

## Using Laser Absorption Techniques to Monitor Diesel Particulate Matter Exposure in Underground Stone Mines

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### ABSTRACT

Underground miners are exposed to some of the highest levels of diesel particulate matter (DPM) in the United States. Therefore, it is important to monitor the exposure of miners to DPM, but it can be difficult because of the complex composition of DPM and the number of interferences. Currently, elemental carbon (EC) is used as a surrogate because it makes up a significant fraction of the DPM and is not affected by interferences. Standard measurement methods for EC can be time consuming and only record end of shift results. In this research, a laser absorption technique that enables one to measure EC concentration in near real time was shown to be a beneficial tool. The real time data showed that the fresh air being drawn into a stone mine was not properly reaching the working area and needed to be redirected to decrease DPM concentrations. The real time data also provided a more accurate efficiency of an environmental cab compared to just using the standard method by detecting the opening of the cab's window and door. The EC optical monitor was also worn by researchers in a mine to show how it can give not only the average concentration for the shift but also reveal when and where a miner is exposed to DPM.

**Keywords:** Laser absorption, diesel, elemental carbon, mining, exposure

## 1. INTRODUCTION

Long-term exposure to elevated concentrations of diesel exhaust is a concern, because diesel particulate matter (DPM) is believed to be a possible carcinogen.<sup>1-3</sup> Exposure to elevated concentrations of diesel exhaust has also been linked to health effects such as eye and nose irritation, headaches, nausea, and asthma.<sup>4-6</sup> Underground miners are exposed to some of the highest levels of diesel exhaust in the United States. Therefore, the Mine Safety and Health Administration (MSHA) has promulgated rules to limit the exposure of metal/nonmetal underground miners to diesel particulate matter (DPM) (personal exposure limit of 438  $\mu\text{g}/\text{m}^3$  for the 2007 interim limit and 200  $\mu\text{g}/\text{m}^3$  for a final limit effective in 2008).<sup>7-8</sup> In order to promulgate this rule, one issue that had to be overcome was how to measure for DPM.

DPM is a complex mixture of particulate elemental carbon (EC) or soot, particulate and particle bound organic carbon (OC), sulfates, some metals, etc.<sup>9</sup> In the mining environment, mass measurements of DPM are prone to interferences from other sources of aerosols (mineral dust, cigarette smoke, etc.) and are not sensitive enough for measuring the concentrations near the final limit (below 200  $\mu\text{g}/\text{m}^3$ ). Therefore, a surrogate was needed to determine DPM exposure.

Both elemental carbon and total carbon could be potential surrogates since both can be accurately measured at the concentrations needed using National Institute for Occupational Safety and Health (NIOSH) method 5040 and are major components of DPM. At first, total carbon (TC) was considered by MSHA to be the most adequate surrogate for DPM because TC accounts for over 80% of the DPM<sup>7,9,10</sup> while EC to DPM ratios more drastically vary depending upon load on the engine. However, the EC and OC particles from mineral dust and OC aerosols from the other sources commonly present in underground mines, such as environmental tobacco smoke and oil mist, were found to interfere with the TC analysis. A size selective sampler<sup>11-13</sup> has been shown to effectively segregate the coarse mineral dust from the generally submicron DPM. Unfortunately, the size selective samplers are not very efficient at removing cigarette smoke and oil mist (OC aerosols that generally belong to the same size category as diesel aerosols). Therefore, cigarette smoke and oil mist cannot always be avoided when taking personal samples. In addition to aerosol interferences, when using TC as a surrogate, one has to also account for organic carbon vapor sampling artifacts.<sup>14-16</sup>

As a result, MSHA turned to also using EC as well as TC as a surrogate for DPM for the interim limit since no other sources of submicron EC are known to exist in the metal/non-metal mining environment. EC is also a major component of DPM, and preliminary data shows a good relationship between DPM and EC in underground mines.<sup>17-18</sup> The interim 2007 limit is a total carbon standard of 350  $\mu\text{g}/\text{m}^3$  TC (80 % of the 438  $\mu\text{g}/\text{m}^3$  DPM standard). In order to determine if a mine is out of compliance, both total carbon and elemental carbon are measured. Total carbon is determined in two ways: by the actual NIOSH 5040 measurement and the calculation of TC using the EC measurement (1.3 x EC). If the TC from a sample is above 350  $\mu\text{g}/\text{m}^3$  using both methods, it is considered out of compliance. The sampling strategy for the final limit has not yet been decided.

