CERP
Casting Emission Reduction Program

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Characterization of Fine Aerosols at the Foundry of the Future: Report from the University of California, Davis

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EPA United States Environmental Protection Agency

CISA

AFS

UNITED STATES COUNCIL FOR AUTOMOTIVE RESEARCH
USCAR
DAIMLERCHRYSLER Ford Motor Company General Motors

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Characterization of Fine Aerosols at the Foundry of the Future

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SUMMARY

Aerosol emissions from the pilot scale pours of February 1999, were measured by mass, size and chemical species. The data showed excellent quality assurance in that the sum of the chemical species was highly correlated with, and closely approached the value of the gravimetric mass gain on the filters, and that the species represented in the size resolved samples approximated those in filter sampling. During foundry operations, the PM2.5 aerosol mass prior to the cleaning system was typically 700 to 900 µg/m3 (proposed daily standard of 65 µg/m3) which then requires an aerosol cleaning efficiency of 90% to 94%. The total emission rate per ton of iron poured was similar to recent studies on foundries in Mexico. The PM2.5 mass was dominated by alumino-silicates with a manganese and iron enrichment. The important ultra-fine component (Dp < 0.07 µm) was only a few percent of the total PM 2.5 mass and had a high component of organic matter. A new sampling technique was used to measure trace elements as a function of particle size with a time resolution less than 1 minute, thus closely matching the information from the gas measurements. Dramatic changes occurred in short time intervals, which will be tied to changes in foundry operations and simultaneous gaseous emissions.

EXPERIMENTAL TECHNIQUES

Aerosol emissions from heavy industry are a major component of concern for those living near such activities. These concerns are reflected in ambient air standards of the US EPA:

Name	Title	Size	Mass	Comments
Total Suspended Particulate 1987	TSP	$D_p < 30$ µm	250 µg/m^3	Replaced by PM^{10},
Inhalable Particles	PM$_{10}$	$D_p < 10$ µm	150 µg/m^3	
Fine Particles	PM$_{2.5}$	$D_p < 2.5$ µm	65 µg/m^3	Proposed 1998
Ultra-fine Particles	UF	$D_p < 0.07$ µm	na	No standard: health data causes concern.

In order to measure these parameters, two different sampling systems were used:

1. PM2.5 IMPROVE cyclone with Teflon filter media,
2. Three stage rotating DRUM impactor with after filter (ultra-fines).

The IMPROVE cyclone and analytical protocols (Malm et al, 1994) are accepted by the EPA (Federal Register, Nov, 1996) as the defining method for rural and remote sites in the US, and is one of a very few under consideration for a national speciation monitor. The slitted drum sampler (Raabe et al, 1988, Cahill and Wakabayashi, 1994), was designed to work in conjunction with IMPROVE filters, giving time and size information not possible in a PM$_{2.5}$ system. The IMPROVEd DRUM collects samples on Mylar or Teflon substrates continuously in three size modes:

A. $1.15 < D_p < 2.5$ µm
B. $0.34 < D_p < 1.15$ µm
C. $0.07 < D_p < 0.34$ µm

Analysis for the filters includes mass (gravimetric), hydrogen (PESA), Na through Fe (PIXE), Fe through Pb (XRF) (Cahill, 1996). Analysis for the IMPROVEd DRUM include all of the above except gravimetric mass, but the XRF is now focused polarized x-rays from the Lawrence Berkley National Laboratory (LBNL) Advanced Light Source. Quality assurance protocols are extensive, and are based on not only proper operation of the systems but also the concept pioneered by UC Davis, “integral redundancy”, where key parameters are made by two totally different methods to insure accuracy and precision.

As originally proposed, we reviewed the use of scanning electron microscopy (SEM) and x-ray diffraction (XRD) in the Central Facilities of the Division of Materials Science and Engineering in the College of Engineering for the purpose of characterizing the morphology and particle size of the aerosols. SEM can provide morphology, with the possibility of elemental analysis of individual particles by energy dispersive analysis of emitted x-rays (EDAX). XRD provides complementary speciation by chemical identification of compounds, rather than elements, and size analysis (average and distribution) by line broadening analysis. We continue to plan to use such techniques in the ongoing analysis of aerosols. For this initial study, however, we had a unique opportunity to use the world-class facilities of the National Center for Electron Microscopy (NCEM) at LBNL (near the Advanced Light Source). We specifically used an analytical transmission electron microscope (AEM) with EDAX. This provided images of morphology, particle size, and chemistry on specific, representative samples of aerosols.

