Quantitative determination of haematite and chalcopyrite in metamorphic rocks using infrared spectroscopy

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Abstract . The infrared spectroscopic analysis of metamorphic rock samples from Mamandur multimineral complex was investigated Infrared spectra (4000 cm⁻¹ to 200cm⁻¹) were obtained for 24 samples collected from different sites and altitudes of Mamandur hills The observed results show the presence of quartz, microcline feldspar, sillimanite, magnetite, haematite, chalcopyrite and sphalerite minerals The presence of the peak at 695cm⁻¹ confirms the crystallinity of quartz. The quantitative analysis of iron bearing mineral (haematite) and copper bearing mineral (chalcopyrite) yields an average amount of 14.9% and 4 6% respectively.

Keywords FTIR, mineral identification, chalcopyrite, haematite

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1. Introduction

The scientific studies of the identification of the minerals in ore deposits lead to useful information about the possible origin of the minerals and give great impetus to the industrial development. For this reason, the study of minerals has been a dominant area of research having key role in the economic growth of a nation.

Since the pioneering work of Stubican and Roy [1] in the assignments of infrared bands for minerals through synthesis of known composition and the works of Farmer *et al.* [2], Wilkins [3], Russell *et al*, [4], Russell and Fraser [5] and Flanigen *et al* [6], there has been considerable progress in the development and application of infrared techniques to the study of soil and rock mineralogy. Lyon [7] listed characteristic peaks for a number of minerals and gave the patterns for mineral series. Qualitative analysis of rocks and clays including soil clays have been made by many workers [2,4,8], but the quantitative estimation is found to be meagre.

As a preliminary step to test the applicability of the infrared method to the analysis of whole rocks, the method was first applied to the samples of rock material. In the present study, the infrared analysis has been carried out as a tool to identify the

mineral content of metamorphic rocks collected from Mamandur multimineral complex of Tamilnadu. The qualitative estimation of all the minerals present in the samples and semi quantitative estimation of chalcopyrite ($CuFeS_2$) and haematite (Fe_2O_3) have been attempted.

2. Sample collection

The rock samples used in this study are collected from Mamandur multimineral complex, Tamilnadu at different heights from ground level to 30 feet, numbered as A to F. Some samples are from interior of the complex numbered as M1 to M8 and some more samples are from State Geology Department, Chennai, numbered as S1 to S9.

This deposit was first investigated by the Geological Survey of India followed by the State Geology Department. The exploratory mining was carried out by the Bharat Gold Mines Ltd., Karnataka.

3. Location of hills

The polymetal sulphide deposit (multimineral complex) is situated at about 2.5 kms south east of Mamandur (Lat. N, 12°02'; Long, E, 79°02') falling within the reserved forest limits of Kannankadu in Kallakurichi taluk, Cuddalore district, Tamilnadu [9]. This area

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can be approached by road from Thiruvanamalai railway station (Rs) on the Villupuram Katpadi metregauge section of Southern Railway at a distance of 40 kms south of Thiruvannamalai.

The nature of base metal deposit comprises of sulphide ores mainly of zinc and lead with a small percentage of copper occurring in a garnolithic terrain beloging to the Archean complex of south India.

4. Sample preparation

The samples are usually subjected to various pre-treatments in order to remove organic matter and certain other materials to improve the quality of the spectrum. Wet grinding is carried out by taking 5 to 10 mg of the sample in an agate mortar and then by adding 10 to 15 drops of ethanol. The samples are ground most preferably through hand grinding, avoiding rigorous rotatory motion until ethanol evaporate completely. The 53μ grain-sized samples are mixed with KBr in the ratio of 1:20 and the pellets were prepared, which are of 1mm in thickness and 13mm in diameter [10].

5. Experimental technique

The PYE – UNICAM SP3 – 300 double beam spectrophotometer was used for recording spectra of the samples with a scan time of 7 minutes. The instrument was calibrated for its accuracy with the spectra of a standard polystyrene film. The resolution is $1.5\,cm^{-1}$ at $1000\,cm^{-1}$ region and $3\,cm^{-1}$ at $3000\,cm^{-1}$ region and the accuracy is $\pm 4\,cm^{-1}$ in $4000\text{-}3000\,cm^{-1}$ region and $\pm 2\,cm^{-1}$ in $2000\text{-}200\,cm^{-1}$ region.

