Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. pp. 227-236, 26-30 September 2005, Istanbul – Turkey

CONTINUOUS SEMI-VOLATILE FRACTION MEASUREMENT IN PM_{10} AND $PM_{2.5}$

TH. Petry[1], M. Richter[2], H. Grimm[1], K. Mueller[3] and G. Spindler[3]

GRIMM Aerosol Technik GmbH & Co. KG, Dorfstr. 9, 83404 Ainring, Germany[1]
GIP Messinstrumente, Muehlbecker Weg 18, 06774 Pouch, Germany[2]
Leibniz-Institut für Troposphärenforschung e.V., Permoserstrasse 15, 04318 Leipzig, Germany[3]

ABSTRACT

Different studies have shown that the semi-volatile fraction of $PM_{2.5}$ accounts for 20%…50% of the total $PM_{2.5}$ mass. Semi-Volatiles account for a lower but significant percentage of PM_{10} mass. To determine the appropriate PM_x mass it is important to measure not only the non-volatile fraction but also the semi-volatile content. Semi-volatiles can be lost from filter samples due to the on-going sampling, to gas-solid or even fluid-solid reactions. Also during the conditioning before weighing volatile compounds might be lost. Particulate monitors have used heated sample probes to prevent condensation, but by doing so, they can lose the semi-volatile fraction by heating up the sample. As a result, the data obtained often reflects measurements that have poor semi-volatile capture and PM values are therefore underestimated. With a newly developed real time OPC instrument employing non heated and heated probe sample cycles in the same instrument, it is possible to get a value of PM_x including Volatiles and to calculate a correction (location) factor for existing measurements as well as providing information about particle size distribution within the mass sample. This paper will show results from field tests in US and Germany and results from comparison with other real time and filter analysis. Results support higher PM values, better semi-volatile capture and the potential to calculate a correction factor.

Key Words: PM10, PM2.5, SVC, Semi-Volatiles

1. INTRODUCTION

Current methods of measurement of particulate matter only give a limited amount of information about particles in ambient air. For a better understanding of the possible impact of particles on human health we need information about the mass, size, concentration and composition of particulate matter. Available technologies have limitations with respect to these parameters.

In addition, information about temporal changes is required, making real time measurement desirable. Such data collection is cost effective and provides better source analysis and better understanding of the relationship of particulates measurement to processes occurring in the atmosphere. This information has the

potential to improve our understanding of causality and epidemiology and potential also for better prediction of episodes which may impact on human health.

Much of the data available only provides mean mass values, giving no information about size, distribution and concentration of particles.

A high mass value could come from a few coarse particles or from a huge amount of small particles.

Much of the existing data has been collected using filter methods with direct gravimetric measurement but no temporal information or ral time methods. The commonly used real time technologies have been based on Beta Attenuation Technology, Tapered Element Oscillating Microbalance TEOM (and FDMS), and Optical Particle Counters (OPC). Results are obtained from radiation attenuation, frequency of microbalance oscillation and orthogonal light scatter respectively.

Fine particulate mass in the atmosphere includes non-volatile components such as sulfate, crustal material and elemental carbon which (within instrument resolution) can be easily captured by a variety of techniques. However, also included in the fine particulate matter is semi-volatile matter.

Examples of semi-volatile particles include ammonium nitrate, ammonium sulphate, some organic material and water which is much more demanding to monitor (Eatough et al., 2003)

Different studies (Ten Brink, 2004) have shown that the semi-volatile fraction of $PM_{2.5}$ accounts for 20%...50% of the total $PM_{2.5}$ mass. Semi-volatiles account for a lower but significant percentage of PM_{10} mass. To determine the appropriate PM value, it is important to measure not only the non-volatile fraction but also the semi-volatile content. This importance increases as the focus on smaller particles measurement increases.

Semi-volatiles can be lost from filter samples due to the on-going sampling, to gas-solid or even fluid-solid reactions. Also during the conditioning before weighing semi-volatile compounds may be lost.

Dust monitors using heated sample probes to prevent condensation may lose the semi-volatile fraction by heating the sample.

As a result of the limitations of sampling methods, the data obtained often reflects measurements that have poor semi-volatile capture and PM values are therefore underestimated.

It is necessary to improve the technologies available to increase the efficiency of particulate capture as well as to determine the aerosol mass, size distribution and

concentration in combination/addition with different speciation technologies to get insight into the composition of particulate matter.

In this paper we present for discussion the results of two studies and propose that the results support the notion that using non heated probes results in higher Particulate Mass Sample Readings and that this higher reading can be explained by better captured of semi-volatile compounds.

