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Letter to the Editor

Estimation of Total Organic Carbon in shales through color manifestations

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A B S T R A C T

Recently shale gas resources have emerged as a viable energy source and have become an attractive target because they represent a huge resource. Total organic carbon (TOC) content of shales is one of the key reservoir parameters and for source rock assessment its measurement is the first priority. Here the authors have collected different types of banded inhomogeneous shale samples and have tried to estimate their TOC content by identification of color (intensity) of lithobands (namely coal, dark shale, gray shale and silt) in shales by naked eye by assigning numeric values to the bands based on their color intensity. Total Color Assessment (TCA) of the samples was calculated by dividing summation of the product of the band thickness and their respective color value with total length of the sample. The relationship between TCA and TOC shows significantly high coefficient of determination and hence can be used as a significant first order field tool for estimation of TOC. For TCA <5, the estimated TOC values (calculated from TCA) are very close to the actual TOC values.

1. Introduction

In spite of being the most voluminous rock on the earth's crust, only recently shales have garnered considerable interest due to its emergence as hydrocarbon reservoirs (Montgomery et al., 2005; Varma and Panda, 2010). Shales are fine grained clastic sedimentary rocks made up of clay and silt sized particles. Hydrocarbon generative potential of shales depends on the amount, type and maturity of the organic matter present in it (Tissot and Welte, 1978). Organic matter in shale typically ranges from below 1 wt % to more than 20 wt % and is responsible for in situ gas generation as well as provides storage sites for shale gas in the organic matter micropore structure (Mastalerz et al., 2012). For any source rock assessment, the measurement of TOC (Total Organic Carbon) is a priority and is the first step of quantifying organic richness, though it doesn't indicate the quality (Lewis et al., 2004; McCarthy et al., 2011). Shales exhibit various colors ranging from red to green to gray to black and it was observed that organic carbon content and Fe^{3+}/Fe^{2+} are the main controlling factors for color in shale (Tomlinson, 1916; Pettijohn, 1974; Berner, 1971; McBride, 1974; Hubert and Reed, 1978; Potter et al., 1980; Myrow, 1990). Here we have tried to present a method of estimating the TOC (total organic carbon) content of banded, inhomogeneous shale samples by identification of color (intensity) of lithobands in shales by naked eye. The lithobands were assigned with numeric values based on their color intensity.

Homogeneous colored shales such as red shales, green shales have been excluded from the study and only inhomogeneous, banded shales have been considered. Red shales are red in color due to presence of hematite; green coloration in shales is contributed by chlorite and illite (and glauconite in case of marine shales) i.e. in either case the colors are contributed by mineral matter type and not by its organic matter content. Here the coloration is controlled by Fe^{3+}/Fe^{2+} ratio– a higher ratio will result in red coloration and lower ratio will result in green coloration; the former may be converted to the later by reduction of Fe (McBride, 1974; Hubert and Reed, 1978; Potter et al., 1980). If carbon is present in sufficient amount, it favors the reduction of Fe^{3+} to Fe^{2+} (Potter et al., 1980). Mineral like pyrite (FeS_2) in which Fe is in $+2$ state, is not an important pigment that contributes to color (Berner, 1971) and hence darker coloration of shales is ultimately controlled by its organic matter content. Here for the purpose of study authors have investigated inhomogeneous, banded borehole shale samples with wide variation in TOC content from Raniganj basin, West Bengal, India.

2. Materials and methods

Twenty nine inhomogeneous, banded shale samples of Raniganj Formation (Upper Permian age) from different parts of Raniganj coal basin were chosen.

2.1. Macroscopic study

Macroscopic study of the shale samples comprised identification of lithobands and then assigning a color value to the lithobands of the samples. Four types of lithobands (Fig. 1a) have been identified (Coal, Dark shale, Gray shale and Silt) and were assigned with numeric values based on their color intensity. Highest numeric value of 8 was assigned for any coaly band present in the sample due to their stronger impact on the TOC content of the sample. Numeric value of 4 and 2 were assigned to dark shale and gray shale bands present keeping in mind their probable higher and lower

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impacts respectively on the TOC content of the sample. Likewise a value of 1 was assigned to white/whitish silt layer present in the studied samples, as it will have lower impact on the TOC content with respect to the above mentioned three bands. Thickness of each band present in the sample was measured and multiplied with the color value. The summation of the product of the band thickness and their respective color value is obtained. To obtain the total color assessment (TCA), weighted mean is calculated when the above summation is divided with the total length of the sample as shown in Equation (1).

$$\text{Total Color Assessment (TCA)} = \sum(\text{Band length} \times \text{Color value}) / \sum \text{Band lengths} \quad (1)$$

For the study, the following band rules were adopted: (i) for a coaly horizon to be considered as a lithoband, the minimum vertical thickness should be 1 mm; (ii) for non-coaly horizons to be considered as a lithoband, the minimum thickness should be 2 mm; (iii) the lateral continuity of each considerable horizon/layer should be at least 1 cm (in case of core samples). Same part of the sample was used for calculating TCA and TOC content.

The colors were selected following revised geological rock Color chart by Munsell Color, 2009. Coaly band with numeric value of 8 corresponds to N1 shade of the color chart; dark shale with numeric value of 4 corresponds to N2–N4 shades of the color chart. Likewise gray shale and silt layer correspond to N5–N8 and N9 shades respectively (Fig. 1a and b). Defining different lithobands based on consecutive shades present in shales were avoided to minimize complexities that may arise with human eye assessment and for this purpose only 4 gray shades were selected.

