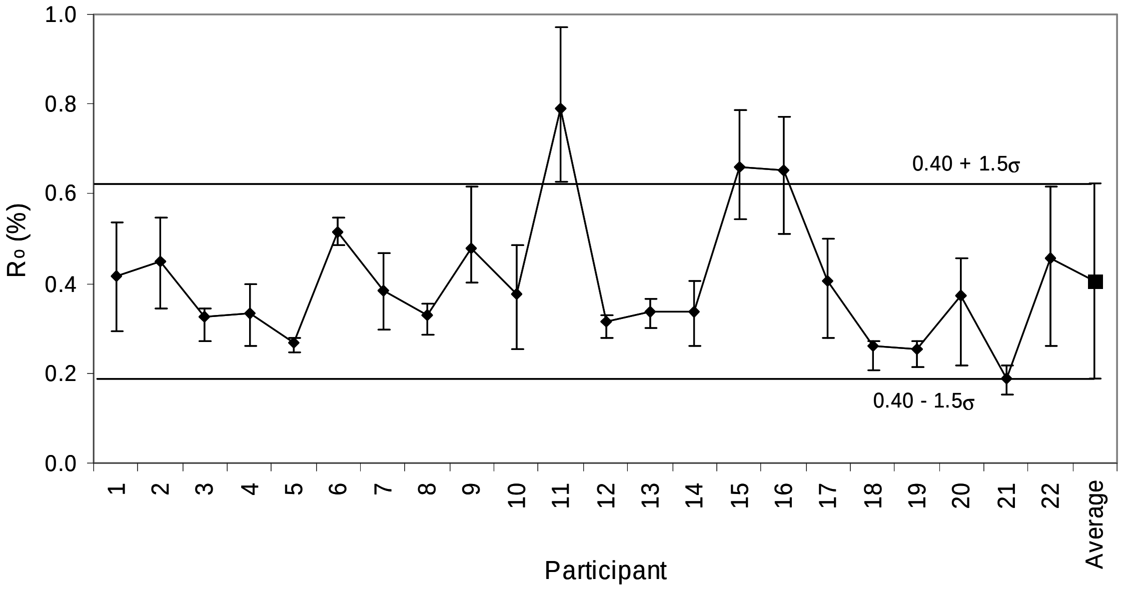

Fig. 13. Scatter of R_o reported by participants for sample PT

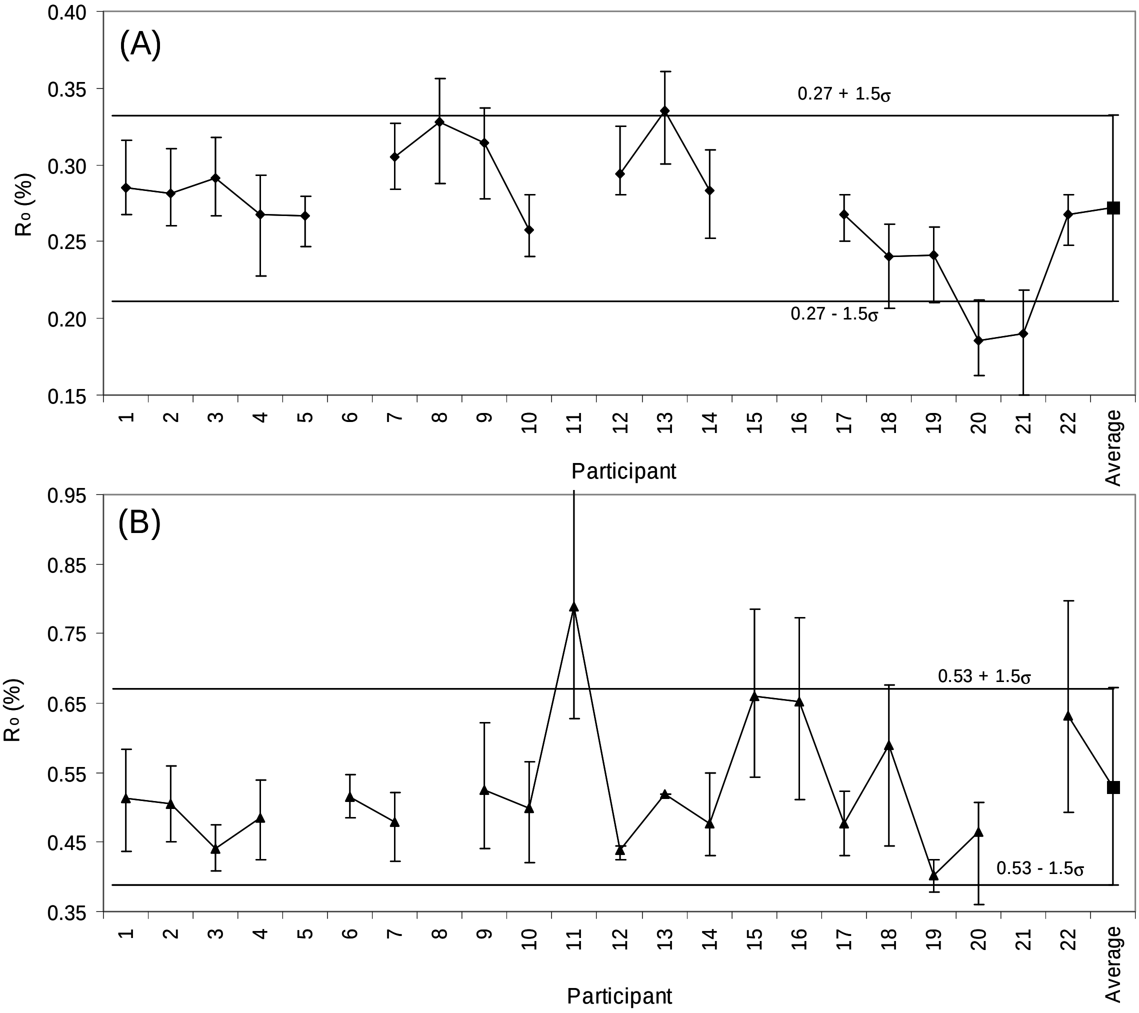

Fig. 14. Scatter of R_o reported by participants for the low (A) and high (B) reflecting populations in sample PT