The standard method for measuring the exposure of DPM in underground mines is to collect the particulate matter in the environment by passing air through a quartz filter at 1.7 lpm for an entire shift and analyze the filters for elemental carbon (EC) and total carbon (TC) by NIOSH Method 5040.<sup>19-20</sup> To avoid mineral dust which can cause an interference to the total carbon measurement, a single-stage impactor having a cut point (diameter of particle collected with 50% collection efficacy) of 0.8  $\mu\text{m}$  @ 1.7 L/min is used.<sup>11-13</sup> At times, a dynamic blank is used to compensate for the absorption of vapor phase organic carbon.

Using the NIOSH method 5040, samples have to be sent to a laboratory to be analyzed with results coming back weeks later. Also, the mine only receives information on a miner's average DPM exposure for an entire shift. A real time method for measuring elemental carbon would give a mine the capability to evaluate where the highest concentrations of DPM are in the mine (i.e. where the miner was exposed to the highest concentration). It would also give the capability of immediately evaluating the DPM concentration when changing different parameters such as ventilation.

Magee Scientific and Sunset Laboratory have stationary instruments that use laser absorption to measure real time EC in ambient air.<sup>21</sup> However, these instruments are too bulky and heavy to be worn by a miner or easily attached to a piece of equipment to monitor actual exposure as the miner is moving throughout the mine. NIOSH has used the same concept of laser absorption and designed a wearable optical monitor to determine real time exposure to DPM. The monitor is small and light enough to be worn, is stable when worn or mounted on a vehicle, and measures EC accurately in concentration ranges seen in underground mining.

This paper describes how the laser adsorption technique can reveal additional information on a miner's exposure to DPM and when evaluating control technologies that cannot be retrieved using the standard sampling method.

## 2. METHODOLOGY

### 2.1 EC optical Monitor

This section is a brief description of the EC optical monitor. A detailed description of the instrument, parameters used (e.g. wavelength), limit of detection, and its accuracy will be presented in a future paper. The basic configuration of the EC optical monitor is a laser passing through a filter with a photodiode detector measuring the laser intensity after the filter. The monitor is plumbed such that a size selective sampler can be attached and outside air can be collected onto a filter at the desired flow rates. A MSA Elf pump is used to draw an air sample at 0.85, 1, 1.7, or 2 lpm. These flow rates were chosen for mining issues in order to achieve the desired cut point for a size selective device (described in further detail in the next paragraph) to avoid dust and to attain the concentration range needed. As EC from the air sample is collected onto the filter, the laser signal will decrease. By calculating laser absorption from this decrease in signal, as seen in Figure 1, a good correlation (r-squared of 0.998) was established between EC measured by NIOSH 5040 and laser adsorption measured using the EC optical monitor. Special consideration to the design of this monitor was given to create a stable and accurate measurement of EC while a miner or vehicle is moving around. The EC monitor was tested in the lab and shown to be stable when being moved and passed the NIOSH 25% accuracy criteria.<sup>22</sup> The details and results of this testing will be included in a future paper.

