About the Project

Certain irregularities in DPM samples taken in mines with high concentrations of sulfide ore dust seemed to indicate that sulfides may interfere with some DPM sampling methods. This study was undertaken to address these concerns and to compare various DPM sampling methods in a high sulfide environment.

The study was performed by CANMET at Noranda’s Brunswick Mining Division in Bathurst, New Brunswick - a lead-zinc mine operating in a massive sulfide ore body. The study was completed in December 1998.

Background

Three common methods for measuring worker exposure to diesel particulate matter (DPM) were evaluated in the study: (1) respirable combustible dust analysis (RCD), (2) size selective sampling (SS), and (3) the thermal-optical (total carbon - TC) method. All methods start with collecting a DPM/dust sample on a sampling filter, which is then evaluated to determine the collected mass (weight) of DPM. In the case of the RCD method, the evaluation involves a controlled combustion of the sample, which burns off the DPM, leaving mineral dust particles behind. The RCD portion is determined by weighing the mineral dust, and subtracting it from the weight of the original material on the filter.

Previous sampling in Canadian mines uncovered cases where RCD measurements had to be rejected because of suspected interference. This led to the suspicion that combustion led to the addition of oxygen to sulfide minerals on the filter, causing the sample to gain in mass during the RCD analysis. The first goal of the study was to investigate the impact of the presence of respirable sulfides on the RCD sampling method. The second goal was to compare and evaluate the three sampling methods (RCD, SS, TC) under high DPM, and mixed DPM/sulfide mineral dust conditions.

Test Program

The experimental sampling program was divided into two one-week segments:

1. in a diesel contaminated atmosphere
2. in a diesel/mineral contaminated atmosphere.

The first part of the study was designed to evaluate and compare the three sampling methods for DPM where no sulfides were present. It was conducted in a non-productive mine area with airborne dust that was composed mainly of DPM. This was achieved by having a scooptram operate in the area under a duty cycle that closely resembled its regular production duties. In order to reduce airborne mineral dust concentration, the operator kept the muck in the scooptram bucket for the duration of the sampling period. Re-entrained dust from the roadway was controlled with water or calcium chloride.

“Diesel/mineral” tests performed in the second week were designed to observe the impact, if any, of respirable sulfide mineral dust on the DPM sampling methods. The objective was to produce airborne mineral dust that contained sulfide material on a background of DPM produced by the same vehicle and operator involved in the previous week. The tests were performed in an actual production area where sulfide-bearing ore had been stored ahead of the study. These materials were hauled back and forth with no attempt to wet the roadway or otherwise control the dust. On the contrary, the operator was asked to use his judgment to try to produce as much airborne mineral dust as possible.

The test vehicle was a Wagner model ST8B scooptram powered by a Detroit Diesel Series 60, DDEC III engine, which had just received regular preventive maintenance at 5328 hrs.
Results

To determine if sulfides had any impact on the RCD results, the ratio of RCD to TC was plotted as a function of sulfide dust concentration. Normally, we would expect that RCD and TC both measure mainly diesel emissions and so their measurements would be closely related. However, if RCD combustion causes the conversion of sulfides to sulfates, then the RCD measurements would vary in relation to the sulfide dusts. The results, however, showed that the quantity of airborne respirable sulfides did not have any significant or direct impact on the RCD values measured, as illustrated in Figure 1 by the RCD line of a near-zero slope.

![Figure 1. Relationship Between Sulfides and RCD/TC Ratio](image)

Results collected in the study show that oxidation of respirable sulfide materials on samples does not cause significant mass increases during the RCD process. It was found that oxidation of these minerals, as well as the combustion of sulfur-bearing compounds from the fuel, results in the formation of gaseous $SO_2$ rather than sulfate particles. The formation of $SO_2$ was confirmed by special laboratory tests (using thermogravimetric and differential thermal analysis). The subsequent interaction of $SO_2$ with the silver from the filter membrane is the probable cause of sample mass increase, where it happens. A very likely source of interference in the temperature range used in RCD analysis is the presence of organo-sulfates in the fuel. The performance of the RCD method can be enhanced by utilizing small pore silver membrane filters and using low-sulfur fuel in diesel applications underground. Smaller pore sizes help keep sulfur bearing minerals on the surface of the filter and away from the silver matrix, while lower sulfur fuel produces DPM with lower levels of organic sulfur, which can produce $SO_2$ upon combustion during the RCD analysis.

The total carbon (TC) concentration, as measured by the thermal-optical method NIOSH 5040, was used to compare and evaluate the RCD and SS gravimetric methods. In "diesel only" measurements, the RCD method overestimated exposures by about 12% and the SS method by 13%. During the "diesel/mineral dust" sampling, RCD underestimated by 10% and SS overestimated by 8%.

In spite of the fact that the three methods did not yield statistically similar results, linear regression analysis relating both the SS and RCD methods to the TC values showed very close agreement in the higher concentration ranges. These results seem to support the finding that lower sulfur fuel and the use of a small pore size (0.8 $\mu$m) silver membrane filters can limit the impact of sulfation of the silver membrane in the presence of $SO_2$.

At low DPM concentrations (< 0.2 mg/m$^3$) both gravimetric methods (RCD, SS) quickly became inaccurate. In many instances, the industry sets action levels at half of the exposure limit. Using this as a rule of thumb and setting this value at 0.3 mg/m$^3$ to gain a safety margin, it could be argued that for high sulfide ore bodies, the gravimetric approaches are adequate only if the exposure limit for DPM is set at 0.6 mg/m$^3$ or above. For lower exposure limits, data collected in the study shows that a gravimetric method may not be precise and/or accurate enough to assess exposure.

Conclusions

Even in a sulfide ore environment, all tested methods (RCD, SS, TC) performed very well. As long as the limits of DPM exposure are at or above 0.60 mg/m$^3$, the gravimetric methods appear to be adequate in sulfide ore mines. Below these levels, alternatives such as the thermal-optical methods should be considered.

For mines where mineral interference is not a problem and/or in applications where DPM is the main source of airborne respirable dust, the RCD method could be used at lower concentrations.