

HAM, who are less hypoxic than their counterparts, the HAC, at the same altitude, may have a selective advantage in a new extreme environment in maintaining routine physical activities. Higher level of SaO₂, if present in an individual, could be of immense utility, especially to mountaineers, trekkers, etc.

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Quantitative estimation of mineral matter in some Indian coals using interactive Rietveld-based full profile X-ray diffraction technique

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Four Indian coals with their relative density fractions have been studied for quantitative estimation of mineral matter by X-ray diffraction technique using Rietveld-based full profile refinement method. The SIROQUANT™ software has been used for this purpose, where Rietveld parameters are adjusted interactively. The mineral analyses are consistent when compared with chemical analyses. Associative nature of mineral matters with macerals in different fractions of coal is observed.

X-RAY diffraction (XRD) technique has been used in the study of Indian coals so far only for identification of mineral phases present, but no quantitative estimation of crystalline phases has been done till date. It is well known that mineral phases play an important role during the commercial utilization of coal, such as in boiler erosion, ash formation and slagging^{1–3}. It is essential to know the proportion of each mineral matter, as it controls the melting and crystallization behaviour in the ternary or quaternary phase diagrams. Hence, only the elemental or oxide compositions of mineral matter in coal are not sufficient for complete understanding of coal utilization processes. In particular, Indian coals are of drift origin, and concentration of mineral matter is higher relative to that in coals occurring in other parts of the world. Hence, quantitative estimation of crystalline phases in coal will also help in understanding the origin and geology of the concerned coal. The present study is an initial step towards quantification of mineral matter of some Indian coals using X-ray powder diffraction profile. Several relative density (RD) fractions of coals have been chosen to find any associational behaviour of minerals with different macerals in coal. The calculated compositions of the oxides obtained from quantitative estimation of mineral matter (in ideal form) have been compared with the actual chemical composition obtained from chemical analysis.

XRD is an important tool for identification of crystalline phases and it is also used for determination of minerals in coal. Identification of minerals in coal is mostly done with powdered raw coal or low-temperature ash

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(LTA) of the coal. XRD was not considered as an authentic tool for quantification of mineral matter due to limitations associated with it, such as dependence of line intensity on mineral crystallinity, preferred orientation of mineral matter while sample mounting and differential X-ray absorption by mineral matter. Nevertheless, several methods, e.g. direct analysis of two-component system, multicomponent system, internal standard analysis of single and multicomponent, and analysis by dilution of sample, etc. were suggested for quantification of mineral phases in rocks by XRD⁴⁻⁷. Some methods were used for semi-quantitative estimation of mineral matters in coal⁸⁻¹¹. The full profile of XRD has the advantage that residual errors caused by intensity aberrations, for example, due to preferred orientation in platy minerals, not completely removed in the specimen preparation stage, or imperfect structural models, tend to be positive and negative over the whole profile leaving the Rietveld phase-scaling factors largely unchanged. Powder data suffer severe limitations due to these problems. Since only d -spacings are measured from a powder diffraction pattern, all the information from the three-dimensional reciprocal space lattice is compressed into one-dimension. Overlap of reflections is the biggest problem for a crystallographer, to decompose the pattern in order to obtain the individual line-profile parameters of each reflection. Rietveld¹² introduced a technique by which a crystal structure model can be refined from an experimental powder diffraction pattern using the method of least squares. A calculated model can be fitted to the observed powder diffraction pattern in order to obtain parameters

which define each reflection. He obtained a formula for the calculated intensity $Y_{\text{cal}}(i)$ at some point i as $Y_{\text{cal}}(i) = \sum_j h_{j(\text{cal})}(i)$, (where $h_{j(\text{cal})}$ is the contribution at i from the j th peak and summation is overall reflections that contribute at the point i), in the background corrected pattern profile of a single-phase, and devised a computer program for structural refinement from the single-phase powder data profile. Rietveld used 14 instrumental parameters, including the mineral (phase) scaling factor, asymmetry, preferred orientation, half-width, instrument zero, line shape and unit-cell parameters. Several authors¹³⁻¹⁶ have extended this approach to quantify crystalline mixtures, including multiphases. The extension allows a calculated XRD profile of each mineral phase to be generated from its known crystal structure and the sum of all calculated patterns to be fitted to the observed XRD pattern of a multi-mineral sample by iterative least-squares analysis, to find optimum individual phase scales. These are then used to determine the mineral percentages in the sample.