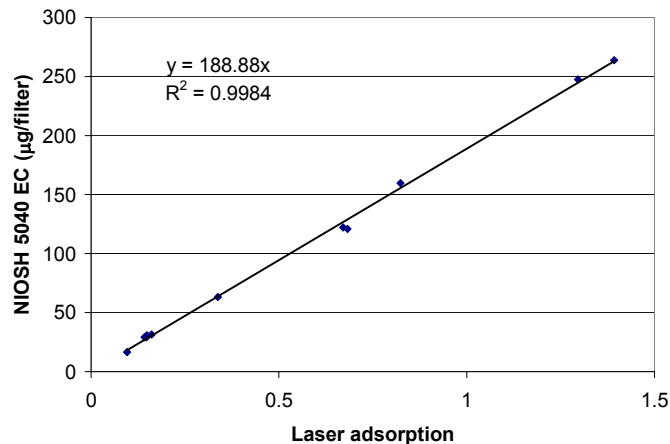


Figure 1: Calibration curve of EC measured using NIOSH 5040 vs. laser adsorption from the EC optical monitor

In order to collect DPM in the mining atmosphere, the collection of dust particles must be avoided. To achieve this, a commercially available impactor designed to separate dust from DPM (SKC DPM cassette) was used. The filter was taken out of the cassette and the impactor was resealed. The impactor and cyclone were placed on a lapel holder which can be attached to the miner's shirt or coveralls or simply strapped to the monitor to not be in the way of the miner. Conductive tubing was then run from the lapel holder to the EC monitor.

## 2.2 Standard sampling setup

In the standard sampling procedure (see Figure 2), the sampling train, consisting of a DPM cassette (SKC, Inc., Eighty Four, PA), a Dorr-Oliver cyclone, and an Elf Escort personal pump (Mine Safety Applicances Company, Pittsburgh, PA) was used to collect ambient air samples at 1.7 lpm (liters per minute). SKC DPM cassettes incorporate an impactor with a 0.8  $\mu\text{m}$  cutpoint and two quartz fiber filters placed in tandem. The filters were analyzed for OC and EC using NIOSH method 5040. This system is designed to be worn by the miner (personal sampling (Figure 2b)) and can be used for area sampling.



Figure 2: (a) The standard sampling setup which consists of an impactor with two quartz fiber filters inside attached to a cyclone in a lapel holder. Tubing connects the lapel holder to the personal pump. (b) The setup is designed to be worn by the miner by attaching the lapel holder to the clothing and the pump to the miner's belt.

## 2.3 NIOSH analytical method 5040

This analytical method analyzes for OC and EC in two different stages. In the first stage, the OC is measured by ramping the oven temperature over four progressively higher temperature steps programmed into the instrument, with the last step being at about 870 °C in a pure helium (He) atmosphere. The EC does not evolve because there is no oxygen ( $\text{O}_2$ ) available for it to react. The evolved OC is oxidized to carbon dioxide ( $\text{CO}_2$ ), reduced to methane ( $\text{CH}_4$ ), and finally measured using a flame ionization detector (FID). In the second stage, the EC is measured by reducing the oven temperature to about 600 °C and then again raising the temperature to about 900 °C in a He/ $\text{O}_2$  atmosphere ( $\text{O}_2$  is now present to react with the EC to form  $\text{CO}_2$ ). The EC is then measured in the same way as the OC. TC is simply the sum of OC and EC. The NIOSH method 5040 also optically corrects for pyrolysis (charring) of OC. This method is explained in more detail elsewhere.<sup>23</sup>

## 2.4 Area Sampling

Area samples were taken at several locations in a stone mine to determine the DPM concentrations in this mine and the effects of the current ventilation system. In a basket on a tripod (see Figure 3), the EC monitor as well as three SKC DPM cassettes (standard setup method for EC and TC) were run for six hours of a shift during actual production of an underground stone mine. A basket was setup at the intake of the mine (fresh air brought into the mine), the return (the exit of the intake air after passing through the whole mine), and at two locations at the working area where loaders were scooping the limestone and loading it into haul trucks. There was also drilling, roof bolting, and scaling at the working areas. The EC monitors were downloaded each day and the EC concentration was calculated using a calibration curve. The quartz filters from the SKC DPM cassettes were analyzed for EC and TC at the NIOSH Pittsburgh Research Laboratory using NIOSH 5040.<sup>23</sup> Samples were taken for three days.

