Chapter 31

X-RAY DIFFRACTION AND IR SPECTROSCOPY OF THREE FORMS OF SILICA AND MINE DUSTS

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ABSTRACT

Different mixtures of the three polymorphs of silica viz. quartz, cristobalite and tridymite are analyzed by x-ray diffraction (XRD) and their IR spectra are investigated by photoacoustic spectroscopy. It is observed that XRD provides a higher resolution to distinguish between the three polymorphs in a sample than IR spectroscopy. In the latter, a sharp band near 617 cm^{-1} is characteristic of both cristobalite and tridymite. A mine dust sample is quantitatively analyzed by XRD and it is shown to contain illite, quartz, kaolinite and calcite.

INTRODUCTION

At present, coal mines are regulated for total dust index as well as for 'free silica' index, the free silica being the three polymorphs of SiO$_2$ viz. quartz, cristobalite and tridymite. In the P7 method adopted by MSHA, free silica is determined by the intensity of the band near 795 cm^{-1} in IR spectroscopy (see e.g. Friedman 1978). Since all the three polymorphs give this band, the method does not distinguish between quartz, cristobalite and tridymite, although most mine dusts are believed to contain only quartz. Collaborative tests with x-ray diffraction (XRD) and IR spectroscopy using laboratory-generated quartz dusts accuracy of the free silica index was limited to only within 25% of the true value 95% of the time (Anderson 1983). In a recent paper, Bish and Chipera (1987) have reviewed the problems and solutions in quantitative analysis of complex mixtures by XRD.

In this paper, we address the questions of developing criteria for distinguishing between quartz, cristobalite and tridymite using IR spectroscopy and XRD, and apply the criteria to a laboratory-generated dust and a coal mine dust. It is noted that a new method viz. the Rietveld method of quantitative analysis (Rietveld 1969) may be able to minimize many of the problems encountered in the analysis of coal mine dusts using XRD.

EXPERIMENTAL SECTION

The samples of pure quartz, pure cristobalite, tridymite with a mixture of quartz, quartz with a mixture of cristobalite, tridymite, and kaolinite, and a mine dust sample were investigated in this work. The XRD spectra were recorded with a fully automated Rigaku/DMax diffractometer in the 2θ range of 5° to 75°, at a scan speed of 1°/min and a scanning interval of 0.01°, using Cu-k$_\alpha$ radiation. For identification of the minerals, the data from the JCPDS files were used.

The IR spectra of the samples were recorded employing the photoacoustic spectroscopic technique, since in this technique no sample preparation is needed and powder samples can be run as obtained. The spectra were recorded with an FTIR spectrometer (Mattson Instruments Cygnus 100), equipped with a photoacoustic cell (MTEC Model 100). Some details of the photoacoustic spectroscopy of silica particles