RESULTS

The results of the studies are presented in the following order:

1. Filter data, PM2.5, 2/16 and 2/17
2. Filter data, ultra fine particulate, 2/16 and 2/17
3. Impactor data, three sub 2.5 µm fractions, 2/17 only
4. Electron Microscopy data, 2/16 and 2/17

Data on the pre-production pours will be analyzed further by a variety of methods, with completion scheduled for August 1, 1999. The results of the pilot scale pours of February 16 and 17, 1999 are also being subjected to additional analytical techniques of possible relevance to FOTF conditions. We shall inform CERP of these subsequent analyses in the course of our ongoing interactions.

1. Results of filter analyses, PM2.5, Feb. 16 and 17, 1999

Seven PM2.5 mode filters were collected during the pilot scale pours of February 16 (2) and February 17 (5). The data are taken from the exhaust duct after the pour, cool, and shake activities but before the aerosol cleaning system.

The aerosol concentration rose rather slowly from the beginning of production, with the first two hours representing less than ½ the eventual peak and steady state values. There then followed a period at which the values between about 650 and 900 $\mu g/m^3$ followed by a tailing off after production was ended, in this case around 1 PM. Also, we also present the organic matter fraction of the aerosol, representing about ¼ of the mass on February 17.

The results of the seven $PM_{2.5}$ mode concentration measurements are presented in a few ways, along with the two ultra fine filters which will be discussed in the next section. The mass of aerosol as weighed is compared to the sum of all species analyzed, and is a key indicator of the quality of the analysis. The sum of species, measured in vacuum and without nitrates included, was highly correlated with the gravimetric mass ($r^2 = 0.98$) and with a ratio 81% of the gravimetric mass. This is in fact typical of these types of measurements, as in ambient air sampling, water and other volatile species (light organics, some nitrates) are removed from the filters in the compositional analyses. The fact that these fresh aerosols have 19% volatiles in conditions in which water is probably not a major factor could indicate that light, adsorbed organics are a larger fraction of the mass than in typical organic samples.

An example of the complete compositional analysis for one of the filters taken during steady state FOTF operations is the which represents the period from 1: 30 to 3:30 PM, 2/16/99. The mass is dominated by alumino-silicates with organic matter, estimated from bound hydrogen, the other major component. Manganese and iron are both enhanced over typical crustal averages. A number of trace elements were also seen.

2. Results of filter analyses, ultra-fine particles, Feb. 16 and 17, 1999

Ultra-fine particles are generally defined as having diameters roughly below 0.07 µm in diameter. In some studies, such particles disproportionately damage lungs in laboratory animals especially if they are insoluble and thus remain for extended periods of time in the lung. Such insoluble ultra-fine particles are characteristic of some high temperature industrial processes, and one of our major goals was to evaluate their presence or absence at FOTF.

The ultra-fine fraction was measured twice during the two days of the pilot scale pours, Feb. 16 and 17. Each filter represents roughly 6 hr. of integrated time, of which about 4 hours were during steady state FOTF operations. As can be seen, they represent a tiny fraction of the $PM_{2.5}$ mass, averaging 30 µg/m3 or about 5% of all aerosol mass. Through the comparison of the ultra-fine and $PM_{2.5}$ composition, the most striking difference is the ultra-fine data has a much higher fraction of organic matter, shown by the hydrogen values. Organic matter in this sample was roughly 20 $\mu g/m^3$ while alumino-silicates were about 6 $\mu g/m^3$. In addition, significant amounts of sulfates (2 $\mu g/m^3$) and salt (0.7 $\mu g/m^3$) were seen. While the exact nature of the organic matter is not known, it would generally indicate species that, unlike alumino-silicates, would be removed from the lung fairly rapidly. It should also be noted that the loss of volatile matter (water, volatile organics) was higher in the ultra-fine fraction than for the $PM_{2.5}$ fraction.

3. Results of impactor analyses, Feb. 16 and 17, 1999

This study pioneered the application of continuously collecting time, size, and compositionally resolved aerosols from foundry operations using the IMPROVEd DRUM impactors. In this type of sampling, particles are impacted onto slowly moving greased substrates, segregating them in to size modes and collecting them for future compositional analysis. It is hoped by this technique that a close coupling between aerosol, and production and foundry operations can be achieved. It is also hoped that the aerosol data can be taken at a short enough time scale to match the minute by minute data on gas measurements.

