# Determining the Quartz Content of Respirable Dust by FTIR

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Informational Report
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# DETERMINING THE QUARTZ CONTENT OF RESPIRABLE COAL MINE DUST BY FTIR

by

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ABSTRACT

Following the promulgation of the Federal Coal Mine Health and Safety Act of 1969, the Mine Safety and Health Administration (MSHA) instituted a program for establishing the respirable dust standard in a coal mine when the free silica content of the respirable dust in the mine atmosphere is in excess of five percent. The analytical method used to determine the amount of silica in dust samples has been modified in the past to coincide with improvements in technology and instrumentation. With the procurement of a Fourier transform infrared spectrophotometer, it has been demonstrated that the silica analysis can be performed more precisely and with a substantial savings in time.

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## INTRODUCTION

It has long been known that the presence of quartz (free silica) in coal mine dust increases the hazard associated with the exposure of miners to coal dust. This was evident from studies conducted in the United States in the 1930's and 1940's[4,5] and resulted in the establishment by the Bureau of Mines in 1948 of a dust exposure limit when the dust in the mine environment was found to contain more than five percent quartz. At the time of promulgation of the Coal Mine Health and Safety Act of 1969, the Congress of the United States responded to this recognized hazard by stipulating that a formula be developed for lowering the allowable respirable coal dust limit to which mine workers are exposed when the content of the dust is found to contain more than five percent quartz. Such a formula was developed and on March 10, 1971, became part of Title 30 of the Code of Federal Regulations. The reduced standard was determined by dividing the percent quartz into the number 10 (i.e., reduced respirable coal dust standard = 10/percent quartz). Use of this formula was continued under the Federal Mine Safety and Health Act of 1977, which amended the 1969 Act, and is included in Parts 70.101, 71.101 and 90.101 of Title 30 of the Code of Federal Regulations.

In order to determine the quartz content in coal mine dust samples, the Mine Safety and Health Administration (MSHA) equipped a laboratory and established a procedure for the analysis. From 1971 through January, 1980, the laboratory procedure for performing the quartz analysis was referred to as the "KBr Method"[6]. This method consisted of ashing the dust from one or more samples in a muffle furnace at high temperature (800°C). Sufficient dust to give a total mass of from one to four milligrams was required. The ashed residue was combined with potassium bromide (KBr) and pelletized under high pressure. The pellet was analyzed on a dispersive infrared spectrophotometer to determine the quartz content of the sample.

In February, 1981, the method used to prepare the sample for analysis was changed. Instead of high temperature ashing and pelletizing of the ash with KBr, the sample was ashed in a low temperature asher and then redeposited onto a membrane filter for analysis. The advantage of this method (referred to as the "LTA Method")[7] was in being able to use a single sample (containing a minimum of 0.5 mg of dust) on which to perform the analysis. The low temperature asher (operating at a temperature of approximately 120°C) utilizes radio

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4/ Bloomfield, J. J. et al: Anthraco-Silicosis Among Hard Coal Miners. U. S. Public Health Service Bulletin 221, 118 p. (1935).

5/ Flinn, R. N., J. E. Seifert, H. E. Brinton et. al: Soft Coal Miners Health and Working Environment. U. S. Public Health Service Bulletin 270, (1941).

6/ Goldberg, Samuel A., Bureau of Mines Procedure for Determing Quartz Content of Respirable Coal Mine Dust. BuMines IC 8545, 1972, 10 pp.

7/ Goldberg, S. A., T. F. Tomb, et. al: MSHA's Procedure for Evaluating Quartz Content of Respirable Coal Mine Dust. MSHA IR 1152, 1984, 13 pp.

frequency energy to generate an oxygen plasma to destroy the collection filter and the carbonaceous material present in the sample. This method, which was collaboratively tested by SRI International under contract with NIOSH and the Bureau of Mines[8/], was further modified to correct for kaolinite. Kaolinite also absorbs infrared energy at 800 $cm^{-1}$ (the position of the analytical absorbance measurement for quartz) and thus interferes with the quantification of quartz in coal mine dust samples.