Taylor¹⁷ developed a personal computer-based software, SIROQUANTTM, using Rietveld refinements for quantitative estimation of up to 25 mineral phases at a time from a conventional X-ray diffractogram. The Rietveld parameters can be refined interactively in the program. The adjustments may be performed for variations due to atomic substitution, layer disordering, preferred orientation, amorphicity and other factors used in the standard pattern. The SIROQUANT software has been used by several workers¹⁸⁻²¹ for mineral quantification of whole-coal samples by XRD. The results have been found to be consistent with other analytical results.

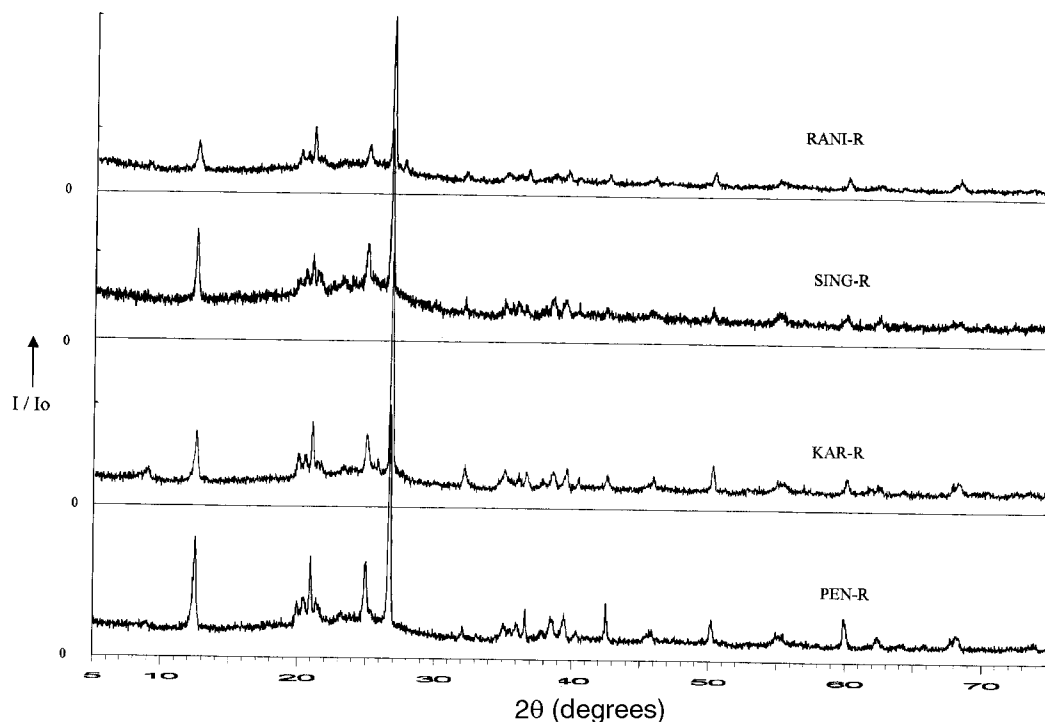


Figure 1. X-ray diffractograms of four raw coals.

RESEARCH COMMUNICATIONS

Four coal samples from Raniganj, South Karanpura, Singrauli and PENCH-KANHAN coalfields, which are named as RANI, KAR, SING and PEN, respectively are studied using XRD for quantification of mineral matter. Each coal sample has been further fractionated into two different RD fractions, which corresponds to the enrichment of vitrinite or inertinite content. Vitrinite-rich fractions are RD cuts at < 1.3 (RD) for PEN, < 1.5 (RD) for KAR and < 1.4 (RD) for RANI and SING coals, whereas inertinite-rich fractions are RD cuts > 1.4 (RD) for PEN and > 1.5 (RD) for KAR, RANI and SING coals. Vitrinite-rich, inertinite-rich and raw coals are designated as V, I and R, respectively, after the name of the coals. Thus, for example vitrinite-rich fraction from Singrauli coalfield will be referred as SING-V.

The size of samples as received was nearly $210\ \mu\text{m}$. They were ground to $15\ \mu\text{m}$ size in an agate mortar in alcohol for half an hour and air-dried to get rid of any moisture and alcohol. XRD patterns of the samples were

then recorded in the D-8 ADVANCE (Bruker AXS, Germany) diffractometer with Bragg-Brentano geometry, using parallel beam $\text{CuK}\alpha$ radiation from 5 to 75° in 2θ with 0.02° step interval and $2\ \text{s/step}$ count-time. The minerals were identified with reference to the JCPDS Powder Diffraction File.