The values of 1, 2, 4 and 8 of the bands are kept in geometric progression [scale factor (a) = 1, common ratio (r) = 2] to encompass the fact that a coaly band in shale will have much higher impact on the TOC content of the sample with respect to the non-coaly bands.

2.2. TOC determination

Rock Eval-VI was used for carrying out Rock-Eval Pyrolysis and TOC analysis of the samples. For this, the samples were washed, dried, crushed to powder and screened through BSS 60 mesh size. The crushed samples were well homogenized before carrying out experiments. Rock-Eval analysis is essentially a two step process, involving pyrolysis in an inert atmosphere (nitrogen) and combustion in an oxic atmosphere (air). The pyrolysis begins by heating the sample at 300 °C which releases the S1 fraction (mg HC/g), releasing volatile compounds, such as short chain lipids and other small volatile compounds. This stage is followed by a temperature rise of 25 °C/min until 650 °C, which releases the S2 fraction (mg HC/g). S1 and S2 are measured by flame ionization detection (FID). Hydrocarbons which are released during this stage are due to cracking of heavier and larger molecules (Taylor et al., 1998; Peters et al., 2005). Hydrocarbons that form the S2 peak represent the present hydrocarbon generating capability of the rock (Taylor et al., 1998). During the pyrolysis step, S3 carbon dioxide and carbon monoxide (mg CO/g) are measured continuously by infrared (IR) spectroscopy. The sample is then transferred to an oxic chamber and heated to 850 °C, burning off all remaining organic matter (OM). This produces the residual carbon (RC) fraction (wt % measured by IR) and the TOC is derived from the sum of these fractions (Lafargue et al., 1998). The TOC values of the studied samples are shown in Table 1.

3. Results and discussions

Initially values in arithmetic progression 1, 2, 3 and 4 were assigned to the bands and the relation (between TOC and TCA) and was tested with a linear fit (R^2 = 0.62), quadratic fit (R^2 = 0.875), exponential fit (R^2 = 0.964) and cubic fit (R^2 = 0.950) separately. Though the exponential and cubic plots show high coefficient of determination (R^2), the standard error of estimate (S) is also high (S = 0.197 for exponential fit and 2.772 for quadratic fit; Table 2).

The values in GP (1, 2, 4, and 8) were then used and were subsequently tested with a linear fit (R^2 = 0.788), quadratic fit (R^2 = 0.960), exponential fit (Fig. 2a; R^2 = 0.976) and cubic fit (Fig. 2b; R^2 = 0.982). Compared to the exponential and cubic plots with values in AP, the plots with values in GP show higher coefficient of determination (R^2) and lower standard error of estimate (S = 0.159 for exponential plot and 1.666 for cubic plot; Table 2). Thus the above data supports the values taken in GP of the color bands. However when the color value of coal was increased many folds with respect to the other 3 lithobands, the correlation between TCA and TOC was seen to fall. For example when values of 1, 3, 9 and 27 (a = 1, r = 3) were given to silt, gray shale, dark shale and coal bands respectively, the coefficient of determination dropped and standard error of estimate increased for both exponential and cubic plots [R^2 = 0.925 and S = 0.286 for exponential plot; R^2 = 0.977 and S = 1.880 for cubic plot]. Similar fall was observed when values of 1, 4, 16 and 64 (a = 1, r = 4) were given to the respective horizons (Table 2). Thus the color values of the bands in GP with scale difference (a) 1 and common ratio (r) 2 is the most appropriate one. TCA (with values in GP where a = 1, r = 2) of the samples vary from 1.21 to 6.17, while the TOC content varies from 0.82 to 46.30 wt % (Table 1).

Logarithmic values with base 2 [the value of base being equal to r of the GP series; in this case common ratio (r) = 2] of both TOC and TCA were taken and the plot between the two was tested with a linear fit (Fig. 3; R^2 = 0.969). Here by multiplying a factor (F_{TOC} = 1.75) with $\log_2$ (TCA) gives the estimated $\log_2$ TOC. It thus represents: $\log_x$ (TOC) ∝ $\log_x$ (TCA), where x = integer; $x > 1$ (in this case x = 2). The thus estimated TOC values are close to the measured TOC values (Table 1) within a range of 0–2 ($2 < E^{TOC} > 0$; E^{TOC} being expected TOC), except for samples A1, R18, U21 and CC3 i.e. those with TCA >5 and correspondingly very high TOC (Table 1). This essentially means that for samples with TCA >5, the TOC content increases many fold and cannot be estimated precisely by the above method. However a TCA value >5 would obviously indicate a horizon which is highly rich in organic matter. The method shows a higher level of accuracy for TCA ranging from 1 to 5. Thus for samples with TCA<5,

$$F_{TOC}[\log_2(\text{TCA})] = \log_2(\text{TOC}) \quad (2)$$

where F_{TOC} = 1.75 (in this case study)

3.1. Applicability of the findings

The authors have identified 4 lithobands (silt, gray shale, dark shale and coal) that dominantly occur in shaly sequences. The objective of giving a color value (1, 2, 4 and 8 respectively) to these