MEASUREMENT OF AIRBORNE DIESEL PARTICULATE IN A COAL MINE USING LASER RAMAN SPECTROSCOPY

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INTRODUCTION

The goal of this research has been to develop the Laser Raman Quantitative Analysis (LRQA) method to measure the composition of respirable particulate, i.e. the fractions of coal and of diesel particulate, in the mine ambient air. In earlier Bureau of Mines sponsored research, we successfully demonstrated that the LRQA method could be used to measure the fraction of Diesel Particulate Matter (DPM) in coal/diesel particulate mixtures which were prepared in the laboratory.[1] The immediate objective was to test and refine this LRQA method on samples collected in a diesel underground coal mine.

Specific objectives required to meet this goal include:

1. Develop in-mine sample collection methods which will insure sufficient particulate loading on filters for LRQA.
2. Develop methodology for in-mine collection of reference samples ("coal-only" and "diesel-only" filters) which are required for quantitative LRQA.
3. Analyze precision and accuracy of the LRQA method.
4. Compare composition measurements with another analytical method, i.e. the University of Minnesota /Bureau of Mines size-selective sampling Micro-Orifice Uniform Deposit Impactor (MOUDI) method.

An advantage of the LRQA method is that it allows analysis of filters which have been collected by a method similar to that used to determine the respirable dust concentration in US underground coal mines. No new sampling instruments and techniques are required. Transfer of sample from collection substrate to analysis substrate is not necessary. Furthermore, other analyses can be made on the same sample since the technique is nondestructive.

The health effects of diesel exhaust, especially particulate, are a concern in the underground workplace. The constituents of DPM include insoluble carbonaceous particle agglomerates, adsorbed or condensed soluble organic compounds, trace metals, and low level sulfates. Many of the organic compounds are mutagenic and some are known carcinogens.[2,3]

Measurements made in underground mines with diesel equipment have shown that DPM may contribute as much as 60 % of the 2.0 mg/m^3 respirable coal mine dust standard.[4] While coal dust has been an important health concern for a number of years, the concern about DPM is more recent.[5] Measurement of pollutant concentrations is prerequisite to engineering control of the airborne particulate and gaseous pollutants to which a miner is exposed in a diesel underground coal mine. At the present time, there is no fully-proven quantitative analysis method which can distinguish between diesel and coal particulate.

EXPERIMENTAL

The mine air particulate samples were collected in a manner similar to that used for gravimetric respirable dust sampling in underground coal mines. Respirable dust was sampled using a personal sampler which draws mine air at 2 L/min through a 10 mm nylon preseparator and then through a filter at 2 L/min. Diesel/coal samples were collected in triplicate (collection times varied from 2.95 to 7.27 hr). Smaller Gelman A/E glass fiber particulate collection filters (25 mm filters instead of the normal 37 mm diameter) were used to assure filter loadings close to 0.10 mg/cm^2 and preferably 0.15 mg/cm^2. This 0.1 mg/cm^2 nominal level was determined by LRQA of various filter loadings above and below this level in previous studies. Only 8% of the samples fell below 0.07 mg/cm^2 with the majority falling in the 0.1 to 0.4 mg/cm^2 range (72%). Three locations were sampled for the diesel/coal mixtures each day: near the feeder-breaker, in the return, and on the ram car within 2 feet of the operator (as designated in Figure 1.

As part of a systematic approach to monitoring diesel emissions for control of mine air quality, we also measure ambient air pollutants and CO_2 concentrations.[6] This approach, developed at Michigan Technological University (MTU), provides a means to relate air quality measurements to engineering controls. The CO_2 concentration, which is related to the fuel consumption and airflow per unit of diesel power used, is related to the DPM fraction. A typical value of 13 mg/m^3 /%CO_2, determined from previous sampling in a number of metal mines, was used to calculate this CO_2—derived DPM value. The DPM concentration estimated using the % CO_2 does not compare well with LRQA values; % CO_2—is expected to be a rough indicator only.