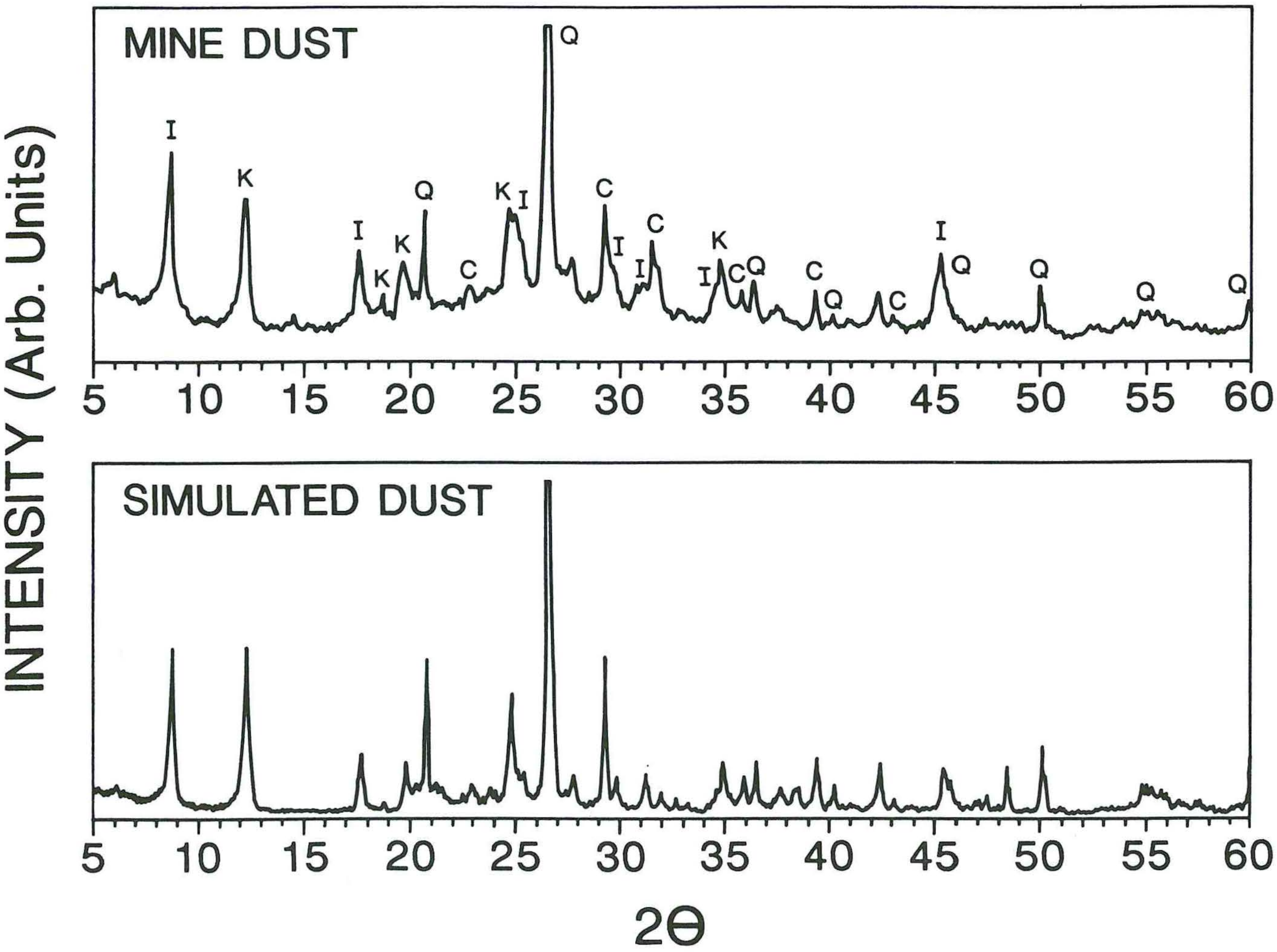

Figure 1. X-ray diffraction patterns of the natural and laboratory generated dust samples.

are given in one of our recent papers (Seehra and Pandurangi, 1989).

EXPERIMENTAL RESULTS AND DISCUSSION

X-Ray Analysis:

In Fig. 1, we show the diffraction pattern of a coal mine dust and a simulated spectra of the dust. The comparison shows near perfect agreement between the two spectra. The simulated spectra was obtained as follows: First the peaks in the dust sample were identified using the JCPDS files. Besides α-quartz, the other mineral present were illite, calcite and kaolinite. Non-overlapping strong peaks for each of these minerals were then selected for quantification purposes. The calibration curves for semiquantitative analysis were obtained using XRD of the binary mixtures of quartz with all minerals mixed in various proportions. Knowing the values of relative integrated intensity ratios of selected peaks of illite, kaolinite and calcite with respect to the quartz peak at $2\theta = 26.66°$ in the dust sample, the amount of these minerals with respect to quartz were determined by comparing with the calibration curves. All spectra were recorded under similar conditions and the effectiveness of the procedure was then tested using a laboratory-generated dust based on the estimated values of the minerals (Fig. 1).