For each sample, five pellets were prepared and the spectra were taken in the region of 4000 to 400 cm^{-1}. The best one containing well resolved maximum number of peaks, is taken for
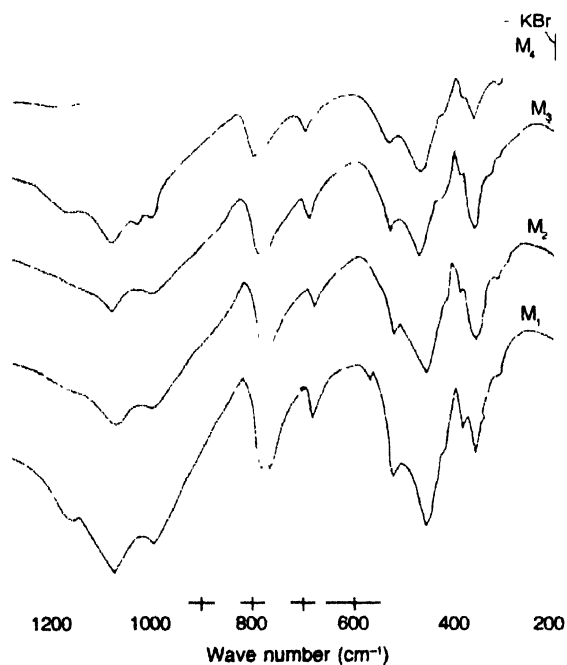

Figure 1. Infrared absorption spectra of Mamandur rock samples collected from interior portion of the mines (sample nos. M_1 to M_4 and KBr).

analysis. Some of the representative spectra are shown in Figures 1-3. Since no absorption peaks are present in the region of 1200 to $4000\,cm^{-1}$, the trace of the spectra in the region of 200 to 1200 cm^{-1} is only shown.
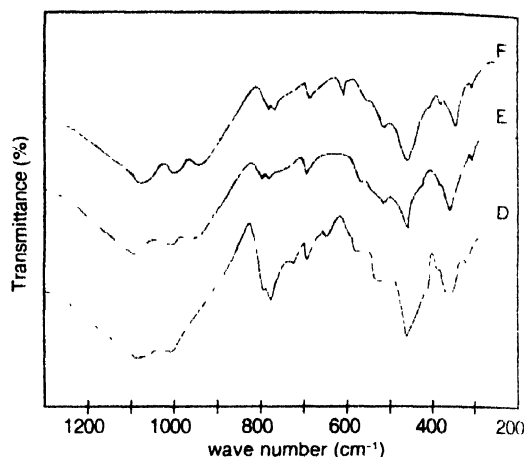

Figure 2. Infrared absorption spectra of Mamandur rock sampl from different heights (3 to 60 feet) (sample nos. D to F)
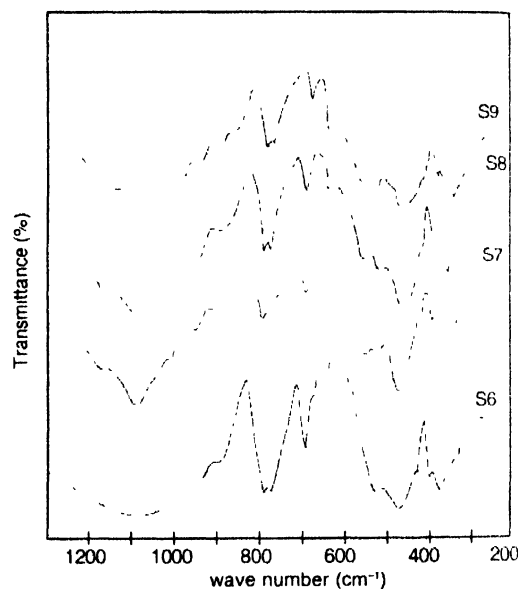

Figure 3. Infrared absorption spectra of Mamandur rock samples obtained from the state Geology Department, Chennai (sample nos. S_6 to S_9)

6. Results and discussion

The infrared spectra of all the samples collected from Mamandur multimineral complex have been recorded and are shown in the Figures 1-3. The observed absorption frequencies from the sample spectra are tabulated in Tables 1-3.