Four "diesel-only" tailpipe particulate matter samples were collected from each of 3 Ram Cars using the portable Emissions Measurement Apparatus (EMA). The EMA, developed at MTU, is illustrated in Figure 2.[1] The EMA is a tailpipe apparatus designed to instantaneously and dynamically dilute the exhaust to a dilution ratio of about 20:1. A 63 mm diameter Pallflex T60A20 filter was used to collect particulate (ca. 1.5 min sampling time).

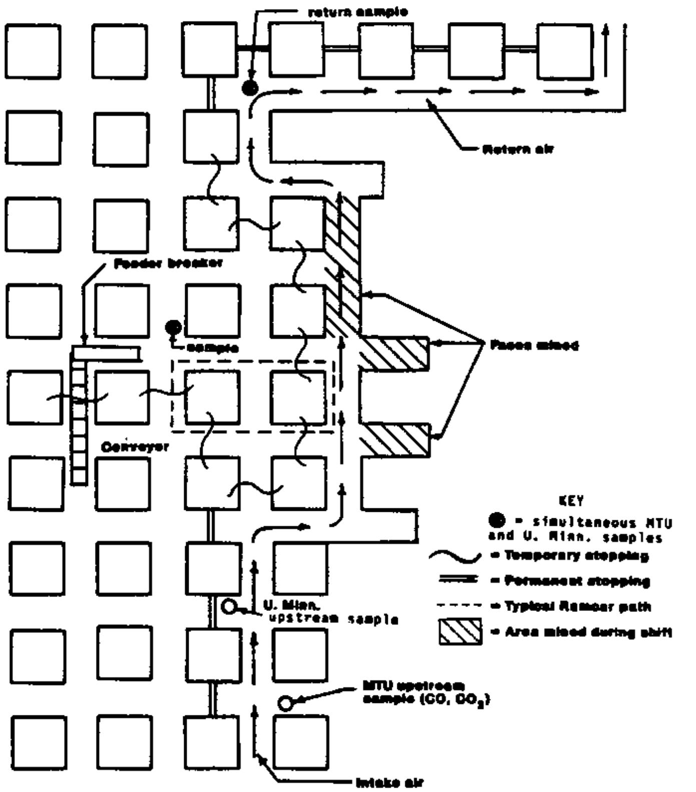

Figure 1. Schematic of coal mine section defining sampling locations.

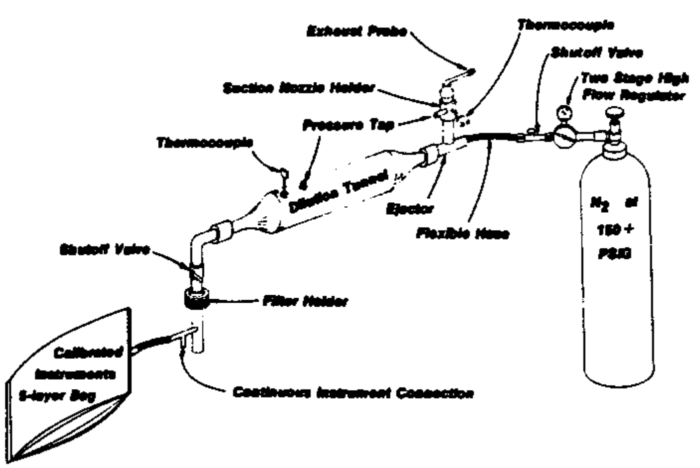

Figure 2. Schematic of emissions measurement apparatus (EMA-2) which is used to collect diesel-only tailpipe samples.

apparatus designed to instantaneously and dynamically dilute the exhaust to a dilution ratio of about 20:1. A 63 mm diameter Pallflex T60A20 filter was used to collect particulate (ca. 1.5 min sampling time).

"Coal-only" particulate reference samples were taken daily for 4 days next to the continuous miner (CM) scrubber (Figure 3). The collection procedure was similar to that used for the diesel/coal mixture samples. With the high dust concentrations between the cutter and scrubber, respirable coal dust can be collected in 15 minutes or less.