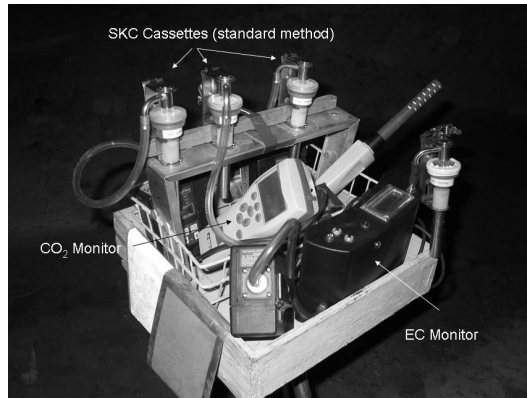


Figure 3: Apparatus for area sampling which includes an EC monitor for real time analysis, SKC DPM cassettes for NIOSH 5040 analysis, and a carbon dioxide monitor.

## 2.5 Sampling in Cabs

In order to minimize the exposure of a miner to DPM, environmental cabs are sometimes used. These cabs are air conditioned and filter out the DPM to provide a cleaner atmosphere for the miner. In order to evaluate the efficiency of a cab, two baskets containing an EC monitor plus three SKC DPM cassettes were made. The baskets were then strapped onto a loader (a Caterpillar 980F) outside the cab. Another identical basket was placed inside the cab of the vehicle where the miner works. The loader was used to clean up areas in the mine and was run during normal production for this stone mine. After about 6 hours of sampling, the samples were removed from the vehicle. These procedures were continued for five days at a stone mine.

The quartz filters from the SKC DPM cassettes were analyzed for EC and TC at the NIOSH Pittsburgh Research Laboratory using NIOSH 5040.<sup>23</sup> The EC monitors were downloaded each day and the EC concentration was calculated using a calibration curve.

## 2.6 Personal Sampling

In order to determine how well the EC monitor could be worn, two NIOSH researchers wore a standard sampling apparatus and an EC monitor as seen in Figure 4. The NIOSH researchers were in the mine to setup samplers for the area sampling mentioned earlier. The researchers first setup samplers at the return, then at the working areas, and finally at the intake. The real time data can show what concentrations the researcher was exposed to in these areas at the time of setup. Since the researchers also wore the standard sampling apparatus, it could also be determined how the EC monitor compares to the standard method when being worn. As in the previous studies, the quartz filters from the standard method were analyzed for EC using NIOSH 5040.



Figure 4: EC monitor is designed to be worn by a miner. It fits on the miner's belt with a camp lamp and self rescuer.

### 3. RESULTS

#### 3.1 EC optical monitor vs. NIOSH 5040

In the underground mining samples, the EC optical monitor resulted in EC concentrations comparable to the standard method (Figure 5). The difference between the two methods was less than or equal to 17% for 90% of the samples and less than or equal to 10 % for over 70% of the samples. Two samples showed a difference between 20-25%.