The spectra of the samples indicate the presence of quartz, microcline feldspar, sillimanite, magnetite, haematite, chalcopyrite and sphalerite. The different modes of vibration assigned to the observed frequencies depend upon the fundamental modes of vibrations viz., stretching, bending and lattice modes. The vibrational frequencies of these modes for the species under study vary considerably depending on parameters such as crystal forms, impurities etc.

Table 1. Observed frequency of the absorption bands of the samples (M1 to M8) in the region of 200-1200 cm⁻¹ and the minerals proposed.

Sample number	Observed absorption frequency					Proposed mineral present in the sample	References
M1	1172	1085	798	779	695	Quartz	11-13
	1000	420				Microcline	7,12,14
	575					Magnetite	17
	520	468	390			Haematite	15
	361	323				Chalcopyrite	18,19
M2		1085	797	778	695	Quartz	11-13
	1000	420				Microcline	7,12,14
	520	468	390			Haematite	15
	360	321				Chalcopyrite	18,19
M3		1084	798	780	697	Quartz	11-13
	1005	420				Microcline	7,12,14
	520	468	391			Haematite	15
	361	323				Chalcopyrite	18, 19
M4	1172	1085	798	778	695	Quartz	11-13
	1030	1000	420			Microcline	7,12,14
	520	468	390			Haematite	15
	361	323				Chalcopyrite	18, 19
M5	1172	1085	798	779	697	Quartz	11-13
	1000	422				Microcline	7,12,14
	521	468	392			Haematite	15
	361	323				Chalcopyrite	18, 19
M6	1172	1085	798	778	695	Quartz	11-13
	1000					Microcline	7, 12, 14
	575					Magnetite	17
	540	520	467	390		Haematite	15
	360	323				Chalcopyrite	18, 19
	797	776				Quartz	11-13
	468	391				Haematite	15
	361	323				Chalcopyrite	18, 19
M9	468					Haematite	15
	361	323				Chalcopyrite	18, 19

Table 2. Observed frequencies of the absorption bands of the samples (A to F) in the region of 1200-2000 cm⁻¹ and the minerals proposed

Sample number	Height in feet	Observed absorption frequency				Proposed mineral present in the sample	References
		1034	793	779	697	Quartz	11-13
		1000	720	640		Microcline	7,12,14
		540	575	468	390	Haematite	17
		361	323			Chalcopyrite	15
							18, 19
		1085	797	778	697	Quartz	11-13
		1000	797	778	420	Microcline	7,12,14
		575				Magnetite	17
		520	467	390		Haematite	15
		361	321			Chalcopyrite	18, 19
		1085	798	780	697	Quartz	11-13
		1005	420			Microcline	7,12,14
						Magnetite	17
		520	468	391	575	Haematite	15
		361	323			Chalcopyrite	18, 19
		1084	798	779	697	Quartz	11-13
		1000	720	640	420	Microcline	7,12,14
15		575				Magnetite	17
		520	468	390		Haematite	15
		361	323			Chalcopyrite	18,19
		1085	798	780	697	Quartz	11-13
		1000				Microcline	7,12,14
45		960				Sillimanite	11,13
		560	520	390		Haematite	15
		361	323			Chalcopyrite	18, 19
		1085	798	780	697	Quartz	11-13
		1000				Microcline	7,12,14
60		960				Sillimanite	11,13
		560	520	390		Haematite	15
		361	323			Chalcopyrite	18, 19

From Tables 1-3, the observed IR absorption bands at 1085, 798, 779 and 697 cm⁻¹ for all the samples and a band at 1172 cm⁻¹ (S3 - S6, S7, S9, M1, M4 - M6) confirms the presence of quartz (SiO_2) [11-13]. The absorption at 1172 and 1084 cm⁻¹ may be assigned to Si-O asymmetrical stretching vibration and peaks at 798, 779 and 697 cm⁻¹ may be due to symmetric stretching vibrations. The results observed in the present study are similar with the results obtained by White [12] and Saksena [13]. The appearance of the peak 697cm⁻¹ confirms the crystallinity of the quartz [2]. The intensity of this 697 cm⁻¹ peak shows the nature of crystallinity. If the quartz is in crystallized form, then one can infer that all the other minerals are also crystalline in nature because quartz crystallizes finally during magmatization.