The use of heated and non heated measurement cycles within the same instrument, can provide valuable indicative measures of the proportion of semi-volatiles in any given site in a cost effective and efficient manner. It is possible that this data can be used to calculate a site specific correction factor for other data. By incorporating this into an OPC based instrument additional useful information is obtained about particle size distribution within the overall mass measurement.

2. METHOD

Optical Particle Counter (particle counting with the method or orthogonal light scattering) instruments are widely used to measure particle counts and mass of ambient aerosols. Optical Technology draws on the principles of classic MIE theory.

The GRIMM monitors for this trial use light scattering technology for single particle counts in which a semiconductor laser serves as the light source. The ambient air to be analysed is drawn into the unit via an internal volume controlled pump at a rate of 1.2 litres/minute. The pump also generates the necessary clean sheath air which is filtered and passes through the sheath air regulator back to the optical chamber. This is to ensure that no dust contamination comes in contact with the laser-optic assembly. This particle free airflow is also used for the reference zero test during the auto-calibration.

The inlet air is usually unaltered prior to introduction to the light scattering chamber. The scattered signal from each particle passing through the laser beam is collected at approximately 90^{o} by a mirror and transferred to a recipient diode. The Grimm optical system measures the scattered light at 90 deg. to the incident beam from individual particles as they pass through the optical system and therefore changes in the refractive index of the particles, by any altered parameters, has minimum or no effect on the measurement. After a corresponding reinforcement, the signal of the diode is recorded with a multi-channel size classifier. A pulse height analyzer then classifies the signal transmitted in each channel. These counts are stored in the data storage card for future analysis.
To prevent condensation, the monitor incorporates a special sample probe drying system and does not alter the sample.

The new generation OPC instrument has been designed so that it can operate with the sample inlet probe unheated or heated and the results of both measurements are processed and the difference calculated.

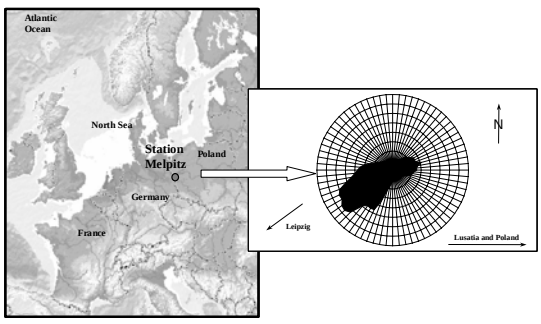
The instrument first measures the total amount of particles (including semi-volatiles in the ambient air with the standard non heated probe and obtains PM 10 and PM 2.5 values. The sample inlet is then heated to 100 C stripping Semi-Volatiles and in the second measurement the Non-Volatile fraction is calculated.

The difference between the two results is the semi volatile fraction of the ambient air. By processing both cycles, it is possible to get the mass value of the semi volatile fraction. The system is mobile and is installed in a robust weatherproof housing. This allows for mobile measuring campaigns, hotspot measuring or source apportionment. Three field tests were conducted.

The first field test was conducted by the Brigham Young University and the DRI in 2003. There were two field campaigns, the first in July 2003 in Roubidoux,CA and the second in December 2003 in Fresno, CA. Two OPC instruments using heated (to 100 C) and non heated probe measurements were compared to RAMS (Real Time Ambient Mass Sampler ; a TEOM (using a sample inlet heat of 50^{o}), a differential TEOM and a TEOM FDMS system.

In the third field test (conducted by the Troposphaeren Institut in Leipzig, Germany) the results from a single OPC unit using 10 minute cycles of heated and non heated probe data collections were compared to the results of High Volume Sampler Collection and the results of further chemical analysis of the High Volume Filter Sample.

The OPC with the nan heated and heated sample inlet were compared against three co-located High Volume Sampler Digitel DAH80 equipped with a PM_{10}, a $PM_{2.5}$ and a PM_1 sample head. The location for the field test was the Melpitz Research Station of the Troposphaeren Institut in Leipzig. This site was well suited for the field test because it is located in a plain with a rural background. The main wind direction is south-west bringing Atlantic air with emissions from middle Europe. The second wind direction is east. This brings mostly dry air from high pressure areas with heavy anthropogenetic pollution from the countries in eastern Europe.