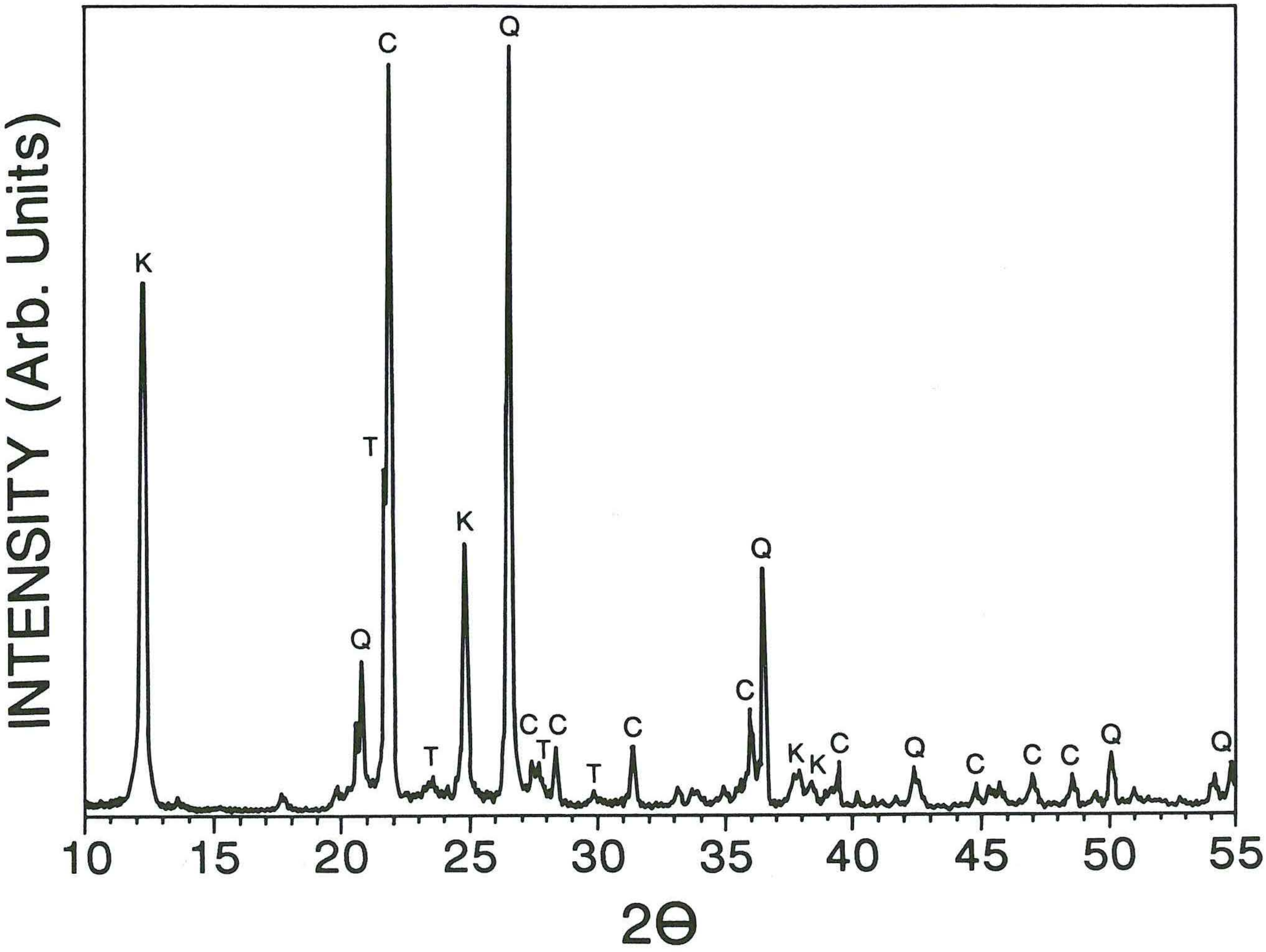

Figure 2. X-ray diffraction pattern of a mineral mixture containing equal amount (by weight) of quartz, cristobalite, tridymite and kaolinite.