The current procedure using the dispersive infrared spectrophotometer requires manually drawing a baseline and measuring the height of the infrared energy absorption peak at 800 $cm^{-1}$. The determinant error associated with this analysis is due in part to the instrumentation and in part to the analyst. In order to enhance the analysis for quartz, MSHA procured a Perkin-Elmer Model 1750[9/] Fourier transform infrared spectrophotometer (FTIR) in 1987. An FTIR spectrophotometer was chosen because of the improvement in precision, reduction in analysis time, increase in sensitivity and the capability of automation made possible by the different operating principles of an FTIR spectrophotometer.

A dispersive spectrophotometer uses a grating and slit system to divide the infrared radiation emitted by the source. The infrared energy reaching a sample at any given time is limited to that of a single frequency or a small band of frequencies. The grating (which selects the frequency) and strip chart recorder move simultaneously and a spectrum of the transmission (or absorption) of infrared energy versus the frequency of the energy is plotted.

An FTIR employs an interferometer to obtain information about the transmission of infrared energy of all wavelengths (simultaneously) emitted by the infrared source and passed through the sample. The interferometer of an FTIR contains a fixed mirror and a moving mirror, the position of which is determined by a helium-neon laser. The information obtained when a sample is scanned is digitally stored as transmission intensity versus mirror displacement and is known as an interferogram. The instrument's computer then performs a Fourier transform of the interferogram to separate the multiplexed signal into individual frequencies and to produce the desired absorbance versus frequency spectrum. Figure 1 shows a typical interferogram of quartz and the infrared spectrum calculated from the interferogram.

Since there are no entrance or exit slits in the FTIR, a greater amount of energy reaches the detector, resulting in increased sensitivity. The laser tracking of the moving mirror results in greater precision of the wavelength measurement, permitting multiple scans to be averaged, thereby minimizing random noise and increasing the signal to noise ratio of the absorbance

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8/ Anderson, Clairene C.: Collaborative Tests of Two Methods for Determining Free Silica in Airborne Dust, SRI International Contract No. 210-79-0059 prepared for NIOSH, BuMines, October 1983, 158 pp.

9/ Reference to specific equipment, trade names or manufacturers does not imply endorsement by MSHA.