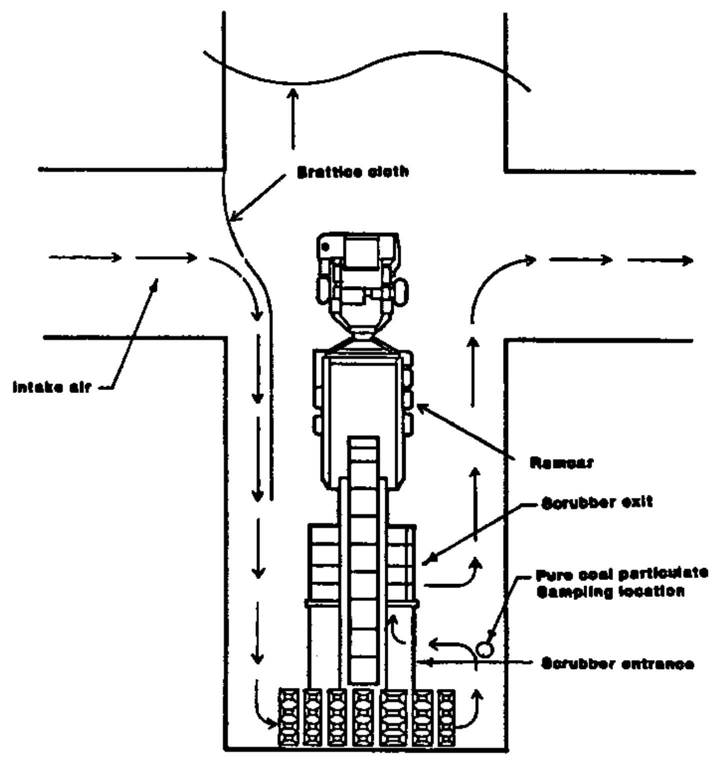

Figure 3. Illustration showing location of coal-only particulate sample collection.

After weighing to determine the respirable dust concentration, the filter is mounted on a sample spinner and analyzed by LRQA. No transfer of the particulate to a different filter is required. Samples are rotated to prevent decomposition in the laser beam.[1] The schematic in Figure 4 depicts the LRQA instrumentation.

The LRQA spectral scan procedures have been designed to test for sampling inconsistencies which might arise from sample decomposition in the laser beam. Four spectra are collected, a pair at each of two different radii on the spinning filter. The individual spectra are designated as "1x spectra." The sum of the two spectra at one radius is designated as a "2x spectrum." Any decomposition in the laser beam will

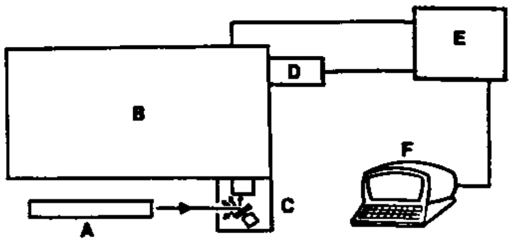

Figure 4. Schematic diagram of Raman instrumentation used to collect coal/diesel particulate spectra.
A) Argon-ion laser
B) Spectrometer (double monochromator)
C) Sample chamber with spinning sample holder
D) Photomultiplier tube
E) Interface between spectrometer and computer
F) Computer used to control spectrometer and to analyze spectra

be apparent upon comparison of two 1x spectra. Comparison of two 2x spectra will indicate radial inhomogeneity. This procedure also allowed detection of radial sampling inhomogeneities on a filter which are caused by particle size segregation. The sum of all four 1x spectra is designated as a "4x spectrum," and is representative of a given filter.

LRQA samples have been collected simultaneously with the size-selective sampling method being developed at the Twin Cities Research Center (TCRC) and the University of Minnesota.[4,7] The latter samples were collected by University of Minnesota personnel. MOUDI samplers, used for this purpose, separate the particles into size fractions on the basis of their aerodynamic diameters and densities.[7] This side by side collection allows direct comparison of the fractions of diesel and coal in the mine air measured by the two methods. All samples were collected during one week of underground air sampling during August, 1987, in the Kerr McGee Galatia Mine.