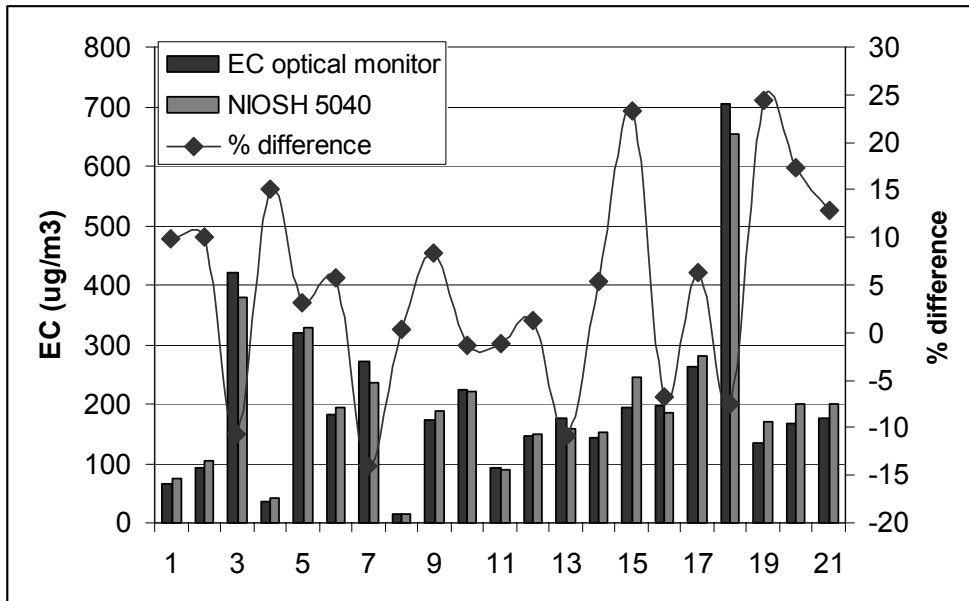


Figure 5: The EC concentrations measured by NIOSH 5040 and EC monitors were similar in field samples. The difference was calculated using the following equation:  $\% \text{ difference} = (\text{EC}(5040) - \text{EC}(\text{monitor})) / (\text{average}) \times 100$

These differences between the two methods are comparable to differences reported between samplers in other field studies.<sup>24-25</sup> (Note: Besides analytical and sampling errors, spatial variability can cause additional error for field analysis.) When measuring dust samples under simulated mining conditions, the differences between samplers was as high as 25%.<sup>24</sup> When measuring for silica in cabs, spatial variability caused the coefficient of variation to be over 20% at times.<sup>25</sup>

#### 3.2 Determining the Effects of Ventilation

Since DPM concentrations are being regulated, various control technologies are being implemented in underground mines to decrease DPM exposure. One type of control technology is ventilation (drawing or pushing fresh air into the mine and diluting the DPM). The EC monitor can give vital information to evaluate the effects of a mine's current ventilation and any adjustments made by the mine. For example, in this study, when sampling in the working area of a limestone mine, the time weighted average (TWA) EC concentration for 6 hours was  $653 \mu\text{g}/\text{m}^3$  (via the standard method). The EC monitor measured a TWA of  $704 \mu\text{g}/\text{m}^3$  EC (similar to the standard method) for the same time period, but it also showed the impact of the ventilation system. As seen in Figure 6, the concentration of DPM was not steady throughout the shift and did not spike at times during the shift. Instead the concentration of EC in that area of the mine slowly built up over time.

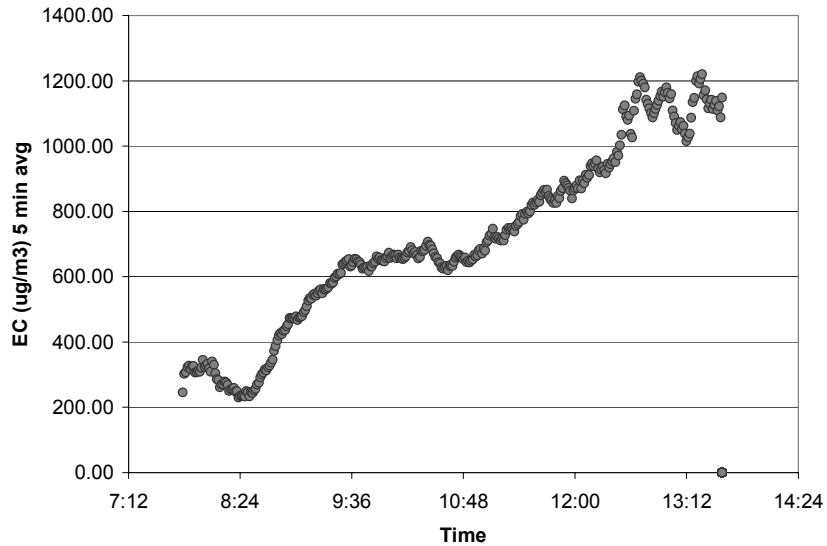


Figure 6: The EC concentration using a 5 minute running average over 6 hours of a shift at a working area in a limestone mine.