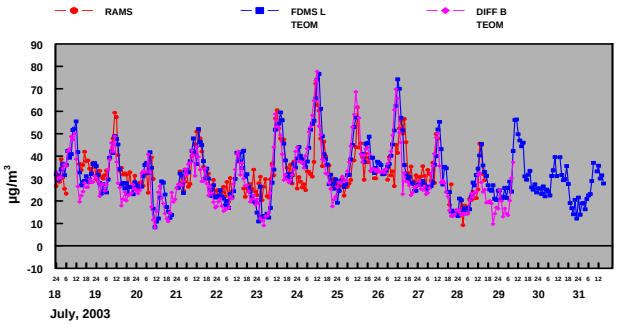


Measuring was conducted in the time from February 26 to April 26, 2004 for a total of 88 days. The daily mean temperatures were ranging from -2 to 18°C. Weather conditions were changing frequently.

3. RESULTS AND DISCUSSION

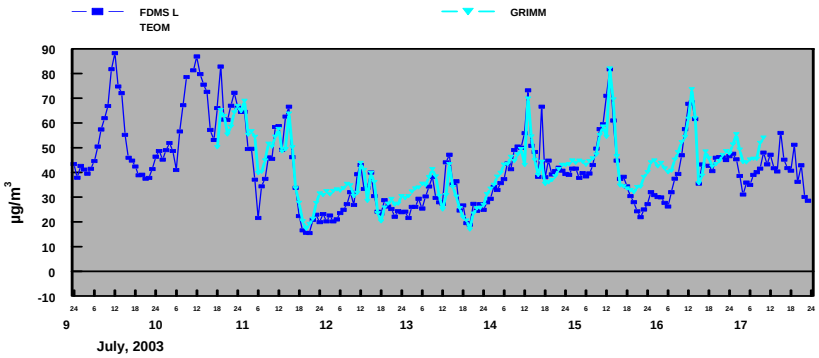
3.1 Roubidoux Study

The measurement of $PM_{2.5}$ by the GRIMM monitor in Roubidoux was evaluated by comparison with the RAMS, FDMS and Differential TEOM, each of which were in agreement with each other, and each of which have been shown to measure total fine particulate mass, including both the nonvolatile and semi-volatile components (Grover et al., 2004). However, each of these instruments uses a Nafion dryer in the inlet stream and does not measure the fine particulate water content. The comparisons between these three instruments has been

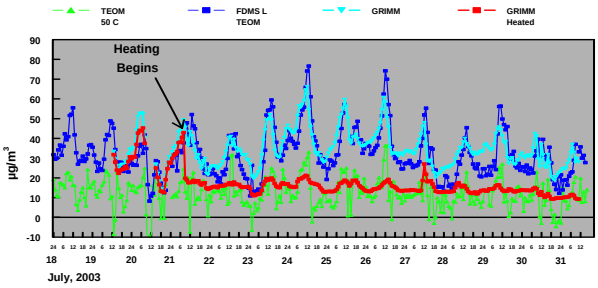


previously given (Grover et. al, 2004). For the purposes of this paper, the GRIMM monitor is compared to the average result obtained with these three instruments. This comparison is shown for data obtained during July 2003 at Rubidoux, CA during two different time periods. During the first time period from 11-17 July FDMS and Differential TEOM data were obtained, but no RAMS data were available. During the 20-30 July period data were available from all three comparison instruments.

Peaks in the $PM_{2.5}$ concentrations generally occurred during the mid-day period for each sampling day. This was a time of significant secondary ammonium nitrate and semi-volatile organic material formation. Relative humidity was general low during this mid-day time period. The GRIMM and comparison monitor results are in good agreement during these periods of low relative humidity, Indicating that the protocols used to convert the GRIMM monitor volume distribution data to a $PM_{2.5}$ mass concentration are robust.



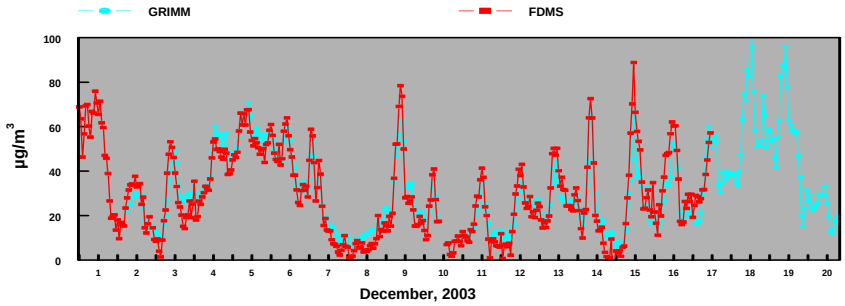
Additional information on mass measurement by the GRIMM monitor were obtained by comparison of the GRIMM monitor results with those obtained with a conventional TEOM monitor operating at 50 ^{o}C and a GRIMM monitor with a inlet heated to 50 ^{o}C. These data are compared to the conventional GRIMM results. As expected, both the heated TEOM and heated GRIMM results give $PM_{2.5}$ measurements which are lower than obtained with the other instruments. This can be attributed to the loss of some of the semi-volatile ammonium nitrate