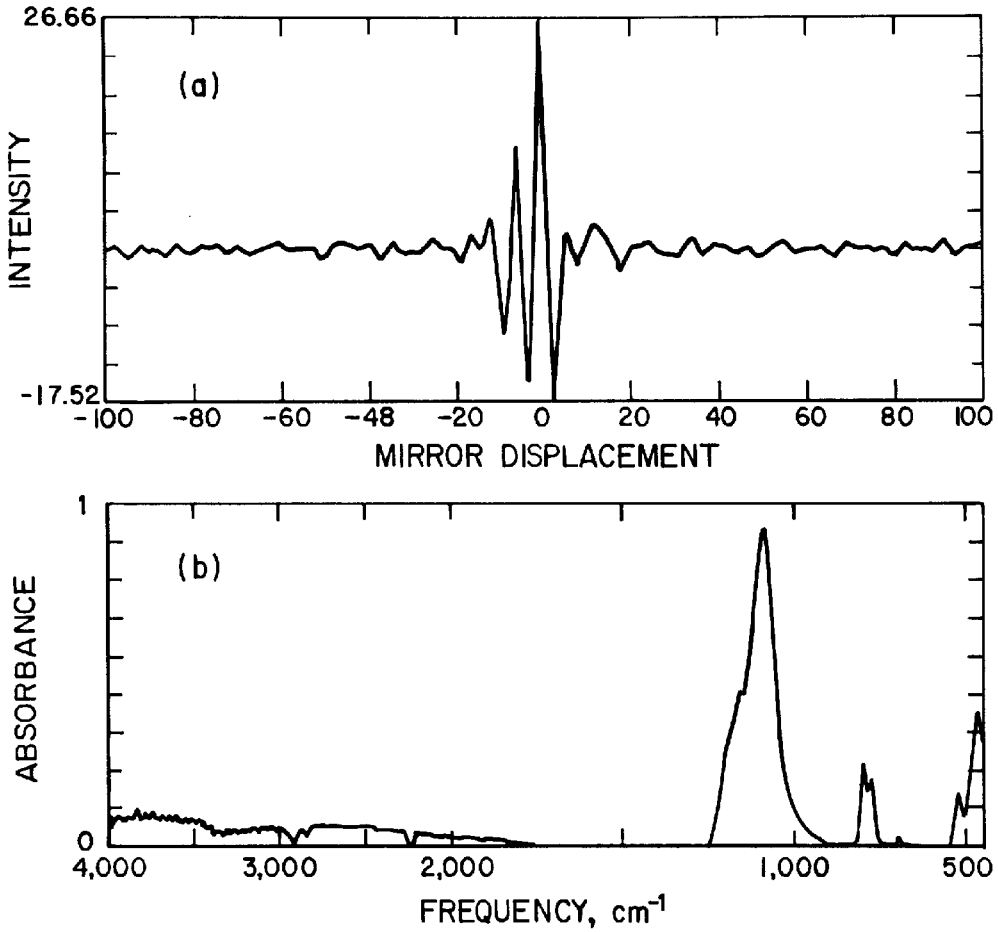


Figure 1. - Example of an FTIR interferogram (a) and the transformed infrared spectrum (b) for -5 micrometer Minusil standard quartz material.

spectrum. Precise duplication of the analytical frequencies and computer control of the calculations with the FTIR eliminates the error associated with the electromechanical components of the dispersive instruments and the necessary manual measurements of frequencies and peak intensities.

This paper describes the experimental work conducted to determine the precision achievable with an FTIR and to show that results obtained are comparable to results obtained with presently used (Perkin-Elmer Models 683 and 681) dispersive (grating) spectrophotometers.

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## EXPERIMENTAL

In order to compare the results of samples analyzed for quartz using an FTIR with those obtained using a dispersive infrared spectrophotometer, 25 coal mine dust samples were examined using both types of instruments. The mass of the samples examined ranged from 0.5 to 2.1 milligrams. Each sample was analyzed twice on each instrument.

The samples were low temperature ashed and prepared for analysis according to MSHA Standard Procedure P7[10/]. Quartz determinations obtained from analysis with the dispersive infrared instruments were also in accordance with Procedure P7.

The operating parameters (resolution, baseline points and peak locations) for the FTIR were determined by scanning several samples of pure quartz, pure kaolinite and ashed coal mine dust, and then choosing the conditions which best represent the average sample. A calibration curve relating absorbance at 800 $cm^{-1}$ to micrograms of quartz, in the range from 30 to 200 micrograms, was developed. A calibration for kaolinite relating absorbance at 915 $cm^{-1}$ to absorbance at 800 $cm^{-1}$ was also established.

The micrograms of quartz and the percent quartz for each sample determined using the two instruments were statistically compared by linear regression analysis using the method of least squares fit. The standard error of estimate ($S_{y/x}$), showing the degree of scatter about the regression line, and the correlation coefficient (r), showing the degree of linearity of the data, were also calculated. Data from the replicate analysis of the samples on each instrument were similarly treated.

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10/ MSHA Standard Method No. P7, Infrared Determination of Quartz in Respirable Coal Mine Dust, Oct. 1, 1984, 32 pages.