The drums collected during the pilot scale pour of Feb. 17 are shown below for the three size classes (top to bottom):

A. $1.15 < D_p <$ Inlet
B. $0.34 < D_p < 1.15$ µm
C. $0.07 < D_p < 0.34$ µm

The ultra-fine filters were collected after this sampler. In each case, the initiation of the pilot scale pours is on the far left of the deposit, while the last 1/3 of the strip was taken during the post-pour cool down period.

The analysis of these strips is scheduled for completion on June 22, 1999, but even prior to then, some innovative analysis has been done. Since the nature of the elemental species and their time behavior are desired, the DELTA Group worked closely with the staff of the Lawrence Berkeley National Laboratory (LBNL) at their Advanced Light Source (ALS) to perform x-ray analysis of unequaled sensitivity and time resolution.

The data from the first analyses ever done on industrial aerosols by this technique are shown in Figure 9, 10, and 11. Again, the order is the same as in Figure 6, coarse to fine, while location 80 on the strip represented the beginning of foundry operations. The samples after position 300 were taken after all production had ceased.

There is a great deal of analysis to do on our part before we understand these data, and then a great deal of analysis for comparisons to gaseous data and foundry operations. However, several points are clear from these results. The alumino-silicates dominate the data, with Fe and Mn being the most common species. But the variability during pilot pours is startling; with moderate emissions suddenly enhanced by large spikes of generally short duration. If the source of these spikes were known, perhaps mitigation could be applied to sharply reduce total FOTF emissions.

4. Results of Analytical Electron Microscopy of representative samples from Feb. 16 and 17, 1999

Aerosols were removed from the Mylar substrate using toluene solvent. Then, the Apiezon grease (used in the collection process) was removed. The particulates were dispersed onto C-coated Cu Grids for Analytical Electron Microscopy (AEM) work. The mass mean diameter of this collection sample was 0.24, 0.34 µm. The key elements seen in the EDAX spectrum are Mn, Si, Fe, Zn, and S. The Cu peak can be discounted as coming from the Cu sample grid. The round particle shape is indicative of a high-temperature formation. The chemical spectrum is obtained from the small circular area in the lower, left hand side of the particle. The key elements seen in the EDAX spectrum are S, Si, and K. Spot chemical analyses indicated a relatively uniform chemistry.

The mass mean diameter of this collection sample was 0.069 -0.24 µm. The key elements seen in the EDAX spectrum are K, Si, and S. The holes in the particle are the result of electron beam evaporation of the material, also indicative of an organic phase.

The “halo” around the particle is associated with the volatilization. Unfortunately, the elements C and H, to be expected from an organic, are too light to be detected by EDAX. The chemical spectrum is obtained from the small circular area in the middle of the particle (held briefly enough to prevent “burn through”).

It should be noted that structural information (phase identification) similar to that obtained by x-ray diffraction is available with the AEM technique by the use of selected area electron diffraction.

INTERPRETATION

At this time, data are still arriving from the compositional studies. Two results, however, are to be emphasized. First, early analysis indicates that the total FOTF pilot scale pours have about the same emission rate as similar foundry studies in Mexico.

The second point is that the efficiency of particle removal in the dust reduction systems can now be established - 90 to 94% of PM2.5 mass. This will then meet EPA proposed fine particle mass standards even in conditions of extremely poor ventilation, such as the winter inversion fogs that are common during winter in Sacramento.

Further, specific comments will be forthcoming as we continue to review data from analytical techniques in our ongoing interaction with CERP.

RESULTS AND CONCLUSIONS OF AEROSOL STUDIES

- The newly developed aerosol sampling and analysis protocols are providing very good diagnostic information on aerosols from foundry processes.
- Very large amounts of $PM_{2.5}$ mass are present in the exhaust duct but before the bag house, roughly 800 µg/m^3, during foundry operations.
- Coarse constituents of $PM_{2.5}$ mass are dominated by sand and iron particles, but include important organic matter contributions.
- The ultra-fine ($D_p < 0.07$ µm) component of $PM_{2.5}$ mass was a tiny fraction of $PM_{2.5}$ mass, roughly 30 µg/m^3, and was dominated by organic matter.
- Dramatic differences in aerosol mass and composition were seen in very short time intervals during the pilot scale pours.
- The $PM_{2.5}$ mass emission rate per ton of iron poured seen in the pilot scale pours of Feb 16 and 17 was roughly the same as seen in other modern foundries.

Finally, we are designing the FOTF sampling and analytical protocols in such a way that they can be easily trans-located to other industrial sites or mobile source testing.

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