RESULTS AND DISCUSSION

Coal-only and Diesel-only Measurements and Use

A well defined relationship (equation 1) exists between the diesel/coal composition (y) and the intensity ratio (M) of two bands in the Raman spectrum of a mixture.[1] Figure 5 graphically depicts this relationship. Raman spectra of coal-only and diesel-only samples are shown in Figure 6.

$$1/y = (g'/g)\ \{(r'-M)/(M-r)\} + 1 \qquad (1)$$

y is the percent diesel particulate matter, %DPM, in a coal/DPM mixture. g represents the coal-only intensity and g' represents the DPM-only intensity. The slope in equation 1, g'/g, is the intensity ratio of the two samples and must be obtained when the two components are identically aligned. The coal-only intensity ratio (r) and the DPM-only ratio (r') must be determined to allow quantitative analysis of the mixtures.

The ratio for coal-only filters (r) was determined for 6 filters which were collected on three different days. The 1x, 2x and

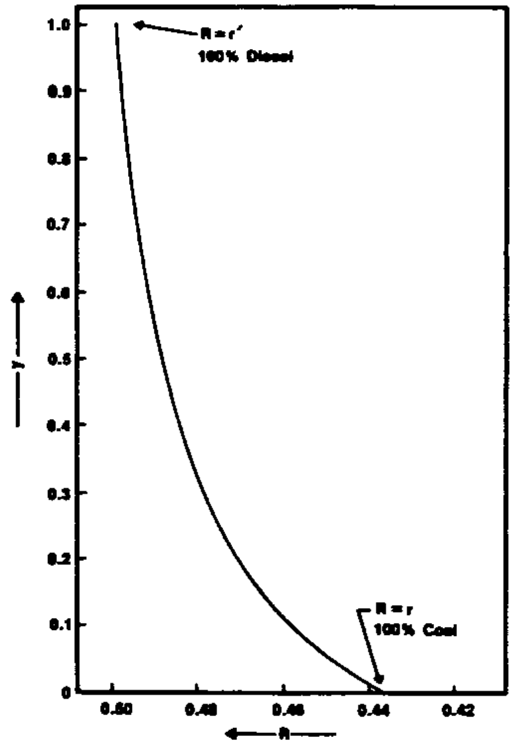

Figure 5. A graphical representation of the dependence of composition, i.e., %DPM (y), upon the experimental intensity ratio (R).

4x spectra demonstrate good reproducibility. This consistency shows that the samples are not decomposing in the laser beam. The mean and standard deviation (SDEV) for the coal-only samples are 0.522 and 0.022, respectively (C.V.=4.3%). This precision is comparable to that expected theoretically for these scan times.[1] The overall accuracy of mixture composition analysis depends on precise measurement of the coal-only intensity ratio (r) and the DPM-only ratio (r').

Spectral ratios have been determined for four DPM-only filters (after-scrubber), collected from two different ram cars. A mean r' value has been calculated by averaging the ratios measured for the four filters (a pair collected from each ram car). Reproducibilities for these are reasonable with an average r' of 0.958 and with a SDEV of 0.089 (C.V.= 9.3%.

Spectral Analysis and Reproducibility

The calculated %DPM values are analyzed statistically to demonstrate spectral reproducibility for a triplicate set of filters. Table I summarizes the %DPM values for one set of diesel/coal mixture filters collected at the feeder-breaker. The %DPM for each filter in column B of Table I are each an arithmetic mean of four 1x spectra. Column C gives the corresponding standard deviations. At the bottom of this table the overall arithmetic mean and standard deviation for the 12 spectra are given. Column D presents the %DPM measured on the summed (4x) spectra, with the mean and

Table I
Statistical Analysis of %DPM for a Triplicate Set of Filters
Collected at the Feeder-Breaker (on 8/10/87)

Column:	B	C	D	F	G
	% DPM for four 1x spectra		% DPM for one 4x spectrum	% DPM for the 2x spectra	
Filter	Mean	SDEV		Inner	Outer
3393	60.4	9.3	65.9	55.6	70.9
4730	61.9	8.7	67.6	62.5	68.9
6337	67.7	8.4	61.7	57.1	65.9
Values for twelve 1x spectra:	63.3	8.8	Values for three 2x spectra, mean:	58.4	68.6
Values for three 4x spectra:	64.9	3.0	and SDEV:	3.6	2.5