In Table 1, we compare the peak positions and relative intensities of the 'natural' dust and 'prepared' dust. The agreement in relative intensity ratios is remarkable, considering that any errors due to preferred orientations or different particle sizes in the standards have been ignored. However, broad peaks and high background of dust sample spectrum compared to the spectrums obtained from standard material is indicative of the influence of small particles or the presence of amorphous material. So the percentage of minerals listed in Table 1 can be considered only as that relative to quartz. We are planning to determine the exact percentage of amorphous component in the dust sample by employing matrix flushing method using a suitable internal standard (Chung 1974).

We next examine the question of qualitative and quantitative analysis of cristobalite and tridymite, if present along with quartz, kaolinite and other components of the mine dusts. To develop a criterion for this purpose, we prepared a homogeneous mixture of nearly equal amounts (by weight) of quartz, cristobalite, tridymite and kaolinite (our tridymite sample had some quartz and minor quantities of unidentified impurities). Fig. 2 shows the x-ray diffractogram of this sample. Kaolinite and quartz give unique intense peaks at $2\theta = 12.34°$ and $26.66°$ respectively. On the other hand, the strong peak for cristobalite at $2\theta = 21.94°$ overlaps that of tridymite, although the two weaker secondary peaks at $2\theta = 31.50°$ and $47.11°$ are characteristic of cristobalite only, and a

Table 1. A comparison of the x-ray diffraction peak positions and intensities of natural and simulated dust samples.

Mineral	Estimated %	Peak position (2θ)		Relative Intensity	
		Natural dust	Prepared dust	Natural dust	Prepared dust
Illite	55.4	8.68	8.71	28.5	28.99
		17.59	17.63	13.14	13.15
Quartz	29.4	26.61	26.65	100	100
Kaolinite	6.8	12.23	12.18	21.31	24.66
		24.7	24.76	18.32	20.02
Calcite	8.4	29.31	29.23	18.91	20.99
		29.65	-	8.63	
		35.85	35.80	7.05	5.74
		39.29	39.32	9.69	9.28

Table 2. A list of primary and secondary x-ray diffraction peaks of kaolinite, quartz, cristobalite and tridymite that can be used for quantitative analysis of a complex mixture.

Mineral	Peak position		Overlap Δ2θ = ± 0.5°
	2θ	d	
Kaolinite	12.34	7.87	Nil
	24.88	3.578	Nil
Quartz	26.66	3.343	Nil
	20.85	4.26	20.52 (Tridymite)
Crystobalite	21.94	4.05	21.64 (Tridymite)
	31.50	2.841	Nil
	47.11	1.929	Nil
Tridymite	21.64	4.107	21.94 (Crystobalite)
	23.29	3.818	Nil
	20.52	4.328	20.85 (Quartz)
	23.00	3.867	23.11 (Kaolinite)

nonoverlapping peak at 2θ = 23.29° is unique to tridymite. In Table 2, we list 2θ and d values of various Bragg reflections that can be used for the analysis of kaolinite, quartz, cristobalite and tridymite. Using this procedure, we note that the mine dust sample of Fig. 1 does not contain any measurable quantities of cristobalite or tridymite.

IR Analysis:

In Fig. 3, we show the IR spectra of various combinations of quartz, cristobalite and tridymite samples obtained by photoacoustic spectroscopy. The objective here is to develop a criterion for the analysis of cristobalite and tridymite in presence of other components of the mine dusts. It is noted that the sharp band at 617 cm^{-1} is unique to cristobalite and tridymite, in that it is not present in either α-quartz or kaolinite. Hence we propose this band for the analysis of cristobalite and tridymite since the P7 method of using the 795 cm^{-1} band for the quantification of silica does not distinguish between quartz, cristobalite and tridymite. In Fig. 4, we show the IR spectra of the mine dust sample. The absence of the 617 cm^{-1} band signifies that neither cristobalite nor tridymite is present in this dust sample, as also inferred from the XRD. However, whereas XRD can in principle resolve cristobalite and tridymite in a dust sample, the IR spectra does not appear to have adequate resolution for this purpose in the mid IR range 4000-400 cm^{-1}.

