A Comparison of XRF and ICP-MS for $PM_{2.5}$ Elemental Analysis in the Chemical Speciation Network

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A comparison of X-ray fluorescence (XRF)—the analytical method currently used by the Chemical Speciation Network—and an alternative technique, inductively coupled plasma mass spectrometry (ICP-MS) to speciate fine particulate matter, which is necessary to determine the source of pollution, and consequently, the most cost-effective control strategies.

In the United States, particulate matter (PM) concentrations have decreased substantially over the last few decades. These lower PM concentrations challenge the current techniques for measuring PM element content in the U.S. Environmental Protection Agency (EPA) Chemical Speciation Network (CSN). Element concentrations are useful as tracers to help identify specific sources of PM and track emission control strategies. Source apportionment has become more challenging now that nationwide regulations have dramatically reduced the largest sources of pollution (e.g., power plants, automobiles/trucks), leaving a diverse mixture of other sources contributing a larger fraction of the PM. The U.S. National Ambient Air Quality Standard (NAAQS) for PM with an aerodynamic diameter of less than 2.5 µm ($PM_{2.5}$) was recently reduced and may necessitate changes in element analysis instrumentation or sample collection to achieve better detection.

CSN measures the chemical composition of $PM_{2.5}$ at over 140 US sites. CSN sites collect $PM_{2.5}$ samples at low flow rates (i.e., 6.7 liters of air per minute or lpm) on large diameter (47 mm diameter) polytetrafluorethylene (PTFE, tradename Teflon) filters, which was appropriate when PM concentrations were higher. These lightly loaded samples are analyzed using X-ray fluorescence (XRF) spectrometry for 33 elements. XRF analysis is performed on the filter sample directly, does not require sample preparation, and does not destroy the sample filter. Therefore, XRF detection limits (DL) are dependent on the sample deposit thickness or density, which has decreased as ambient concentrations have decreased. One option to improve XRF DL is to concentrate the sample deposit by decreasing the filter size and/or increasing the sample flow rate. Another option is to change the analytical technique.

While XRF analysis is a cost-effective and reliable technique for measuring sulfur and soil-related elements, it is not the best available technique for most elements that pose health concerns (e.g., arsenic, selenium, cadmium, antimony, and lead). An alternative technique, inductively coupled plasma mass spectrometry (ICP-MS), has lower DL for many elements of health concern. ICP-MS is more labor-intensive, mainly due to the required sample preparation—thus more expensive to perform than XRF—and is destructive. The optimal analytical approach for a large-scale monitoring network like CSN must be based on a balance of its accuracy, cost, and operational considerations. This article delves into the pros and cons of performing element analysis on CSN $PM_{2.5}$ samples using XRF and ICP-MS.

Elements of Concern

As already mentioned, XRF DL are generally higher than corresponding ICP-MS DL for many elements and can be more than two orders of magnitude higher depending on the element. Elements that often exist in higher concentrations in $PM_{2.5}$ (e.g., silicon, sulfur, potassium, calcium, titanium, and iron) can be measured reliably and cost-effectively by XRF.[1] Laboratory-scale XRF instruments cannot quantify heavier elements in $PM_{2.5}$ samples because the photon fluxes at higher energies do not exceed the background noise. Heavier elements, generally present in lower concentrations in $PM_{2.5}$ and of greater concern to public health, can be more reliably quantified by ICP-MS.[1]

Sample Preparation and Analysis

XRF requires no sample preparation and minimal operator training for routine operations. XRF calibrations are stable, and thus, only performed following major repairs and annual maintenance. Quality control samples are analyzed daily, weekly, and monthly to assess calibration stability. XRF uses both single- and multi-element reference materials for calibration. The current CSN XRF analysis takes approximately one hour to determine the suite of 33 elements.

ICP-MS preparation requires the $PM_{2.5}$ samples be digested into liquid form. The digestion involves strong acids, requires formally trained laboratory personnel, and takes over two hours.[1,2] Vessels for sample digestion must be cleaned thoroughly prior to use (e.g., soaked in acid 24 hours).[1] Many strong acid digestions have been validated/certified for $PM_{2.5}$. Hydrofluoric acid (HF) is optimal to achieve complete digestion, but is dangerous to work with and expensive to dispose of. For CSN, a dilute leaching method may be optimal to balance extraction efficiency with cost and safety. However, dilute leaching methods may result in incomplete extraction of chromium (Cr) and nickel (Ni), as well as silicates which are a major PM source in dusty areas of the country.