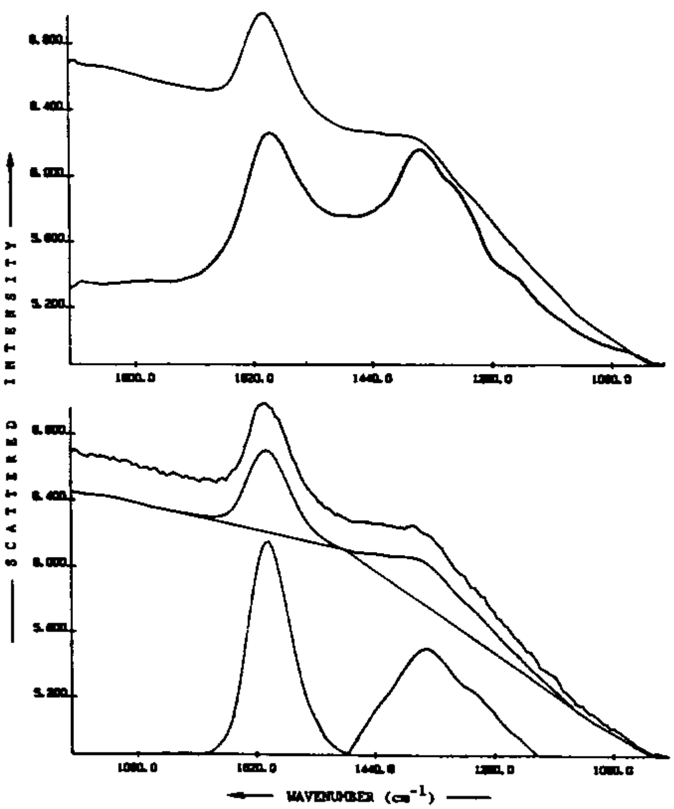

Figure 6. Raman spectra of coal-only and DPM-only filters (top), and baseline subtraction procedure for measurement of the intensity ratio (bottom).

standard deviation for the set of three at the bottom. Note that the standard deviation for the 4x spectra is smaller than for the 1x spectra because of the increased S/N ratio in each summed spectrum. The inter-filter mean composition is 64.9% DPM.

The intra-filter reproducibility is measured by the standard deviation of the %DPM (in column C of Table I) for each filter. The 4x %DPM for each filter (column D) must be consistent with the lx average (column B), and they are in each case. These results indicate that the samples have not changed during the time of measurement in the laser beam.

Table I also compares %DPM values for 2x spectra (each a sum of two lx spectra) collected at two different radii (columns F and G). This comparison shows whether or not the sample is radially homogeneous.

The inter-filter reproducibility is demonstrated by the standard deviation for the three filters (bottom of Table I, column C). In particular, the values in column D provide a measure of the inter-sample precision which can be attained for three filters collected simultaneously. The SDEV of 3.0% DPM demonstrates the high precision attainable. It is comparable to the uncertainty predicted theoretically upon consideration of standard counting statistics and the count time per data point. SDEV values that are higher than this will be found when real sampling differences occur.

Composition Measurements at the Feeder Breaker Ram Car, and Returns

Table II summarizes the DPM compositions at the various mine locations. While we have observed some inconsistencies for some filters, DPM compositions between 60 and 83% (SDEV < 10.5) have been measured with good precision. Samples with compositions outside this range exhibit inconsistencies among the multiple lx spectra. Their origin is under further study.

In some filters the compositions measured at the two different radial positions differ substantially, as indicated by a t-test on the difference of the means (see Table II). Table III presents an example calculation. The null hypothesis that the two sets of data are equal can be rejected at the 95% confidence level if the t-value is greater than 2.9. We can reject the null hypothesis since the observed t-value is 6.4. This result indicates that the compositions measured at these two radii are statistically different. The inner radius has a higher coal content.

Five out of eleven of the filter sets listed in Table II show significant differences between the means for the 2x spectra at the inner and outer radii. These results indicate inhomogeneous deposition which changes the measured coal/diesel ratio. Visual observation also reveals the inhomogeneous particulate deposition on some filters. Therefore steps must be taken to insure uniform deposition.