## DISCUSSION

Table 1 shows the mass of respirable dust for each of the 25 samples analyzed and the mass of quartz determined for the replicate analysis of the samples with the FTIR and dispersive IR (Perkin-Elmer Model 683) spectrophotometers. Table 1 also shows the calculated percentage of quartz determined for each analysis. Figures 2 and 3 are graphical comparisons of the quartz mass and percentage determinations, respectively, obtained for the first analysis of each sample on the two instruments. Also included on these figures are the regression equations showing the relationship derived between the analysis from the two instruments.

The regression equations show that comparative analyses with the two instruments on the same sample will be the same. As shown on Figure 2, the micrograms of quartz determined using the FTIR is approximately 1.5 micrograms more than that determined with the dispersive infrared. This slight

Table 1. - Mass of Quartz and Percent Quartz for 25 Coal Mine Dust Samples Analyzed in Replicate on Both Dispersive IR and FTIR Spectrophometers.

| Sample Number | Sample Mass (mg) | Micrograms Quartz | | | | Percent Quartz | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | FTIR | | 683 | | FTIR | | 683 | |
| | | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 |
| 1 | 0.6 | 58 | 58 | 53 | 59 | 9.7 | 9.7 | 8.8 | 9.8 |
| 2 | 1.7 | 123 | 122 | 118 | 119 | 7.2 | 7.2 | 6.9 | 7.0 |
| 3 | 1.2 | 78 | 77 | 77 | 78 | 6.5 | 6.5 | 6.4 | 6.5 |
| 4 | 0.5 | 45 | 45 | 40 | 48 | 9.1 | 9.1 | 8.0 | 9.7 |
| 5 | 1.0 | 36 | 36 | 32 | 37 | 3.6 | 3.6 | 3.2 | 3.6 |
| 6 | 1.0 | 148 | 146 | 140 | 145 | 14.8 | 14.6 | 14.0 | 14.5 |
| 7 | 2.1 | 151 | 151 | 147 | 150 | 7.0 | 7.0 | 6.9 | 7.0 |
| 8 | 1.6 | 54 | 55 | 54 | 55 | 3.4 | 3.4 | 3.4 | 3.4 |
| 9 | 0.7 | 53 | 53 | 49 | 47 | 7.6 | 7.6 | 7.1 | 6.7 |
| 10 | 0.9 | 53 | 53 | 48 | 50 | 5.9 | 6.0 | 5.4 | 5.6 |
| 11 | 1.4 | 106 | 104 | 96 | 93 | 7.5 | 7.5 | 6.9 | 6.7 |
| 12 | 0.8 | 53 | 52 | 46 | 51 | 6.6 | 6.6 | 5.8 | 6.4 |
| 13 | 0.7 | 51 | 51 | 49 | 50 | 7.3 | 7.3 | 7.1 | 7.1 |
| 14 | 0.5 | 29 | 29 | 27 | 28 | 5.9 | 5.9 | 5.4 | 5.7 |
| 15 | 0.8 | 219 | 219 | 207 | 216 | 27.4 | 27.5 | 25.9 | 27.0 |
| 16 | 1.6 | 152 | 152 | 155 | 157 | 9.5 | 9.5 | 9.7 | 9.8 |
| 17 | 0.8 | 52 | 52 | 54 | 52 | 6.5 | 6.5 | 6.8 | 6.5 |
| 18 | 1.3 | 126 | 127 | 130 | 129 | 9.7 | 9.8 | 10.0 | 9.9 |
| 19 | 1.1 | 142 | 141 | 140 | 144 | 12.9 | 12.9 | 12.8 | 13.1 |
| 20 | 0.9 | 152 | 152 | 146 | 165 | 16.9 | 16.9 | 16.3 | 18.3 |
| 21 | 0.9 | 24 | 25 | 28 | 25 | 2.6 | 2.8 | 3.2 | 2.8 |
| 22 | 1.6 | 100 | 101 | 97 | 101 | 6.2 | 6.3 | 6.1 | 6.3 |
| 23 | 0.9 | 116 | 116 | 115 | 122 | 6.1 | 6.1 | 6.1 | 6.4 |
| 24 | 1.6 | 113 | 114 | 123 | 112 | 7.1 | 7.1 | 7.7 | 7.0 |
| 25 | 1.9 | 109 | 108 | 114 | 108 | 5.7 | 5.7 | 6.0 | 5.7 |