Some possible explanations for this phenomenon are that the number of vehicles working in that area increased causing a rise in DPM concentration, the concentration in the mine continued to build, or the ventilation in that area was not reaching and flushing out the DPM emissions rather allowing the DPM to stagnate and build up throughout the day. Since the number of vehicles at this working area did not increase throughout the shift and we did not see a build up of DPM in other locations sampled at the mine, it is probably the third possibility. This result indicates that a ventilation increase or re-direction could decrease the DPM concentration at the working areas.

In another location of the mine where trucks dump the limestone to be crushed, the 6 hr TWA EC concentration measured by the standard method was  $200 \mu\text{g}/\text{m}^3$  (the EC monitor showed a TWA of  $176 \mu\text{g}/\text{m}^3$  EC). This shows what a miner's exposure would be if working in that area outside of a cab. From real time data (Figure 7), we can see that at this location in the mine, the EC concentration consistently fluctuated back and forth from about 150 to  $250 \mu\text{g}/\text{m}^3$ . This is a result of the fluctuation of truck traffic at the dump area. These data suggest that the ventilation was diluting the DPM since the DPM was not being trapped and built up.

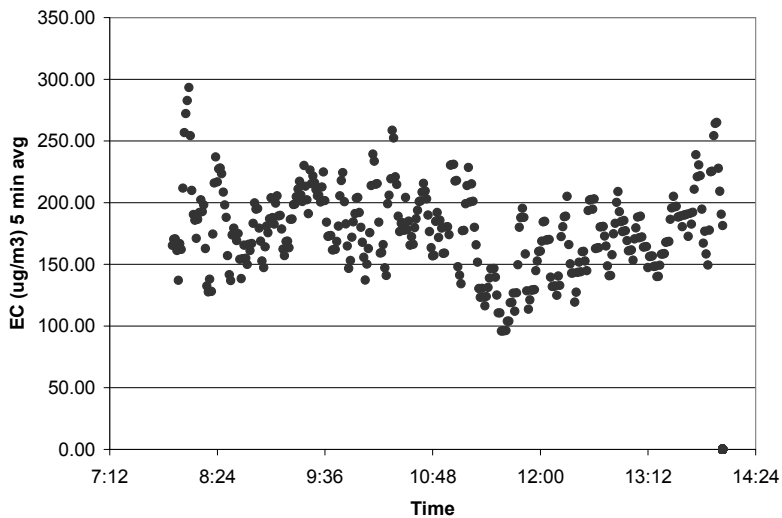


Figure 7: The Near real time EC concentrations for a dumping area of a mine.

### 3.3 Efficiency of Cabs

Another type of control technology used to minimize miners' exposures to DPM is to have an air conditioned cab on the vehicle which filters the particulate. This can be an effective strategy if the cab is working properly and the cab is kept sealed. An example of how the EC monitor can benefit in evaluating a cab's protection effectiveness is provided by sampling inside and outside of a cab in a stone mine. For one day of sampling (test 1), an EC concentration of  $378 \mu\text{g}/\text{m}^3$  for outside the cab and an EC concentration of  $104 \mu\text{g}/\text{m}^3$  for inside the cab using the standard method were measured. This gives about a 73 % efficiency for the cab used on this vehicle. A significantly higher efficiency for the environmental cab was measured on the same vehicle but on a different day with a different driver (test 2). For test 2, the EC concentration outside the cab was  $237 \mu\text{g}/\text{m}^3$  and  $16 \mu\text{g}/\text{m}^3$  for inside the cab. This indicates an efficiency of 93%.