Quantitative estimation of the minerals was made with the help of the SIROQUANT software for each sample by processing the individual diffractograms. This was done by creating the Rietveld-format XRD data (.hkl) files for each mineral present in the samples. Crystal-structure information for individual minerals is obtained from the SIROQUANT databank. ASCII files were obtained by this process, which also includes information about the plane of preferred orientation and data for anomalous dispersion. A task file (.tsk) was created for individual analysis with the listing of the minerals present in the sample. All the diffractograms (Figure 1) have high background due to scattering of X-rays by the or-

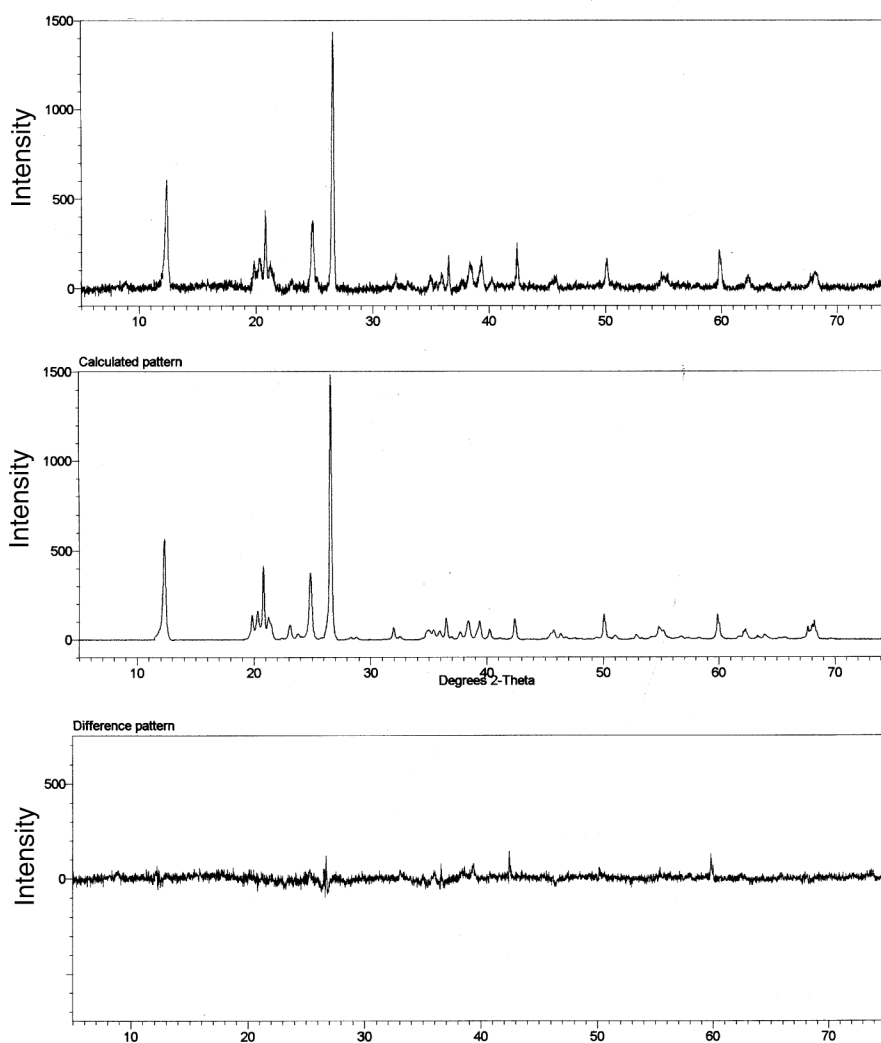


Figure 2. Observed, calculated and difference patterns of PEN-R coal for SIROQUANT analysis.

ganic matrix of the raw coals. The patterns, after background correction, are due to crystalline mineral matter.

The Rietveld parameters were adjusted interactively and the best-fit to the observed diffraction pattern was obtained for individual minerals in the task file. Full-profile fitting of the diffractogram was made by refining parameters like intensities of the individual mineral phases (scale factor), unit-cell dimensions, line-widths, preferred orientations, and global parameters like zero-setting of the diffractometer progressively. At the end of each stage of refinement, weight per cent of each mineral phase and global χ^2 values are obtained. Global χ^2 value signifies the goodness of the fit between the observed and calculated profiles. For a perfect fit, the global χ^2 value approaches 1.0. The March Function²² was used for preferred orientation correction of the siderite phase, and the mineral percentage was adjusted accordingly. A nominal diameter of 15 μm was used for all mineral phases. Final results of the SIROQUANT analysis were obtained from each task when the best possible fit had been achieved between the observed and the computed XRD patterns. Figure 2 shows the experimental, calculated and difference patterns for PEN-R sample. Mineral percentages and χ^2 values thus obtained for all the coal samples are

shown in Table 1. The total error associated with each SIROQUANT analysis may be derived by the equation $e_i \chi^2$, where e_i is the error associated with each mineral.