Table II

Summary of %DPM and Statistical Results to Determine if Inner Radius and Outer Radius Analyses Differ

Sample Location	Date taken	No.*	% DPM Mean**	% DPM SDEV**	C.V. %	Calc. t	t at 0.05	Inhomogeneous at 95% conf.	% DPM*** est. from CO_2 conc.
Feeder	8/10	3	64.9	3.0	4.6	3.8	2.9	yes	ND
	8/11	2	65.1	10.5	16.1	5.9	6.3	-	ND
	8/12	3	47.4	16.4	34.6	7.1	6.3	yes	68.8
	8/13	2	47.9	30.3	63.1	3.6	6.3	-	93.6
Ram Car	8/11	3	48.4	13.4	27.8	6.4	2.9	yes	47.2
	8/12	2	68.2	6.3	9.2	8.1	6.3	yes	65.1
	8/13	2	70.0	10.0	14.2	2.0	6.3	-	54.8
Return	8/10	2	77.9	0.6	0.7	2.0	6.3	-	78.9
	8/11	3	83.1	7.5	9.1	2.7	2.9	-	57.7
	8/12	2	82.4	7.9	9.6	3.0	6.3	-	49.9
	8/13	3	60.7	11.1	18.2	4.1	2.9	yes	59.7

* Number of samples analyzed per set.
** Mean and standard deviation for two or three 4x scans.
*** %DPM estimated from CO_2 concentration in mine.

Table III

Statistical Analysis of %DPM for a Triplicate Set of Filters with Radial Inhomogeneity; Ram Car (8/11/87)

Column:	B	C	D	F	G	H
	% DPM for four 1x scans		% DPM for one 4x scan	% DPM for two 2x scans		Delta
Filter	Mean	SDEV	Mean	Inner	Outer	F-G
2022	68.0	14.1	63.2	39.4	72.7	33.3
2431	51.8	30.3	45.1	20.8	75.6	54.8
6541	20.2	30.8	36.9	00.0	56.8	56.8
Total number of spectra analyzed:	12		3	3	3	3
Mean:	46.7		48.4	20.1	68.4	48.3
SDEV:		31.5	13.4	19.7	10.2	13.0
t :						6.4

Segregation by particle size can cause such inhomogeneity, with the larger particle size coal particulate concentrated toward the center. This natural tendency for nonuniform deposition of particulate on the filter surface has been observed with asbestos fiber collection. Size-selective sampling research has indicated that coal dust tends to exhibit a particle size distribution above +0.7 micrometer with diesel particulate below 0.7 micrometer.[4,7] Improved uniformity of particulate deposition has been achieved for asbestos fiber collection by using a cassette with a cylindrical "extension cowl." It should be pointed out that the observation of radial inhomogeneity demonstrates the sensitivity of the LRQA technique.

Comparison of Compositions as Measured by Different Methods

For two of three simultaneously collected samples there is excellent agreement between the MOUDI and the LRQA results (see 8/12 and 8/13 results in Table IV). The MOUDI gives %DPM values of 46.2% and 62.1%, while the LRQA gives values of 47.4% and 60.7% DPM, respectively. For these two pairs, the overall time spans for collection were comparable and no sampling irregularities occurred. It is important to note that the Raman triplicate filters are collected at the same time and for the whole period (ca. 5 to 6 hr.), whereas the MOUDI samples are collected in sequence. Each MOUDI filter is collected over a 1 to 2.5 hr period. Thus the arithmetic mean %DPM values calculated by the two methods may differ because of the differences in times sampled. For the third measurement (on 8/11), the two methods do not exhibit such agreement. The mean values differ by 25%. During the last hour of sample collection on 8/11, the dust from the mine face did not pass by the samplers. This occurred when the continuous miner broke through the mine face into the adjacent drift, drastically changing the air flow pattern.

The S/N ratio based upon the counting statistics for the scan time used in this study indicates that precision is not limited by the scan time. (A longer scan time will, of course, improve the S/N ratio.) Radial inhomogeneity reduces inter-filter reproducibility. Empirical variables can be controlled to improve precision. These are being optimized in our continuing work.

CONCLUSIONS

The LRQA method has been tested and refined on samples collected in a diesel underground coal mine. The amounts of DPM found at the feeder-breaker, on the ram car or at the returns, are in the range from 37 to 83% DPM. Total respirable DPM ranges from 0.18 to 1.61 mg/m^3 (Table V). Sampling reproducibility (precision) has been confirmed by statistical analysis of results for triplicate filters. Standard deviations below ± 10 % DPM are attainable. This precision is that expected for the scan conditions used. Reproducibility can be improved with longer scan times.

