

Comparability of the Xact Ambient Metals Monitor to Filter Sampling Followed by Analysis by ICP-MS

It has been well established that increased particulate matter (PM) air pollution is associated with adverse health effects (Brunekreef and Holgate, 2002; Kelly et al., 2012). Particulate matter is not a homogenous air pollutant but a complex mixture with chemical and physical characteristics that can change depending on the contributing sources and chemical processes in the atmosphere. Understanding the chemical composition of PM can help provide insight into its toxicity and sources. Trace metals, although they constitute a low percentage of overall mass, are important contributors to the toxicity and in many cases can serve as markers for specific sources and source categories.

Airborne particulate composition is typically determined by collecting PM on filters using high volume or low volume filter samplers (TE-6070, Partisol 2025) followed by chemical digestion and analysis by analytical methods such as Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Filters are usually collected by continuously sampling over a period of 24 hours and then analyzed in the laboratory several weeks later. This approach is time consuming, labor intensive and results in data with low temporal resolution. This makes it difficult to correlate variability in reported concentrations with meteorology or to detect variability in emissions. This Technical Note focuses on two of the many peer-reviewed studies that have compared the Xact 625i to standard ambient particulate sampling followed by metals analysis by ICP-MS.

The Xact 625i Ambient Metals Monitor can address some of these limitations by allowing the measurement of metals concentrations in PM₁₀ and PM_{2.5} metals on much shorter time scales (from 4 hours to as little as 30 minutes). Air is sampled through a low volume (16.7 l/min) particulate matter size-selective inlet and drawn through a filter tape. After sampling is complete the resulting PM deposit is then advanced into the analysis area where the sample is analyzed by Energy Dispersive X-ray Fluorescence (EDXRF) for selected metals while the next sample is collected. The resulting metals concentrations are reported in nanograms per cubic meter (ng/m³).

As for all analytical techniques, quality and accuracy are vital to using the data appropriately. To this end, how well Xact compares to traditional analytical methods has been evaluated in several studies. This technical note outlines two of these studies – one undertaken by the King's College in London, and one by the U.S. EPA under the Environmental Technology Verification (ETV) program.



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King's College Evaluation

In this study (Tremper et. al), three different field campaigns were conducted: one at a traffic site in central London (Marylebone Road), and two industrial sites (Pontardawe in Wales and Tinsley in Sheffield see Figure 1). There were two different sampling campaigns on Marylborne Road, one lasting about 9 months and another for 3 months. The instrument also spent about 2 months in Tinsley and about 1 month in Pontardawe - resulting in a little over a year's worth of comparison data gathered over a period of about three years from 2014 to 2017. In all cases, reference method sampling was done using Thermo Scientific Partisol 2025 and the filter sample was subsequently digested and analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The average of 24 one hour Xact samples were plotted against the integrated twenty four hour average for each filter sample and a Demming least squares regression (Demming, 1943), which considers variability in both the X and Y variables, was performed on the data for each element. An example plot for lead (Pb) is shown in Figure 2. Elements where there were a significant number of days with concentrations above the detection limits of both analytical methods were compared.



Figure 1: Sampling Locations



Figure 2: Example Regression Plot

Figure 3 shows the slope and correlation coefficients for multiple elements including (Ba, Cr, Cu, Fe, K, Mn, Ni, Pb, V, and Zn). Perfect agreement would be indicated by unity for both the slope and the correlation coefficient. The slopes for these elements range from a low of 0.87 for vanadium (V) to a high of 1.10 for manganese (Mn) while correlation coefficients range from 0.89 to 0.99. In short, comparison shows that the Xact has excellent agreement with ICP-MS over a wide range of elements.



Figure 3: Slopes and Correlation Coefficients for Kings College Study



US EPA ETV Study

The Environmental Technology Verification program was established by the United States Environmental Protection Agency (USEPA) to "facilitate the development of innovative environmental technologies through performance verification." The Xact 625 was evaluated by the USEPA under this program (Battelle, 2012) during a field deployment of an EPA owned Xact 625 for a period of approximately 80 days in Marietta, Ohio. This location was chosen in part because of the close proximity several industrial sites, restricted air flow due to localized terrain (i.e. the Ohio River valley) and because of previous sampling in the area had identified high concentrations of manganese (Mn) and other metals in ambient particulate matter.

The Xact 625 was installed in a temperature-controlled trailer and a Thermo Scientific Partisol Plus 2025 sampler was co-located with the Xact 625's sampling head on the roof of the trailer (a photo of the sampling trailer can be found in Figure 4). Filter samples were collected on 47mm Teflon filters and sent every two weeks to a lab contracted by EPA for analysis of metal concentrations by ICP-MS using EPA Standard Method IO 3.5 including sample digestion with hydrofluoric acid (HF), laboratory blanks, fortified blanks, internal standards and tuning solutions.



Figure 4: Sampling Trailer Used During the ETV Study



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In this study, the Xact 625 measured 23 different elements while laboratory analysis was performed on 19 different elements. Comparisons were made between the Xact and ICP-MS when concentrations reported by the Xact were above its quantitation limit and when elements reported by the laboratory were above the method detection limit. In all, five elements (Ca, Mn, Zn, Se and Pb) had significant data above both the quantitation limit of the Xact and the detection limit of the laboratory ICP-MS analysis. For these elements the Xact daily average was calculated from the 24 individual hourly data points and plotted against the integrated daily filter average. A standard linear least square regression analysis was performed to assess the comparability of the Xact data with laboratory methods. The results of the regression analysis are shown in the figures below.



Figure 5: Regression analysis for Zn

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Figure 6: Summary of slopes and correlation coefficients for the ETV study

Slopes of the best fit regression line range from a low of 0.82 for calcium to a high of 1.06 for lead indicating good agreement between the Xact and reference method sampling followed by laboratory analysis by ICP-MS. In addition, the correlation coefficients range from 0.93 to 0.99 indicating a high degree of precision in the comparison between the two methods. Many of these elements also showed excellent agreement over a wide range of concentrations from a low of 1 ng/m³ for Se to over 1000 ng/m³ for zinc and manganese.

These are but two examples among many demonstrated the comparability of the Xact with other analytical methods and that the Xact can provide users with reliable data that can subsequently be used for source identification and understanding health effects.

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