The appearance of bands at 1030 and 1000 cm⁻¹ due to Si (Al)-O stretching vibrations, 727 cm⁻¹ due to Si-O-Al compound vibrations, 640 cm⁻¹ due to Al-O coordination vibrations and 420 cm⁻¹ due to Si-O stretching vibrations suggest the presence of microcline ($KAl_2Si_3O_8$), another form of potash feldspar, mostly occurs in metamorphic rocks [7,12,14]. On the lines of White [14], the presence of the peak in the range 770-720 cm⁻¹ confirms that the feldspar structure is in disorder state. It disturbs the Al/Si order in the structure. The IR absorption spectrum of the samples (S3 to S8, E and F) show weak shoulder peaks at 960 and 890cm⁻¹ due to tetrahedral SiO_4 group, which are the characteristic frequencies of sillimanite (Al_2SiO_5) [11,13]. Even though the presence of sillimanite is identified in some samples, the characteristic peak shows no importance from the scope of the present work, it is of importance in ceramic industry. On the basis of the characteristic of the IR absorption bands for haematite (Fe_2O_3) by McDevitt and Baun [15], the presence of the bands at 560, 540,520, 468 and 390 cm⁻¹ in our samples, may be due to the presence of haematite. From Tables 1-3, the differences observed in the locations of the IR peaks may be due to the isomorphous substitution, impurities, crystal defects

Table 3. Observed frequency of the absorption bands of the samples (S1 to S9) in the region of 1200-2000 cm⁻¹ and the minerals proposed

Sample number	Observed absorption frequency				Proposed mineral present in the sample	References
S1	1085	798	779	697	Quartz	11-13
	1005				Microcline	7,12,14
	468	390			Haematite	15
	323	300			Sphalerite	18,19
S2	1085	798	779	695	Quartz	11-13
	1000				Microcline	7,12,14
	520	468			Haematite	15
	300				Sphalerite	18,19
S3	1170	1082	779	788	697	Quartz	11-13
	1005	640	420		Sillimanite	7,12,14
	960	890			Microcline	15
	520	468	390		Haematite	18, 19
	361	323			Chalcopyrite	
S4	1172	1082	798	779	697	Quartz	11-13
	960	890			Sillimanite	7,12,14
	560	520	468	390	Haematite	15
	360	323			Chalcopyrite	18, 19
S5	1172	1082	798	779	697	Quartz	11-13
	1000	640	420		Microcline	7,12,14
	960	890			Sillimanite	11,13
	575				Magnetite	17
	520	468	390		Haematite	15
	361	323			Chalcopyrite	18, 19
S6	1082	797	778	695	Quartz	11-13
	640	420			Microcline	7, 12, 14
	960	890			Sillimanite	11,13
	520	468	390		Haematite	15
	361	323			Chalcopyrite	18, 19
S7	1170	1082	797	779	697	Quartz	11-13
	640	420			Microcline	7,12,14
	960	890			Sillimanite	11,13
	540	468	391		Haematite	15
	361	323			Chalcopyrite	18, 19
S8	1170	1082	797	779	697	Quartz	11-13
	640	420			Microcline	7,12,14
	960	890			Sillimanite	11,13
	540	468	391		Haematite	15
	361	323			Chalcopyrite	18, 19
S9	1172	1082	797	779	697	Quartz	11-13
	640	420			Microcline	7,12,14
	960	890			Sillimanite	11,13
	540	468	391		Haematite	15
	361	323			Chalcopyrite	18, 19

and the degree of crystallinity [16]. Hence, the IR absorption peaks of the haematite present in our samples, need not be located at the same frequencies as that obtained by other workers.