CONCLUSIONS

The main conclusion of this work is that it is possible to detect cristobalite and tridymite in the presence of quartz and kaolin and that x-ray diffraction provides superior resolution than IR spectroscopy for this purpose. In addition, good agreement is obtained between a simulated spectra and an actual spectra of a mine dust sample using XRD. We are now in the process of developing the Rietveld method for a more refined quantitative analysis of mine dusts using XRD. In this method, crystal structures of possible components of a dust are needed and cell parameters are varied to yield the best fit without any calibration. These results will be reported in due course.

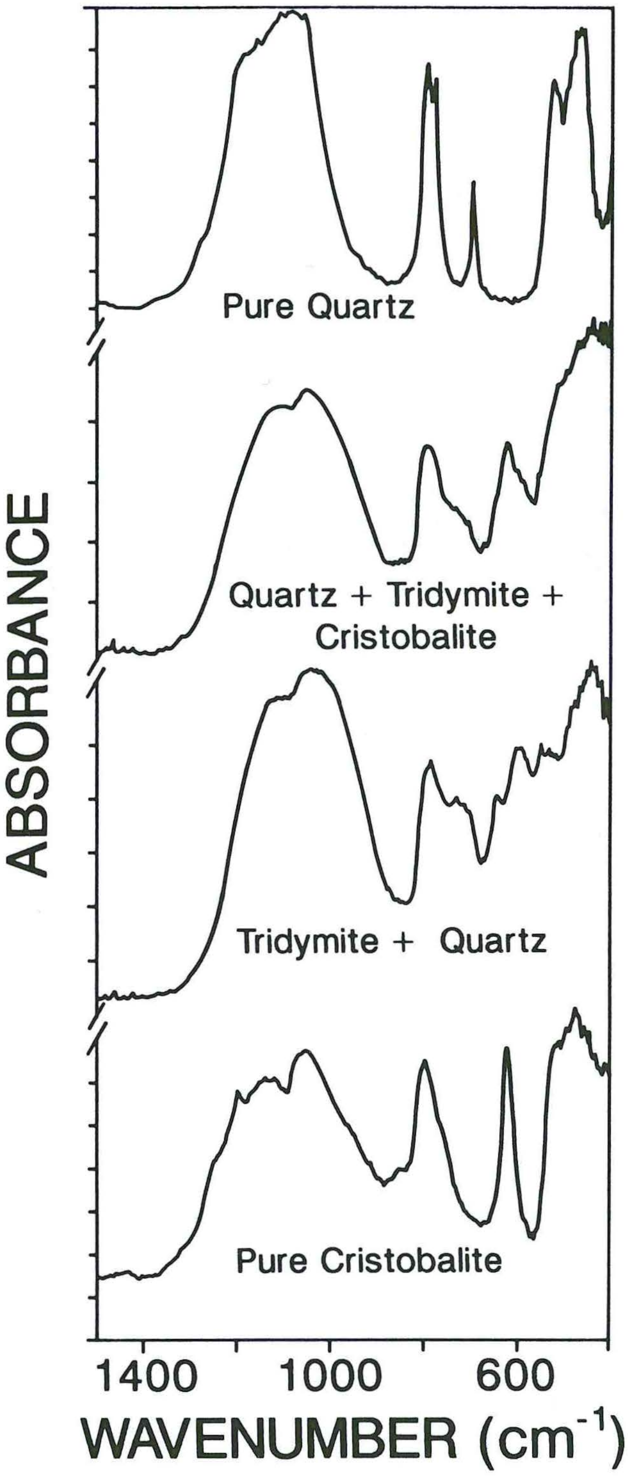

Figure 3. FTIR-Photoacoustic spectra of various mixtures of quartz, cristobalite and tridymite.