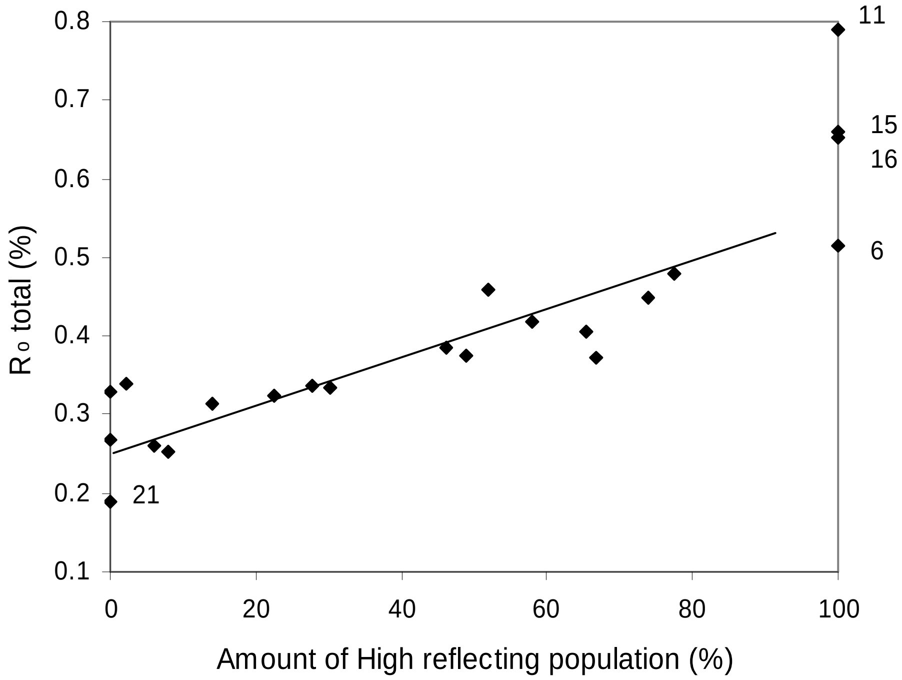

Fig. 15. Variation of the total average reflectance as a function of the amount of high reflecting vitrinites for the sample PT. The labels correspond to the participant number