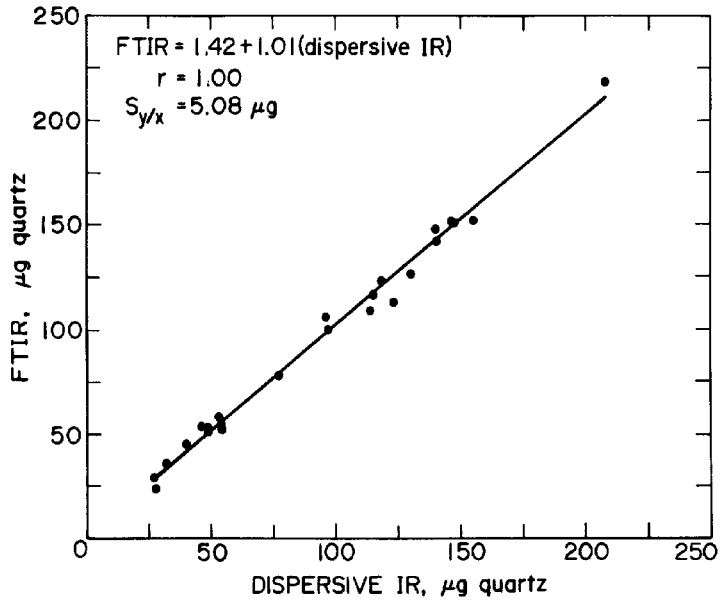


Figure 2. - Comparison of the mass of quartz determined on 25 coal mine dust samples analyzed with FTIR and dispersive IR spectrophotometers.

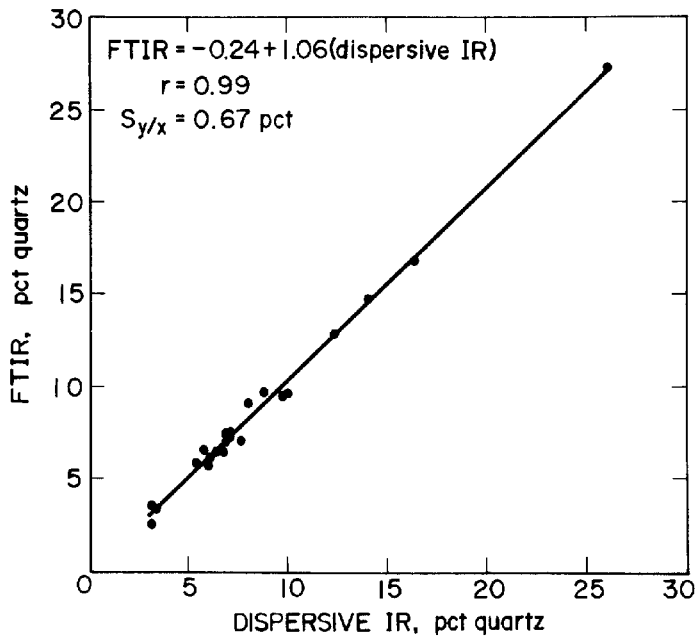


Figure 3. - Comparison of the truncated quartz percentages determined on 25 coal mine dust samples analyzed with FTIR and dispersive IR spectrophotometers.

dissimilarity is most likely attributed to calibration differences since the instruments were calibrated at different times using samples prepared from different standard quartz slurries. A calibration bias of this magnitude would have little effect on a quartz percentage determination because in MSHA's enforcement program, the percent quartz determined is truncated to the whole percent before the value is used to establish the applicable dust standard. A sample of 0.5 mg (the minimum amount of sample analyzed) would require a quartz percentage of more than 5.6 before the FTIR bias would cause the percentage determination to change one percent (i.e., five versus six percent). The fact that this difference has no effect on a percent quartz determination is confirmed on Figure 3 which shows that truncated percent quartz determinations from the FTIR analysis are the same as those obtained with the dispersive IR.