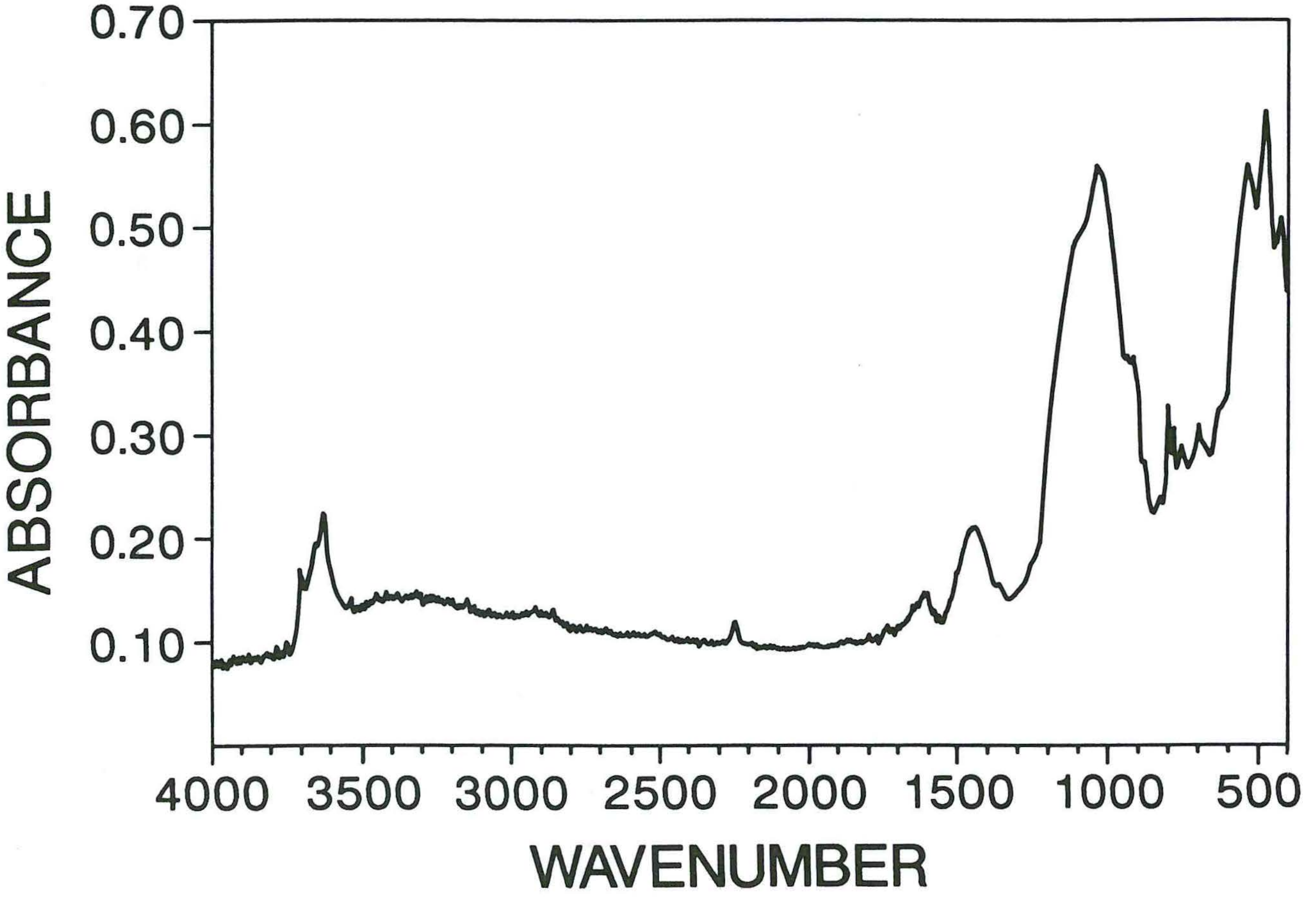

Figure 4. FTIR-Photoacoustic spectrum of the mine dust sample.

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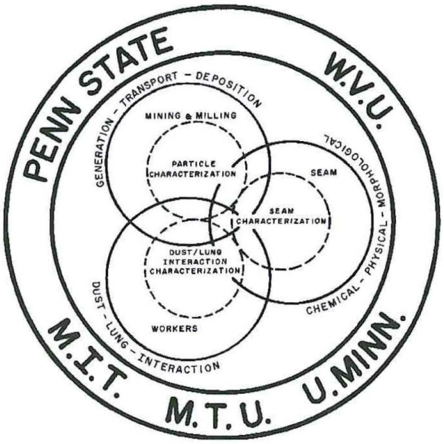

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