

Use of low-volume PM_{10c} FRM sampler

As noted in our previous consultation, the uniformity of this sampler's collected deposit needs to be established if XRF is used as the analytical method. Attachment 1 illustrates the need for such a determination with an example of a non-uniform sample collected with a different (non FRM) sampler. The elements Pb and Fe, presumed associated with different particle size classes, show quite different deposition patterns in this example. As the x-ray beam fluoresces only the central portion of the filter, the ratio of reported loading to ambient concentration varies accordingly. XRF analysis of filters from this sampler would thus respond differently to fine Pb particles from fume sources and coarse Pb particles from dust sources.

XRF as method of analysis

XRF is cost-effective, is sensitive enough for the levels under NAAQS consideration (see below), and fits well with other aspects the Agency's monitoring strategy and infrastructure. It has not previously been used for a NAAQS, however, and this first application raises issues of calibration (see below), standardization (see below), and sample uniformity (noted above) that wet-chemical methods do not present. I think Dirk Felton's suggestion to establish XRF as an FEM with ICP-MS as the FRM is worth considering, with the caveat that methods requiring extraction and digestion raise their own accuracy issues.

Adequacy of XRF bias, precision, and detection limit

The adequacy of XRF measurement capabilities depends on the MQOs (measurement quality objectives) established for the analytical method, which in turn depend on the DQOs (data quality objectives) established for compliance monitoring. In today's discussion it was noted that DQOs required to protect public health will themselves depend on the level and form eventually chosen for the NAAQS. With all these considerations yet to be finalized, there are nevertheless certain points that are already clear.

Detection: The NAAQS level proposed in the Federal Register is in the range 0.1-0.3 ug/m³. The existing CSN and IMPROVE networks demonstrate reliable (95% probability) XRF detection of non-spurious Pb at filter loadings of 5-7 ng/cm² (Attachment 2). For the low-volume PM_{10c} FRM sampler, this corresponds to a real detection limit of about 0.003 ug/m³, more than an order of magnitude below the lowest contemplated NAAQS level.

Precision: The declared goal for collocated precision is a 15% CV at 90% confidence. Quality assurance for IMPROVE includes regular XRF reanalyses of a fixed collection of about 70 representative ambient samples. Over 20 reanalyses have been performed of each sample at approximately monthly intervals, yielding some 70 well-determined analytical CVs. The typical (median) CV obtained for Pb has been 13% ([Trzepla-Nabaglo and White, 2008](#)). These results do not reflect flow and other sampling uncertainties but do include observations at all concentrations, with a (relatively low) mean loading of about 12 ng/cm². As Dirk Felton observed, precision for collocated samples will be sensitive to the minimum concentration included in the calculations.

Bias: The declared goal is a system bias within 10% at 95% confidence. Demonstrating attainment of these tolerances with XRF is likely to be a challenge. The need to verify that the sample deposit is uniform has already been noted. The other main difficulty will be the absence of a suitable NIST-traceable standard for calibration. NIST (2002) offers “air particulate on filter media” as SRM 2783, with a certified Pb loading of about 32 ng/cm², but gives a 95%-confidence uncertainty of about 17% for this value. I am not aware of any peer-reviewed examination of the claimed accuracies of commercially available calibration foils, or even consistency among different foils.

Specific analysis details in the FRM

Some aspects of XRF analysis require more prescriptive detail than the draft FRM gives them. The most important are two that relate to method accuracy.

Audit filters: Bias is to be assessed “through an audit using spiked filters.” The preparation of spiked standards for XRF analysis is significantly more complicated than simply depositing a known quantity of standard solution on a glass-fiber hi-vol filter and letting it dry, as is now done. Deposit uniformity is needed for quantitative XRF, as noted above. Achieving this uniformity in a liquid deposit on a Teflon membrane is likely to require attention to surface phenomena. The most relevant spiked filter would be created by actually sampling a pure Pb-containing aerosol and determining the Pb loading from the weight gain. XRF results for such a filter could be compared directly with those for ambient samples, but the production of such filters would require development and validation.

Protocols: The principals of EDXRF are universal but there is no standard protocol for implementing them, as the Agency discovered two years ago in its effort to “harmonize” XRF reporting from different labs used by their PM_{2.5} speciation networks ([Gutknecht et al., 2006](#)). Different instrument systems use different x-ray spectra generated by different configurations of source anode, secondary target, and spectral filter, different geometries of irradiation and detection, and different spectral decomposition software based on different interpretive strategies. Much of the spectral processing in commercial instrument systems is proprietary and invisible to the user, making it difficult to confirm which lines are used and how they are de-convoluted. Will the Agency undertake to certify certain commercial systems for use?

For whatever analytical method is used, field blanks should be routinely exposed and analyzed to detect possible contamination in the field and laboratory. CSN and IMPROVE both report loadings below 3.5 ng/cm² in 95% of their routine field blanks (Attachment 2), significantly exceeding the FRM’s proposed filter acceptance criteria (requiring 90% to be less than 4.8 ng/cm²).

Method interferences

I know of no additional method interferences.