From the spectra of the some samples (S5, M1,M6, B,C and D), the peak at 575 cm⁻¹ corresponding to magnetite (Fe_3O_4) is

broad, diffused and very well resembles with the spectra of magnetite obtained by Kodama [17]. With reference to the nature of peaks, the content of magnetite in our samples is meagre. The presence of the chalcopyrite $(Cu_2 SFe_2 S_3)$ in all samples except S1 and S2, can be explained by appearance of the IR absorption peaks at 372, 365-360 and 323 cm⁻¹ which are the characteristic peaks of chalcopyrite [18,19]. In the sample number S1 and S2, sphalerite (Zn, Fe)S is also present as is evident from the presence of the characteristic IR absorption peak at 300 cm⁻¹ [18,19]. A correlation between Zn-content of sphalerite and the frequency of absorption has been attempted by Liese [18] He found that as the Zn-content increased the frequency of absorption gets decreased. In the spectra of our samples S1 and S2, no such alteration in the position of the IR absorption peaks has been noticed. Hence, the zinc-content may be the same in these samples.

Quantitative estimation of haematite and chalcopyrite

The quantitative estimation through infrared analysis may be achieved using Bouguer – Beer law and the relationship is given by the equation,

$$A = -\log (I/Io) = \log (Io/I) = abc,$$

where A: absorbance, a: absorptivity, b: path length, c: concentration, I_o: intensity of the incident radiation and I: intensity of the transmitted radiation.

This equation states that a straight-line relationship can be obtained from a plot of absorbance against concentration.

In the present investigation, it has been attempted to estimate the amount of haematite and chalcopyrite for all the samples. Nearly pure haematite and chalcopyrite samples have been obtained from state Geology department, Chennai and the respective IR spectra with different concentration of samples are recorded. The peaks corresponding to the characteristic frequency 468 cm⁻¹ of haematite and 361 cm⁻¹ of chalcopyrite are identified and the absorbance at different concentration are reported in Tables 4 and 5. The calibration curves were obtained for haematite and chalcopyrite are shown in Figures 4 and 5.
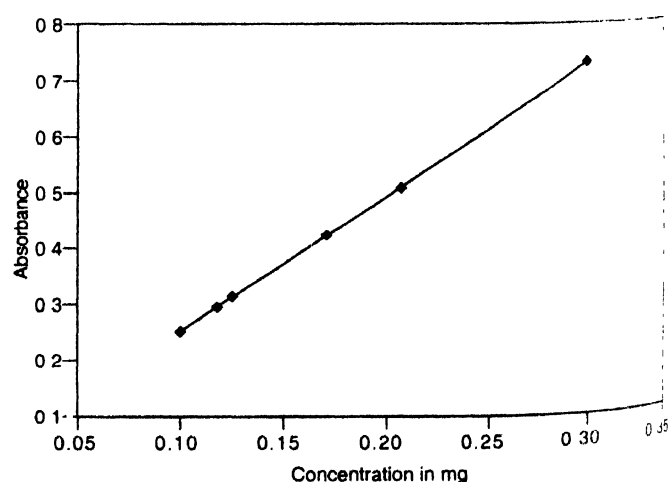

Figure 4. A plot of absorbance *versus* concentration of haematite

Making use of these curves, the amount of haematite and chalcopyrite in different samples of Mamandur are estimated and are given in Tables 4 and 5.
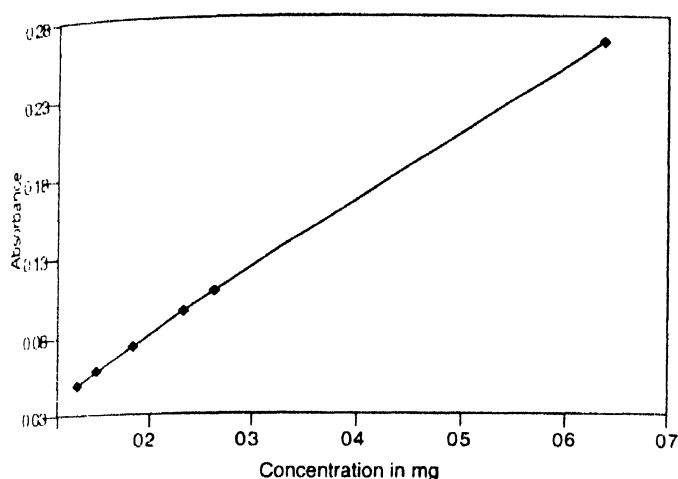

Figure 5. A plot of absorbance versus concentration of chalcopyrite

Table 4. The percentage content of haematite in the rock Mamandur rock samples with reference to the absorbance of 468 cm⁻¹ peak