Figures 4 and 5 are graphs showing a comparison of the replicate analysis of the 25 samples on the Model 683 and FTIR, respectively. The regression equations defining the relationships between the comparative measurements and the standard error of estimate and correlation coefficient for the regression equations are also included on these figures. Although the equations show that an analysis with both instruments is highly reproducible, a comparison of the standard error of estimates shows that the variability associated with an FTIR analysis is 85 percent less than that obtained with the dispersive instrument.

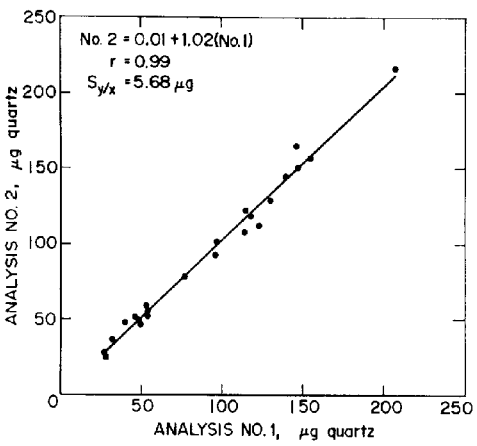


Figure 4. - Replicate analyses for mass of quartz determined on 25 coal mine dust samples analyzed with dispersive IR spectrophotometer.

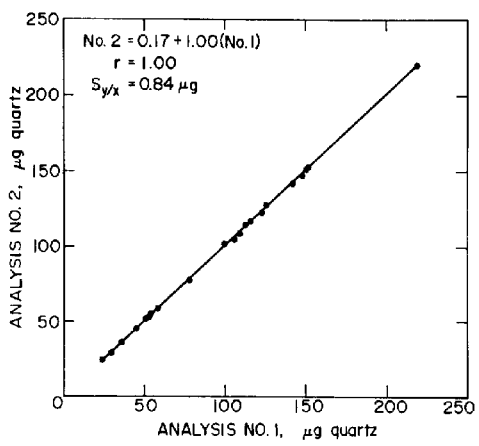


Figure 5. - Replicate analyses for mass of quartz determined on 25 coal mine dust samples analyzed with FTIR spectrophotometer.

The quantity of kaolinite in each of the 25 coal mines dust samples was similarly determined with each of the instruments. A comparison of the kaolinite determinations is shown in Figure 6. Figures 7 and 8 show the comparison of replicate analysis with both instruments. The regression equation determined for the micrograms of kaolinite on the FTIR versus that on the dispersive IR (Figure 6) indicates that kaolinite mass determinations obtained with the FTIR will be approximately 10 percent higher than those obtained with the dispersive unit. This small dissimilarity in measurements between the two instruments is also attributed to instrument calibration differences. Comparison of the standard error of estimates established for the regression equations for replicate kaolinite analysis (Figures 7 and 8) shows that the precision of a kaolinite determination obtained with the FTIR spectrophotometer is also approximately 85 percent better than that obtained with the dispersive IR spectrophotometer.