The RD fractions have been considered in this study to find any associative behaviour of minerals with macerals. Indian coals are of drift origin, and hence quartz and kaolinite are the bulk of the mineral matter. Siderite is present in all samples. KAR-I and RANI-I coals contain illite, and RANI-I and RANI-R contain microcline. Siderite, being the denser among all these minerals, was expected to be enriched in the higher density cut fractions, i.e. the inertinite fractions, but it is actually enriched in the lower RD fraction, i.e. in the vitrinite-rich part. Illite concentration has increased in the inertinite fraction of KAR and RANI coals. These may be due to the fact that siderite and illite are inherently associated with vitrinite and inertinite respectively, from the coalification process.

Oxide compositions have been calculated from the SIROQUANT mineral composition (Table 2), where stoichiometric compositions of mineral phases are used. Chemical compositions of inorganic matter for each fraction have been determined by conventional wet chemical method (Table 3). Chemical compositions have been re-

Table 1. Mineral composition (in wt%) of coal samples using SIROQUANT (numbers in brackets are percentage of error associated with the mineral)

Mineral	RANI-R	RANI-V	RANI-I	KAR-R	KAR-V	KAR-I	SING-R	SING-V	SING-I	PEN-R	PEN-V	PEN-I
Kaolinite	35.1 (1.3)	48.6 (2.6)	33.2 (1.3)	39.8 (1.0)	31.5 (1.5)	38.1 (1.2)	58.6 (1.7)	49.5 (2.9)	47.7 (1.8)	48.6 (1.1)	48.5 (2.0)	57.4 (1.2)
Quartz	54.0 (1.3)	46.3 (2.4)	56.6 (1.5)	46.9 (0.9)	48.4 (1.3)	42.3 (1.1)	39.3 (1.3)	41.3 (2.6)	41.3 (1.5)	46.0 (1.0)	43.0 (1.6)	42.6 (1.0)
Siderite	4.7 (0.6)	5.1 (1.4)	3.9 (0.8)	10.9 (0.5)	15.9 (0.9)	4.2 (0.4)	2.1 (0.5)	9.2 (1.4)	11.0 (0.8)	5.4 (0.4)	8.5 (0.6)	–
Illite	–	–	1.9	2.4 (0.6)	4.2 (0.9)	15.4 (1.1)	–	–	–	–	–	–
Microcline	6.2	–	4.4 (0.5)	–	–	–	–	–	–	–	–	–
χ^2	2.78	2.54	2.59	2.95	3.19	2.91	2.69	2.80	2.63	3.30	3.08	2.96

Table 2. Calculated oxide compositions as obtained from SIROQUANT mineral analysis

Oxide	RANI-R	RANI-V	RANI-I	KAR-R	KAR-V	KAR-I	SING-R	SING-V	SING-I	PEN-R	PEN-V	PEN-I
SiO ₂	78.8	75.5	81.16	73.44	72.68	72.41	73.15	71.83	71.27	75.32	73.04	75.37
Al ₂ O ₃	15.9	21.03	15.20	18.52	15.72	22.66	25.42	21.81	21.08	21.0	21.4	24.63
FeO	3.08	3.46	2.60	7.39	11.03	2.96	1.43	6.36	7.65	3.68	5.56	–
K ₂ O	2.22	–	1.04	0.65	0.57	1.97	–	–	–	–	–	–

Table 3. Chemical analysis of inorganic matter in coals

Oxide	RANI-R	RANI-V	RANI-I	KAR-R	KAR-V	KAR-I	SING-R	SING-V	SING-I	PEN-R	PEN-V	PEN-I
SiO ₂	63.3	55.34	64.48	61.04	59.6	61.48	57.94	50.96	57.28	59.2	57.8	60.84
Al ₂ O ₃	22.48	28.15	22.83	25.00	24.03	27.56	26.19	30.98	27.99	26.35	24.49	28.43
Fe ₂ O ₃	4.79	3.79	3.19	6.99	9.58	5.59	9.98	7.78	8.38	5.59	5.59	3.19
TiO ₂	1.84	1.68	1.76	0.96	1.68	0.64	2.12	2.04	1.84	1.96	1.52	1.84
P ₂ O ₅	0.79	1.53	1.47	0.65	0.61	0.21	0.66	0.5	0.44	0.30	0.20	0.14
SO ₃	0.19	0.82	0.69	0.26	0.47	0.27	0.69	1.32	1.3	1.73	3.11	1.52
CaO	3.4	4.61	2.08	1.33	0.93	0.75	0.94	2.51	0.74	2.71	4.33	1.96
MgO	0.71	1.77	0.85	0.57	0.31	0.29	0.66	1.98	0.6	0.56	0.61	0.72
Alkali + undetermined	2.5	2.31	2.65	3.2	2.79	3.21	0.82	1.93	1.43	1.60	1.95	1.36