Attachment 1: material excerpted and annotated from Nuclear Instruments and Methods in Physics Research B 160 (2000) 126-138 Elemental composition and sources of air pollution in the city of Chandigarh, India, using EDXRF and PIXE techniques

H.K. Bandhu, Sanjiv Puri, M.L. Garg, B. Singh, J.S. Shahi, D. Mehta, E. Swietlicki, D.K. Dhawan, P.C. Mangal, Nirmal Singh

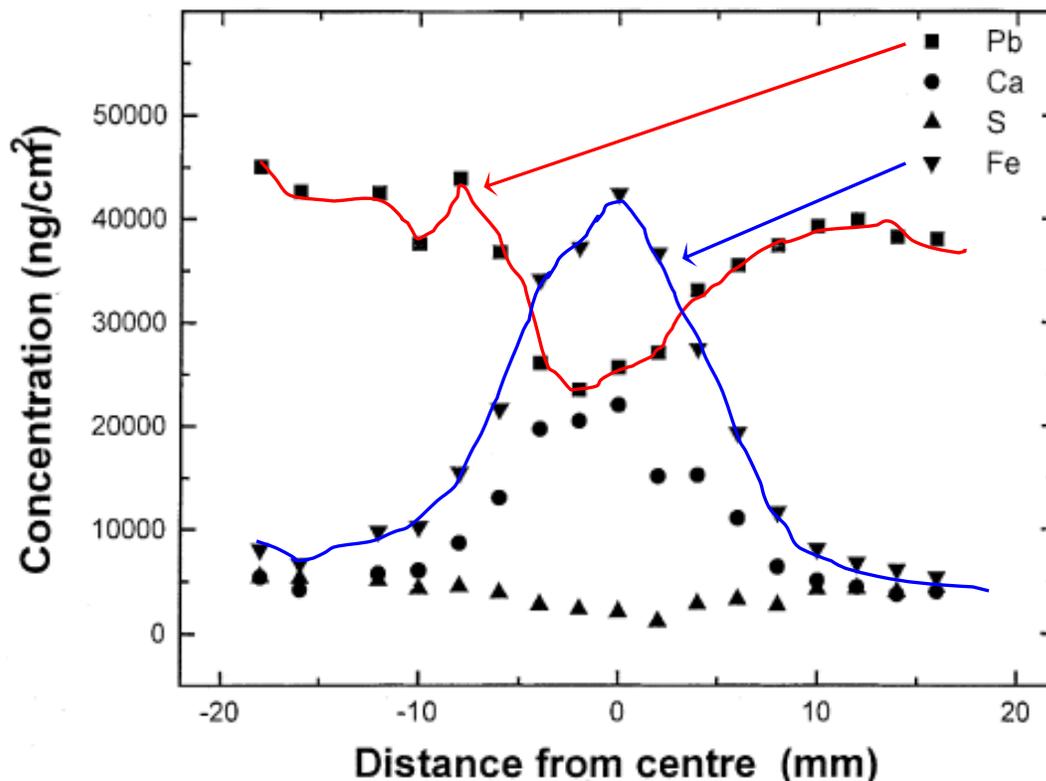


Fig. 5. Aerosol loading distribution for different elements as a function of distance from the center measured using 2 mm proton beam.

Samples were collected on 47 mm diameter, 0.8 μ m pore size, cellulose nitrate filter papers (Microdevices, Ambala, India). Filter paper was mounted in an aerosol filter holder (Millipore, Cat No. xx50 04700) having an inlet dispersion chamber to produce optimum particle distribution on the surface of the filter. The air through the filter paper was sucked at a flow rate of 12 l min⁻¹ with the help of diaphragmatic vacuum pump (Millipore, Cat. No. xx55 22050) and critical orifice (Millipore, Cat. No. xx50 000 00). The flow rate was monitored periodically for each sample with a rotameter and no cases of reduction of flow rate due to filter clogging were experienced during the sampling. The collection surface was directed downward to prevent particle collection by sedimentation and the filter holder was protected with a rain cover. All the sampling sites chosen for sampling were located on the flat roof of building tops 40-60 feet high.

Attachment 2: material excerpted and annotated from
 Environ. Sci. Technol. 2008, 42, 5235–5240

An empirical approach to estimating detection limits using collocated data
 Nicole P. Hyslop and Warren H. White

TABLE 1. Summary of STN and IMPROVE L_c estimates, L_D estimates

element	network	L_c 95th percentile (90–99th percentiles) (ng cm ⁻²)	L_D 95% detection probability (92–97% probability) (ng cm ⁻²)
Pb	STN	3.5 (1.8–8.1)	6.5 (6.3–7.0)
	IMPROVE	3.1 (2.6–4.2)	5.1 (4.8–6.0)
		↑ From field blanks	↑ From collocated sampling

To avoid type I errors a *critical limit* L_c is set such that measurements above that limit indicate the analyte is present with a high level of confidence. For a given probability α of type I error, L_c is the minimum value satisfying the inequality

$$\Pr(\hat{L} > L_c | L = 0) \leq \alpha \quad (1)$$

To avoid type II errors, a *limit of detection* L_D is set such that atmospheric concentrations of the analyte at or above that threshold will be detected with a high level of confidence. L_D is dependent on L_c because the analyte must be measured above L_c to be considered present. For a given probability β of type II error, L_D is the minimum value satisfying the inequality

$$\Pr(\hat{L} < L_c | L = L_D) \leq \beta \quad (2)$$