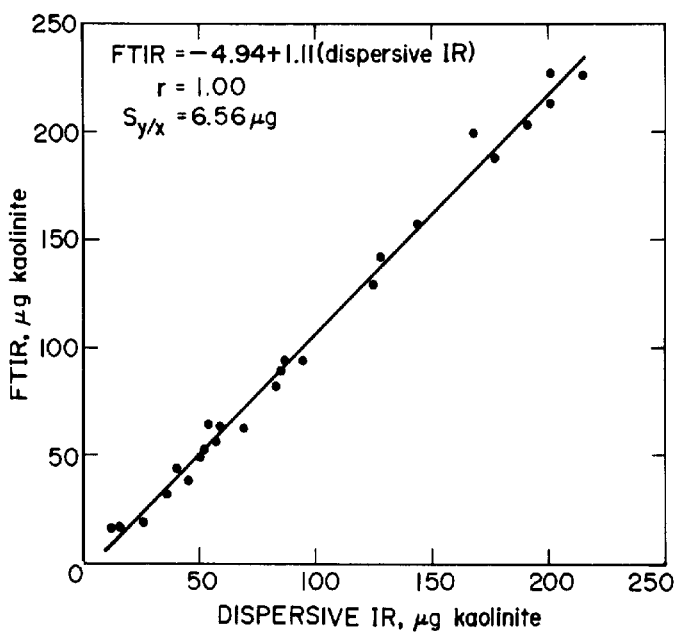


Figure 6. - Comparison of the mass of kaoline determined on 25 coal mine dust sample analyzed with FTIR and dispersive IR spectrophotometers.

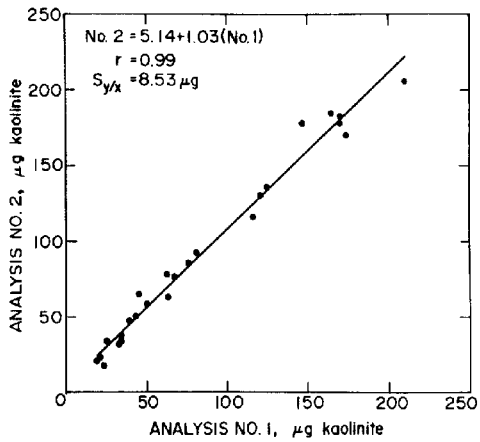


Figure 7. - Replicate analyses for mass of kaolinite determined on 25 coal mine dust samples analyzed with dispersive IR spectrophotometer.

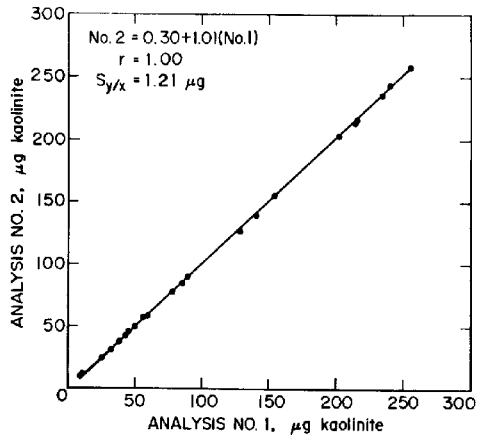


Figure 8. - Replicate analyses for mass of kaolinite determined on 25 coal mine dust samples analyzed with FTIR spectrophotometer.

## SUMMARY

In May, 1987, MSHA procured a Fourier transform infrared spectrophotometer (FTIR). The purpose for obtaining this instrumentation was to upgrade the procedure used to analyze coal mine dust samples for quartz content. FTIR spectrophotometry offers the advantages of increased sensitivity and precision as opposed to the currently used dispersive infrared spectrophotometer.

Prior to using the FTIR spectrophotometer to routinely analyze coal mine dust samples for quartz content, 25 coal mine dust samples were analyed using both FTIR and dispersive infrared spectrophotometry and the results compared using linear regression analysis. Comparison of the results showed that analyses performed with the FTIR were the same as those obtained with the dispersive infrared spectrophotometer. The comparison also showed that the precision of silica and kaolinite measurements obtained with the FTIR spectrophotometer was 85 percent better than that obtained with the dispersive IR spectrophotometer. Experience with the FTIR has also demonstrated that the potential for manual errors associated with the establishment of baselines and the measurement of peak heights has been eliminated and that the time for sample analysis is reduced.