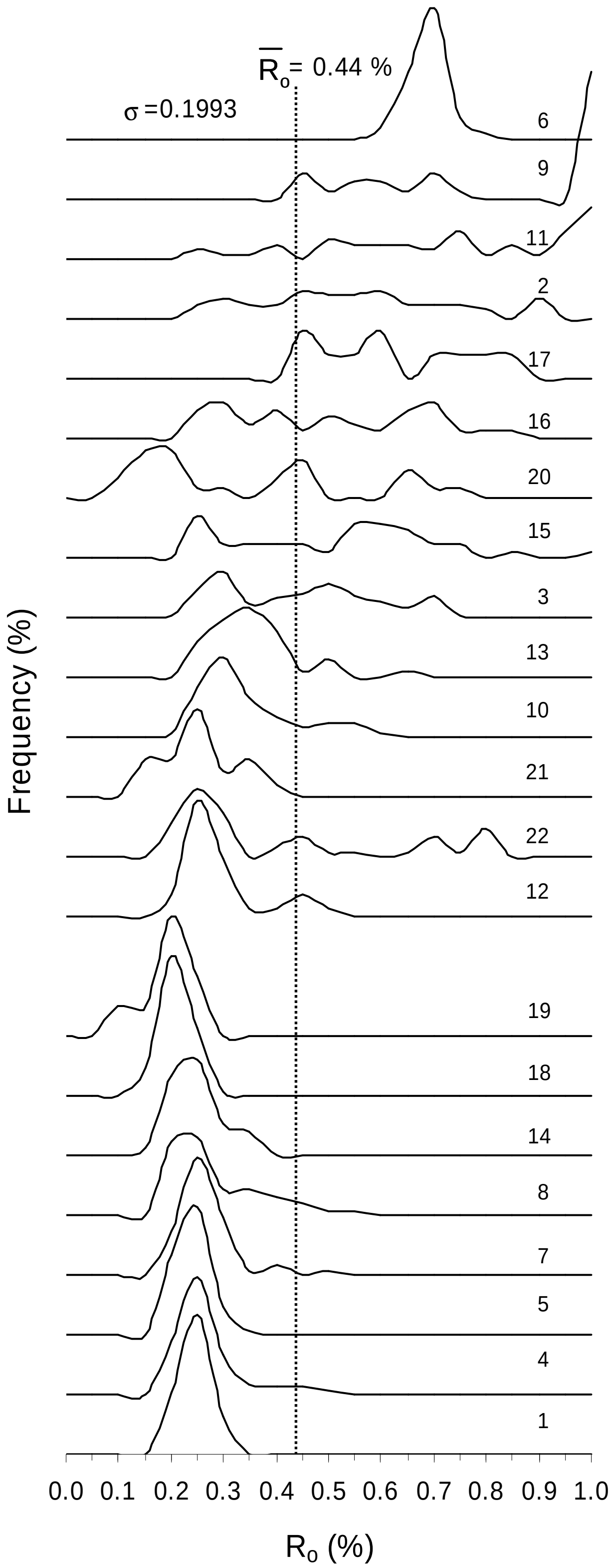

Fig. 16. Histograms of IS (the dotted line corresponds to the group mean reflectance ($\overline{R_o}$) and σ is the standard deviation of the group)