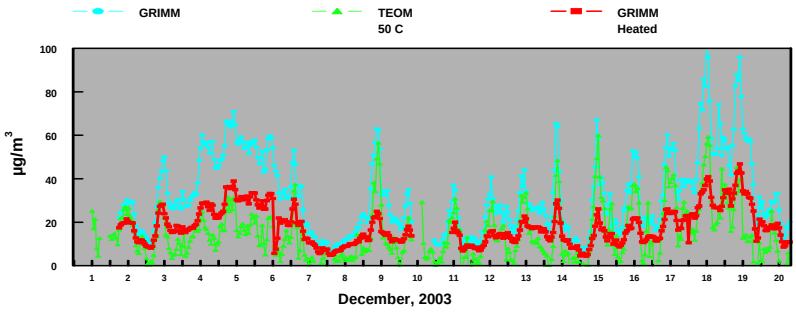
and semi-volatile organic material from the sampled particles at the elevated temperature. The 50 °C TEOM monitor results tend to be somewhat lower than the GRIMM measurements and to have greater diurnal variability. This can probably be attributed to the retention of particles on the heated filter of the TEOM monitor with subsequent continued loss over time as the composition of the sampled aerosol changes. The difference between the unheated GRIMM and comparison samplers which has been attributed above to the measurement of fine particulate water content by the GRIMM monitor is not evident in the heated GRIMM monitor results. This is expected at the elevated temperature of the sampled aerosols in the heated GRIMM monitor.

3.2 Fresno Study

The results obtained in the study at Fresno, CA in December 2003 present results for the GRIMM monitor, the heated GRIMM monitor, the FDMS and Differential TEOM monitors for the first two weeks of the study. The comparison among the various samplers for the data at Fresno are similar to the results seen at Roubidoux.



However, the diurnal pattern in the data is quite different. High concentrations of $PM_{2.5}$ were seen each evening. This can be attributed to a combination of the development of an inversion layer in the early evening, together with the contribution of evening rush hour and wood smoke emissions to the $PM_{2.5}$ present at Fresno.



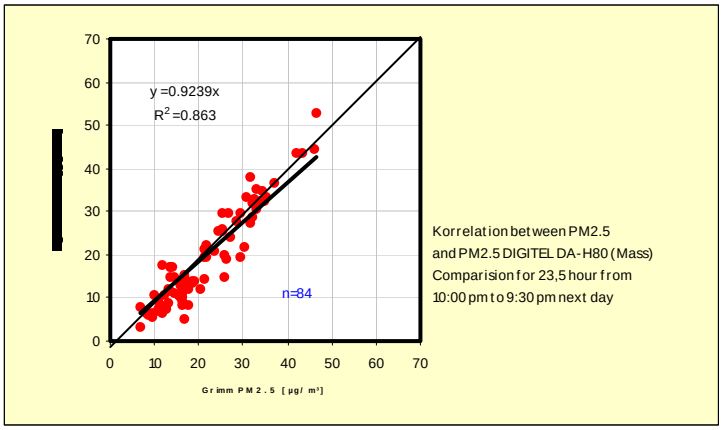
Generally low concentrations are seen during the day. The GRIMM and comparison monitors often give comparable results for both the mid-day and early evening time periods, Important exceptions to this pattern are seen during the prolonged inversion present during December 3 - 6, when the GRIMM monitor was frequently higher than the comparison data in the evening. This is also the time of significant ammonium nitrate formation. Another time period of interest is the early evening data for December 12 and 15. During these two time periods the comparison FDMS data was higher than the GRIMM monitor data by 10 to 15 $\mu g/m^3$ for just 2 or three hours close to midnight. The reasons for this observed difference are not now know. Consistent with results obtained in Roubidoux, the GRIMM monitor with a heated inlet measures significantly less material, presumable not accounting for the particle bound water and much of the semi-volatile ammonium nitrate and semi-volatile organic material.