Sample number	Height in feet from ground level	Absorbance in mg	Concentra in mg	% Content of haematite
M1	–	0 287	0 12	19 18
M2	–	0 227	0 09	14 63
M3	–	0 357	0 15	21 90
M4	–	0 104	0 04	7 75
M5	–	0 138	0 06	13 51
M6	–	0 136	0 05	13 02
M7	–	0 086	0 03	3 50
M8	–	0 106	0 04	7 75
A	3	0 341	0 14	30 33
B	6	0 368	0 15	26 00
C	9	0.120	0.05	11 39
D	15	0 249	0 010	13 00
E	45	0.082	0 03	13 12
F	60	0 106	0 04	9.11
S1	–	0.170	0.070	4 81
S2	–	0.079	0 052	4.48
S3	–	0.180	0 072	13 13
S4	–	0.285	0 115	7 90
S5	–	0 399	0 0160	30 80
S6	–	0 619	0 240	12.63
S7	–	0.205	0.080	19 29
S8	–	0.681	0.275	18 90
S9	–	0.628	0.252	15 40

Table 5. The percentage content of chalcopyrite in the rock Mamandur rock samples with reference to the absorbance of 361 cm⁻¹ peak

Sample number	Height in feet from ground level	Absorbance in mg	Concentration in mg	% Content of Chalcopyrite
M1	–	0 96	0 023	3 73
M2	–	0.16	0 039	6 33
M3	–	0 27	0 066	9 82
M4	–	0.06	0 015	2 80
M5	–	0 92	0 022	5 30
M6	–	0 53	0 013	3 01
M7	–	0 16	0 040	5 60
M8	–	0 19	0 046	6 51
A	3	0 142	0 034	7 37
B	6	0.238	0 058	7 94
C	9	0 669	0 016	3 64
D	15	0 132	0 0032	4 16
E	45	0 027	0 007	2 87
F	60	0 038	0 009	2 04
S1	–	0 542	0 021	3 23
S2	–	0 238	0.019	2 98
S3	–	0 087	0 020	3 73
S4	–	0 051	0 012	0 82
S5	–	0 182	0 044	5 72
S6	–	0 748	0 018	4 80
S7	–	0 543	0 013	3 13
S8	–	0 259	0 063	4 33
S9	–	0 249	0 060	3 66

From Table 4, it is observed that the haematite (in the samples M1 to M8) contents are found to be varying from 3.50 to 21.90%. Similarly for the samples A to F collected at different heights, the percentage content (by weight) of haematite varies from 9.11 to 30.33%. For the samples S1 to S9 the percentage values varies from 4.48 to 30.80%. From Table 4, it is evident that the haematite-content in the samples A to F found to decrease with increase of height.

From Table 5, it is observed that the percentage content of (by weight) chalcopyrite for the samples M1 to M8 is found to vary from 3.01 to 9.82%, for the samples A to F, the values vary from 2.04 to 7.94% and for S1 to S9, the values vary from 0.82 to 5.72%. It is also seen from Table 5 that the amount of copper mineral (chalcopyrite) appears to decrease with the increase of height approximately by 70% for the sample numbers A to F. The percentage content of Cu metal works out approximately to be 1.2 when the molecular weight of chalcopyrite is considered.

7. Conclusion

The improved technique outlined in the present paper provides a rapid, reproducible and accurate method of determination of minerals qualitatively and quantitatively. From the above studies, it is concluded that the minerals identified in all samples are quartz, microcline feldspar, sillimanite, haematite, magnetite, chalcopyrite and sphalerite. With reference to the number of peaks in the sample spectra, quartz and haematite are found to be the major minerals. Chalcopyrite and microcline are found to be minor minerals and other minerals are traces.

The quantitative analysis of iron bearing mineral haematite and copper bearing mineral chalcopyrite of all samples yields an average percentage of 14.9% and 4.6% respectively. Both these contents decrease with increase of height.

Out of these three sets (M1 to M8, A to F, and S1 to S9), the percentage content of haematite is highest in the sample number S5 (3 feet above the ground level) as 30.8% and lowest in the sample number M7 as 3.50% and the percentage content of chalcopyrite is highest in the sample number M3 and lowest in the sample number S4.

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