Table IV

Comparison of Compositions Measured by LRQA with those Measured by MOUDI and Those Estimated from %CO_2

Date/ Location	Sample No.	TIME start	TIME stop	TIME diff.	%DPM Est. from CO_2 conc.	MOUDI %DPM	MOUDI Mean	MOUDI SDEV	LRQA % DPM	LRQA Mean	LRQA SDEV
8/11/87	GNA-1	10:19	11:19	60 min.*		47.1					
Return	GNA-2	11:41	12:41	60 min.+		51.7	57.9	14.84			
	GNA-3	13:01	14:01	60 min.++		74.8					
	20	8:20	14:00	5.76hr.	56.7				77.8		
	21	"	"	"	57.2				79.7	83.1	7.5
	22	"	"	"	59.2				91.7		
8/12/87	GNA-4	8:38	11:08	150 min.**		51.7					
Feeder	GNA-5	11:29	13:59	150 min.**		40.7	46.2	7.78			
	30	8:35	13:45	5.17 hr.	-				40.9		
	31	"	"	"	59.5				35.2	47.4	16.4
	32	"	"	"	78.1				66.0		
8/13/87	GNA-6	9:45	11:45	120 min.*		64.9					
Return	GNA-7	12:00	12:49	158 min.*		59.2	62.1	4.03			
		15:34	17:23								
	44	9:36***	17:15	4.87h	53.4				55.3		
	45	"	"	"	60.0				55.3	60.7	11.1
	47	"	"	"	65.7				73.4		

\+ some mining, moving mine roof bolting
++ dust from face not passing samplers
* mining
** hauling
*** pump off 12:51-15:38

Table V

Summary of LRQA %DPM, Total Respirable Dust and Airborne Diesel Particulate Matter

Sample Location	Date Taken	No.**	LRQA % DPM Mean*	Total Respirable Dust, mg/m^3	DPM mg/m^3
Feeder	8/10	3	65.1	0.915	0.596
	8/11	2	65.1	0.582	0.379
	8/12	2	47.4	0.596	0.283
	8/13	2	47.9	0.373	0.179
Ram Car	8/11	3	48.4	1.523	0.737
	8/12	2	68.2	1.158	0.790
	8/13	2	70.0	1.074	0.752
Return	8/10	2	77.9	1.073	0.836
	8/11	3	83.1	1.690	1.404
	8/12	2	82.4	1.957	1.613
	8/13	3	60.7	0.987	0.599

* Mean for two or three 4x scans.
** Number of samples analyzed per set.

Composition measurements for samples collected simultaneously and analyzed by the LRQA and size-selective methods have been compared. The %DPM values obtained for this limited set of samples at two locations are in reasonable agreement. Two out of three %DPM comparisons agree very well, the third does not.

Sampling objectives were attained which make quantitative Raman analysis possible. First, in-mine collection methods have been shown to provide satisfactory particulate loading on filters. Secondly, methods to provide the diesel-only and coal-only reference samples were developed.

We have demonstrated that sample homogeneity on the filter surface can be confirmed by scanning at two different radii. Filter "extension cowls" are expected to remove radial inhomogeneities, and these will be tested in up-coming work.

These results indicate the importance of DPM-monitoring techniques. Optimization of the LRQA procedures will allow increased precision and accuracy. Further comparison of the size-selective and the LRQA methods is needed. Improved monitoring methods that are able to quantify the diesel and coal fractions are prerequisite to the development of adequate control technology.

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We acknowledge the U. S. Bureau of Mines, Generic Mineral Technology Center on Respirable Dust for support of this research (Project No. M101, USBOM No. 2601).

Proceedings of the VIIth International Pneumoconioses Conference | *Part*
Transactions de la VIIe Conférence Internationale sur les Pneumoconioses | *Tome*
Transaciones de la VIIa Conferencia Internacional sobre las Neumoconiosis | *Parte*

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DHHS (NIOSH) Publication No. 90-108 Part I