As seen in Figure 8, the reason for the difference between the two tests is probably because the miner during test 1 was exposed to some DPM due to the cab door or window being open. In Figure 8, inside the cab for test 1, we see a peak of higher EC exposure in one part of the shift and then a higher exposure at the end of the sampling period. The peak would indicate a

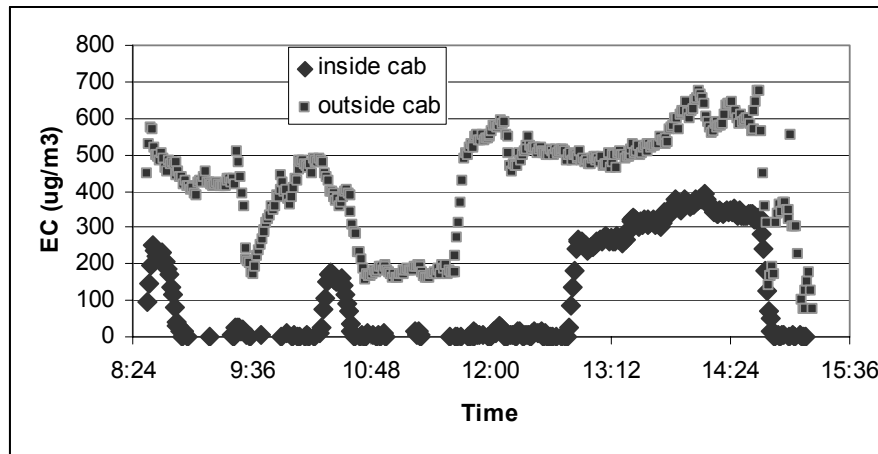


Figure 8: The evaluation of EC concentration in and out of a cab for one day of sampling (test 1). Periodic peaks indicate times when the window or door of the cab was open.

window or door opening and then closing. The higher concentration at the end of the shift could be from the miner slightly opening the window and leaving it open for the rest of the sampling period. If the EC exposure was due to leak or penetration through the filtration system, we would expect the EC concentration to follow the trend of the EC concentration outside the cab (just at a lower value) or possibly build up in the cab. We would also not expect the efficiency to change significantly on the next day of sampling with tests run under similar conditions.

As can be seen in Figure 9, unlike in test 1, the window or door was not opened during the shift for test 2. It seems that after the first initial opening that the cab was closed for most of the day. Thus, the efficiency reading from test 2 is probably closer to the real efficiency of the cab.



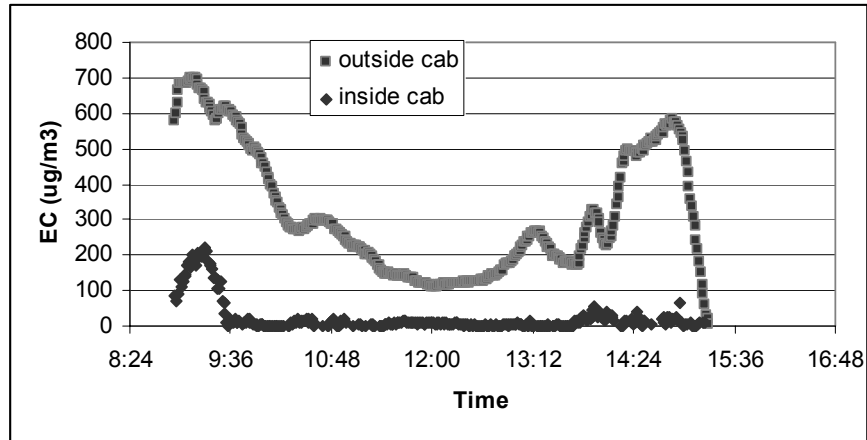


Figure 9: The cab seemed to be sealed for most of the sampling time for the second day of sampling.

In both test cases, the miners were below the regulatory limit for DPM exposure (including the final limit effective in 2008), and the cabs were effective at minimizing the DPM exposure to these miners. However, if one wanted to lower the exposure of the miner from test 1, the information from the real time data suggests that one would have to evaluate how to decrease the number of times the cab was opened.