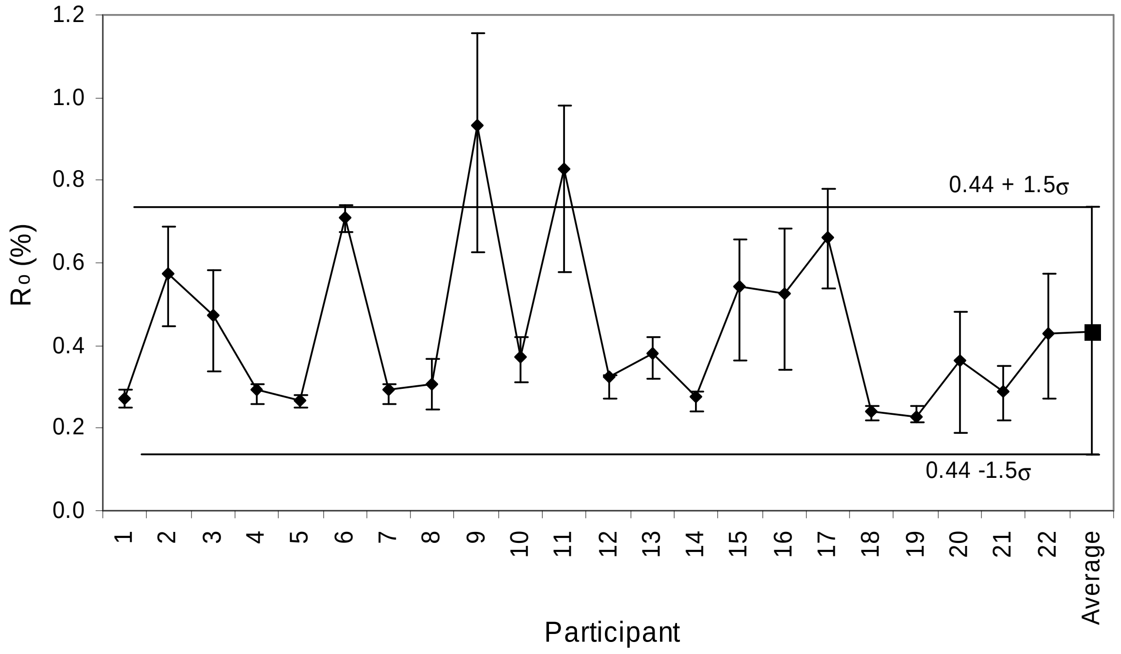

Fig. 17. Scatter of R_o reported by participants for sample IS

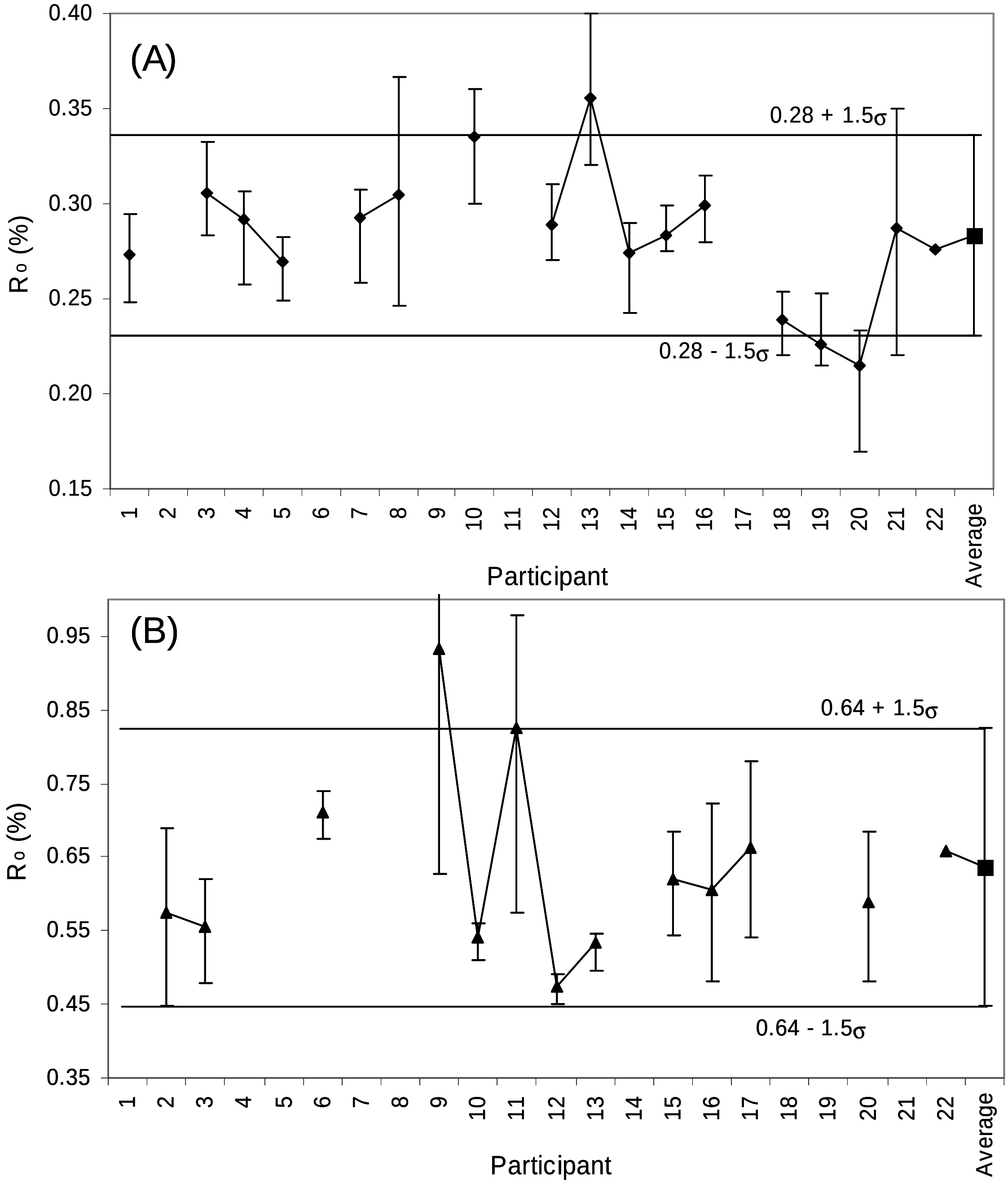

Fig. 18. Scatter of R_o reported by participants for the low (A) and high (B) reflecting populations in sample IS