3.3 Leipzig Study

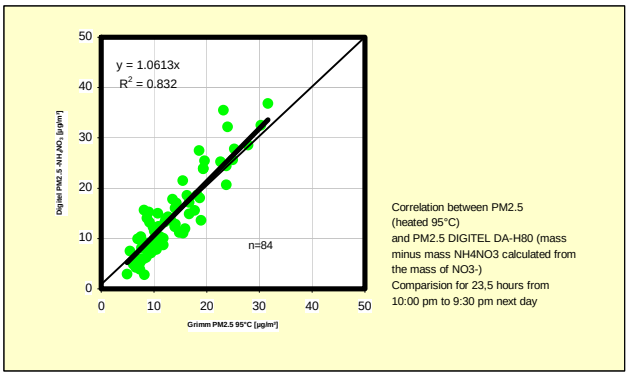
Troposphaeren Institut in Leipzig, Germany

For the field test the OPC with heated and non heated sample inlet were operated in a continuous mode with measuring interval of 10 minutes. The values for PM_{10}, $PM_{2.5}$ and PM1 have been monitored simultaneously. With the High Volume Sampler (HVS) DIGITEL-DHA-80 (30 m³/h flow rate) samples for PM_{10}, $PM_{2.5}$ and PM_1 have been collected on a quartz fibre filter for gravimetric mass measurement and consecutive chemical analysis. Samples have been taken for 23.5 hours (from 10:00h to 9:30h the following day). Of special interest was the amount of NO_3^- and NH_4^+ in the ambient dust. For the comparison a total of 88 filters ware available.

Comparison was made for the PMx values (OPC with non heated sample inlet, gravimetric mass from the HVS filters). A further comparison has been done for the PMx values from the heated OPC with the mass values from the HVS but with subtracted amount for NO_3NH_4, obtained from the chemical analysis.



The comparison showed a good correlation for the PM_x values from the non heated OPC and the values from the HVS. The measurements from the OPC in the 10 minute interval have shown a high temporal resolution of the changing atmospheric conditions. Furthermore the comparison of the values obtained from the OPC with the heated sample inlet and mass values from the HVS without the amount of NO_3NH_4 also showed a good correlation. The results show that the semi volatile fraction changes rapidly and therefore a fixed correction factor cannot be applied broadly.



4. SUMMARY

Measurement of particulate matter in ambient air should be reliable, accurate and sensitive. Information about mass, size, particle composition and temporal patterns is needed for better understanding about the implications for epidemiology and health.

One obstacle to the collection of complete samples has been the potential loss of semi-volatile compounds in filter methods with time and pre-conditioning before weighing of samples. One limitation of most real time methods has been the use of heated sample probes losing volatiles. The significance of this loss increases as the focus on particles less than $PM_{2.5}$ increase. The results of the US field study comparing the Grimm OPC In Non Heated and Heated Sample modes with RAMS and TEOM, TEOM FDMS support the hypothesis that the non heated sample inlet instruments such as the GRIMM OPC used in this study minimise volatile loss as the measurements with the heated probe samples are consistently lower.

The Leipzig study comparing results of Heated and Non heated cycles of measurement with High Volume Sampler mass measurement and subsequent sample speciation, support that volatile loss is the reason for these lower results.

Running heated and unheated instruments side by side at one site can give an estimate of the amount of volatiles on a continuous basis.

We propose that incorporating the capacity to run heated and non heated probe sampling cycles in a portable OPC instrument can provide better volatile capture in the Non heated cycle as well as information about particle mass values and size distribution. Also the comparative results can be used to calculate a correction or location factor for estimating the volatile fraction in the ambient air in a cost effective manner, especially for field companies, hotspot measurement or source apportionment.

REFERENCES

Delbert J. Eatough 2002, Evaluation of the RAMS Continuous Monitor for Determination of PM2.5 Mass Including Semi-Volatile Material in Philadelphia, PA, Journal of Air & Waste Management Association

K.E. Kelly, W.P. Arnott, et al. Sept. 2003, User Guide for Characterizing Particulate Matter, Evaluation of Several Real-Time Methods, Journal of Air & Waste Management Association

Delbert J. Eatough, et al. 2004, Measurement of Fine Particulate Mass, Including the Semi-volatile Constituents, with a GRIMM Monitor
2004th Annual AWMA Conference and Exhibition

Klaus Wittmaak, Lothar Keck 2003, Speciation of aerosol particulate matter by separating and quantifying the volatile and involatile as well as the water-soluble and insoluble fractions, EAC2003

Grover, B.D., Klein, M., Eatough, N.L., Eatough, D.J., Hopke, P.K., Chow, J., Watson, J., Meyere, M.B., Ambs, J., Wilson, W.E. 2004. Measurement of Total $PM_{2.5}$ Mass (Nonvolatile plus Semi-Volatile) with the FDMS TEOM Monitor. 97^{th} Annual AWMA Conference and Exhibition

Xavier Querol et al. 2004, Speciation and Origin of PM10 and PM2.5 in Spain, Aerosol Science 35 (2004)

Harry ten Brink 2004, Artefacts in measuring (the composition of) Particulate Matter in Europe; Atmospheric Environment 38 (2004) 6457