### 3.4 Exposure of DPM to the Miner

The EC monitors can also be worn by a miner to determine DPM concentrations that the miner is directly being exposed to. Figure 4 shows how the monitor would be worn by a miner. An example of the information achieved when a monitor is worn is seen in Figure 10 which shows the exposure of a NIOSH researcher while setting up samplers in an underground stone mine. The researcher was exposed to 200  $\mu\text{g}/\text{m}^3$  EC when setting up samplers at the return. When the researcher moved to the working area, he was exposed to 250  $\mu\text{g}/\text{m}^3$  EC. The concentration of DPM decreased as the researcher set up samplers in areas where fresh air is brought to the mine. The data from the EC monitor showed a TWA for 6-hour of 110  $\mu\text{g}/\text{m}^3$  for the researcher which was similar to the 6 hour TWA of 112  $\mu\text{g}/\text{m}^3$  measured using the standard method (NIOSH 5040).

The above data represent how the EC monitor can give information about when a miner is exposed to the highest concentrations of DPM and where the DPM concentrations need to be decreased. The monitor might also be used to help a miner avoid areas with high concentrations of DPM.

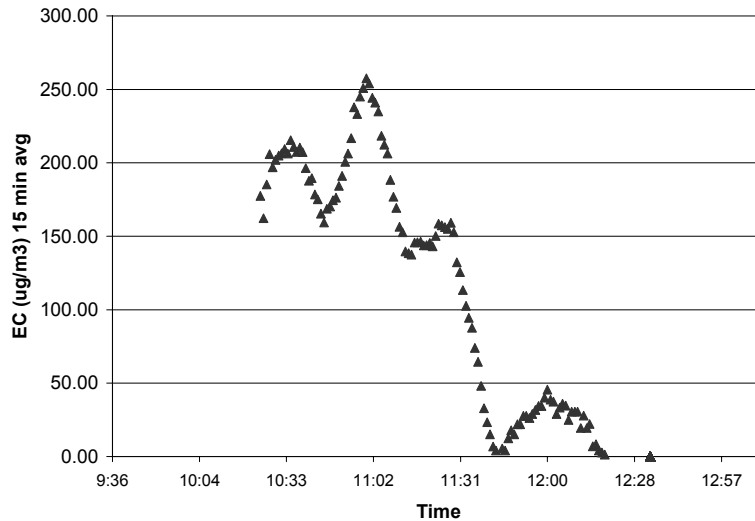


Figure 10: Near real time EC graph showing when a researcher's exposure in the mine over time.

#### 4.0 Conclusion

The standard method for measuring DPM (NIOSH 5040) gives vital information on the average exposure of a miner for an entire shift. However, it can take weeks for test results to be returned and data are limited to the average concentrations. NIOSH has developed a near real time monitor based on laser absorption that can provide more complete information and serve as a beneficial evaluative tool.

For area samples taken at a stone mine, the standard method only provided information on the concentrations of DPM that a miner could be exposed to in a working area, but the real time data revealed that the ventilation was not reaching and flushing out DPM from the working area. It was found that the ventilation needs to be redirected and increased to decrease DPM concentrations in this working area.

Also, the standard method showed that the cab on a vehicle in one stone mine had a 73% (test 1) and 93% (test 2) efficiency depending upon the day. After the near real time data was considered carefully, it was determined that at times, the operator for test 1 had his window or door open in the cab causing some exposure to the outside DPM. The real time data for test 2 showed that the cab was closed for most of the shift. Therefore, the 93% was the more accurate efficiency number.

The EC monitor also showed the concentrations that NIOSH researchers were exposed to when setting up samplers. This demonstrated how the EC monitor can be worn to indicate where and when a miner is exposed to the highest concentration of DPM. This could potentially help a miner avoid areas with high concentrations of DPM.

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