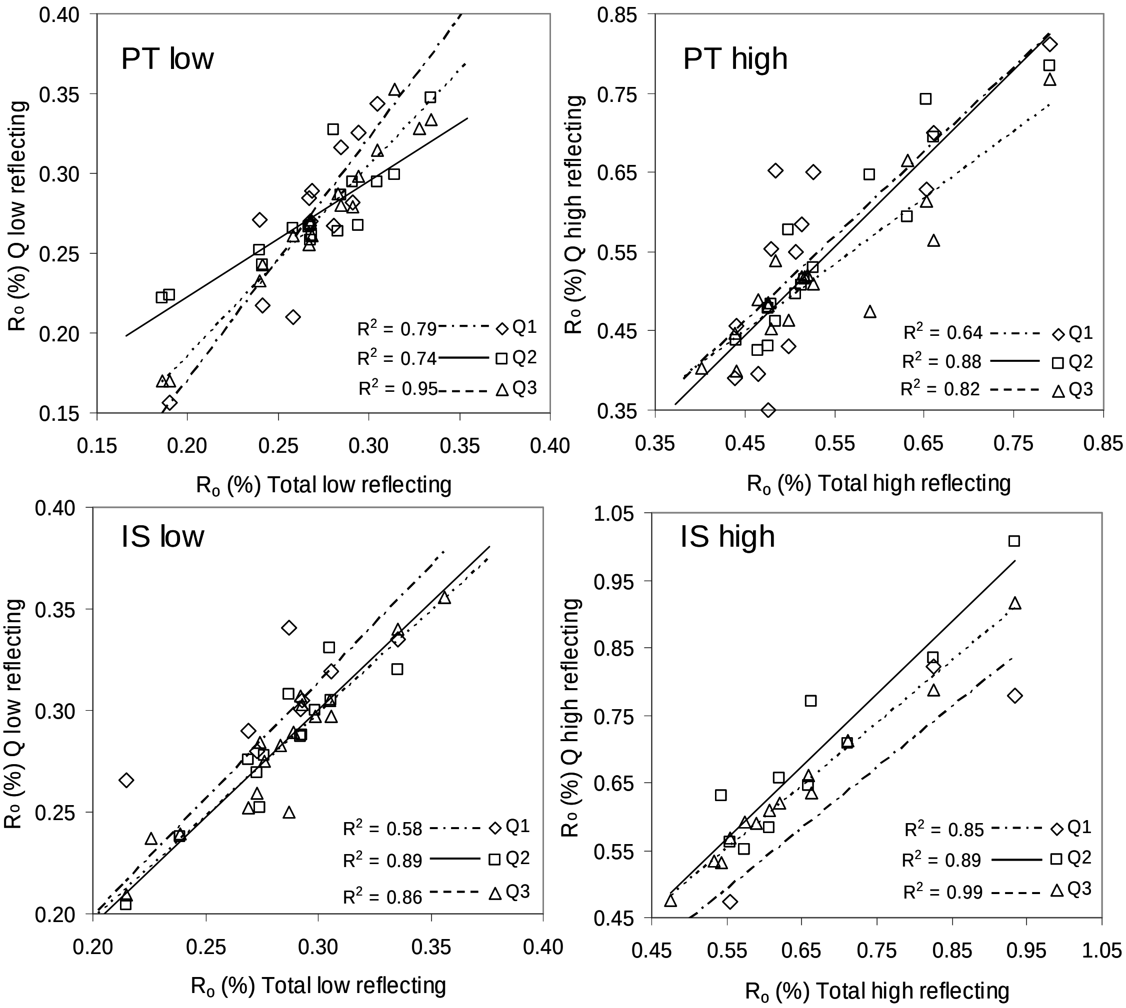

Fig. 19. Total averaged reflectances vs. averaged reflectances of particles classified with a given qualifier for the low and high reflectance populations of samples PT and IS