ICP-MS requires a calibration before each analysis batch (daily) and quality control samples to be analyzed intermittently. Multi-element standards traceable to the National Institute of Standards and Technology (NIST) are commercially available in liquid form and are prepared at multiple concentrations for ICP-MS calibration. ICP-MS analysis takes approximately five minutes to determine the concentrations of most of the elements currently measured for CSN. Bromine and chlorine cannot be determined by the ICP-MS method currently being investigated, but several elements not currently measured by XRF can be measured by ICP-MS with little additional cost (e.g., rare-earth elements such as lanthanum, cerium, neodymium, europium, samarium, terbium, dysprosium, ytterbium, lutetium). Instrument drift can reduce ICP-MS measurement precision.[3] Drift can arise from the state and cleanliness of sample and skimmer cones, or problems in sample introduction systems like nebulizers, spray chambers, peristaltic pumps, and tubing. Optimization of the sample introduction systems and the use of standards can mitigate instrument drift. ICP-MS requires more frequent quality control checks than XRF to monitor drift.

Interferences

Interferences for both techniques can hamper the ability to quantify impacted elements. In ICP-MS spectral interferences arise from atomic or molecular polyatomic ions with the same mass-to-charge ratio (m/z) as the target analyte(s). These interferences can be reduced using collision cell technology, where the collision gas flow rate is optimized based on the elemental recoveries of quality control (QC) materials in a matrix comparable to that of the samples. However, certain ubiquitous and highly variable elements such as oxygen, nitrogen, carbon, and hydrogen contribute to polyatomic species,[4] and it is not practical to run QC materials that mimic the chemical compositions of every site in a national air monitoring network.

XRF interferences result from overlapping characteristic peak energies and matrix effects whereby emitted X-rays are reabsorbed by other particles in the sample matrix. Overlapping peak energies are well-established and addressed using theoretical corrections in the XRF software along with multi-element reference materials.[5] XRF matrix effects are generally small for lightly loaded samples like CSN, thus no corrections are made to address them.[6]

Sample Preservation

ICP-MS is destructive because of the digestion. While ICP-MS analysis can be performed in replicate on the sample digest, the sample digestion step can only be performed once. Therefore, the entire chemical measurement process for ICP-MS cannot be replicated, like ion chromatography which also requires liquid digestion of the samples. In addition, digests are less practical to preserve because of the large volumes, refrigeration requirement, and possible degradation. In contrast, XRF is nondestructive and preserves samples for reanalysis or analysis by complementary techniques, such as ICP-MS. XRF replicate analyses can be performed days or years later to identify analytical drift or the effects of method changes.[7,8]

Reference Materials

Certified reference materials (CRM) that match the matrix of $PM_{2.5}$ on PTFE filters are not available. One legacy CRM—NIST Standard Reference Material (SRM) 2783 (Air Particulate on Filter Media)—continues to be used for XRF calibration. Reference materials that mimic atmospheric aerosols have been successfully generated on PTFE filters in the laboratory but are not independently certified.[9] NIST SRM are available in powder form (e.g., 1633c, 1648a) to evaluate ICP-MS digestion and analysis, although the minimum mass of powder required to get a uniform sample (10–25 mg) is 100 times greater than the typical CSN sample mass (0.1 mg). These large CRM loadings can overwhelm the digestion and thus have limited utility. Ideally, these CRM particles would be deposited on PTFE filters at atmospherically relevant concentrations for analysis by XRF and ICP-MS, challenging all aspects of the measurement processes and facilitating a reliable evaluation and comparison of the two techniques.

Conclusion

An overall cost-benefit analysis of how many elements can be reliably measured, which elements are most important, cost per sample and the value of sample preservation should be applied to the CSN measurements. Any change in methodology will create discontinuities in the measurement record; a period of overlapping measurements is helpful to evaluate these discontinuities. The best data quality may be obtained from a combination of the two analyses, similar to the Canadian National Air Pollution Surveillance program, where XRF measures the lighter elements and ICP-MS measures the heavier elements.[10] ICP-MS analysis typically costs 4–6 times the cost of XRF. To maintain the overall budget, other program costs will need to be reduced to adopt ICP-MS (e.g., fewer sites, samples, or analyses). For example, a CSN site might choose to collect samples every 1-in-6 days instead of 1-in-3 days to offset the costs of ICP-MS analysis. It is also prudent to increase the CSN sample deposit density by decreasing the filter diameter and increasing the flow rate to improve the existing XRF DL, like the IMPROVE network which collects samples on 25 mm PTFE filters at 23 lpm.[11]

The evolution of PM monitoring techniques reflects the dynamic landscape of environmental regulations and technological advancements. As PM concentrations and NAAQS decrease, more sensitive monitoring techniques are required. Now may be time to revise the CSN sampling strategy. **em**

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