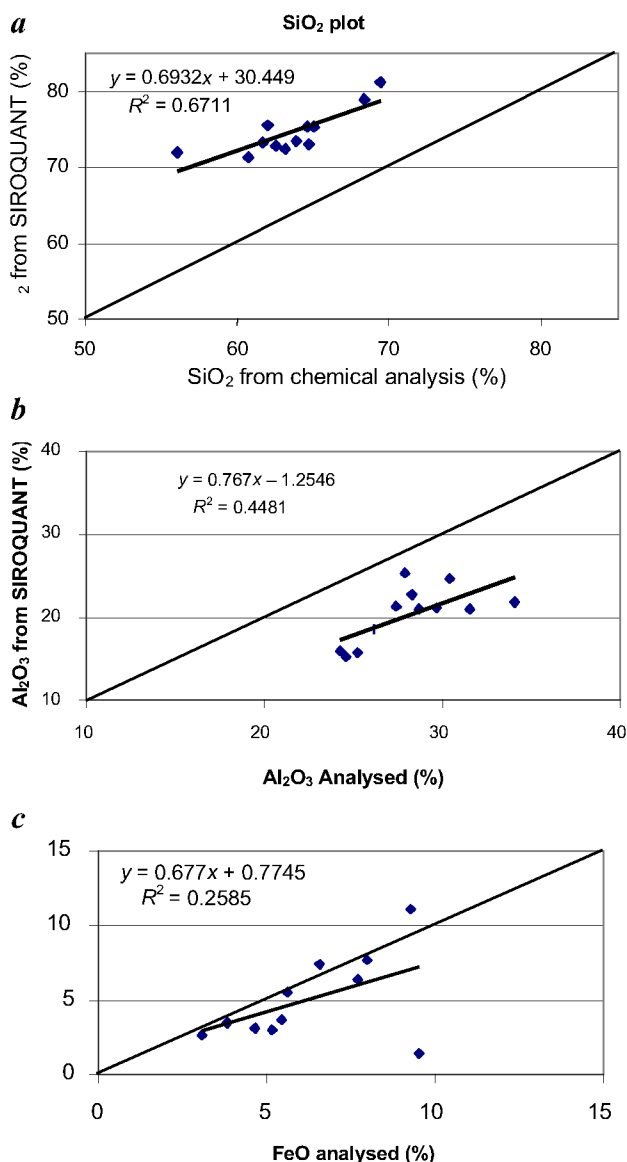


Figure 3. Regression plot of chemical analysis vs calculated oxide composition from SIROQUANT for *a*, SiO₂; *b*, Al₂O₃ and *c*, FeO.

calculated for four oxides, namely SiO₂, Al₂O₃, K₂O and FeO (Fe₂O₃ has been stoichiometrically converted to FeO) and have been compared with the oxide compositions obtained from SIROQUANT analysis (Figures 3). Linear regression lines have been plotted for each component and equation, and the correlation coefficient for each regression line ($y = mx + c$) has been shown.

The regression equations for SiO₂, Al₂O₃ and FeO have slopes of 0.69, 0.76 and 0.67 respectively, which are moderately high, showing the reliability of the mineral quantification by SIROQUANT. SiO₂ values calculated from SIROQUANT are consistently about 10% higher than the chemical analysis data, whereas Al₂O₃ values are lower for similar cases. Linear regression graphs for FeO and Al₂O₃ have lower correlation coefficients and intercepts (R^2 : 0.258, 0.448 and c : 0.774,

1.254), but for SiO₂ the graph has moderately high correlation coefficient (R^2 : 0.67) and intercept (c : 30.39) values. The FeO regression graph gives low correlation coefficient due to one datapoint from SING-R coal, which is an outlier data with unknown reason. If we plot another regression graph for FeO with the remaining datapoints, R^2 increases to 0.846, which is quite high. Siderite is absent in the XRD analysis of PEN-I coal, leading to the absence of FeO in its corresponding calculated oxide composition, and hence has not been considered for comparative study of FeO.

This study is an initial step towards quantification of mineral matter in Indian coals. XRD of coal samples without ashing process and quantification of mineral matter by SIROQUANT technique is in good agreement with chemical analysis and other studies^{19,20,23}. Study of associative nature of minerals with macerals is in progress.

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