Comments on Proposed Pb PM_{10} FRM - Appendix Q Part 50 R. Poirot

An important prefacing comment is that the CASAC Lead Panel has advocated a transition of the Pb indicator from TSP to PM_{10} Pb if, <u>and only if</u>, the level of the standard is set lower than 0.2 µg/m^3. If a level equal to or higher than 0.2 µg/m^3 is selected, the CASAC Pb panel is unanimously opposed to a reduction in the indicator particle size range from TSP to PM_{10}.

What are your comments on the use of the low-volume PM_{10c} FRM sampler as the Pb-PM_{10} FRM sampler ?

Assuming the level of the Pb standard is set below 0.2 µg/m^3, the PM_{10c} sampler would be an appropriate choice for a Pb-PM_{10} FRM sampler.

What are your comments on the use of XRF as the Pb-PM_{10} FRM analysis method?

XRF should be an adequate analytical method for a Pb NAAQS set toward the middle to upper end of the range of levels recommended by EPA staff and the CASAC Pb Panel. If the level is set toward the low end of that recommended range (0.02 µg/m^3), a more accurate analytical method like ICP-MS, with lower detection limits and smaller analytical errors, would be preferable. Consideration should also be given to specifying ICP-MS as the FRM and establishing XRF as a FEM.

What are your comments on the specific analysis & details of the XRF analysis method contained in the proposed Pb-PM_{10} FRM analysis method description?

I think it should be useful and possible to tighten up some of the specific details relating specifically to the determination of Pb by EDXRF. Much of the description sounds more like cautionary guidance rather than prescribed details of specific procedures, and also seems to pertain to XRF analysis of elemental species other than Pb. This raises a related point that it would be best to be very clear up-front about analytical and data reporting procedures for (readily detectable) XRF elements other than Pb that may result at little or no extra cost from the Pb XRF analysis (and would also represent an important reason in favor of the choice of XRF as part of the Pb FRM). Arguably this "supplemental data" would have value for quality assurance and source attribution of the Pb measurements, and if significant additional costs are not incurred, analytical and data reporting procedures could be specified. Similar considerations would also apply if (multi-elemental) ICP-MS were selected as the Pb FRM. Along similar lines, clear guidance should also be provided on whether (or not) there should be PM_{10} mass measurements conducted on the Pb FRM filters. Possibly the Agency would want to provide for an optional national analytical contractor, as has proved effective for IMPROVE and STN networks. Alternatively, some consideration should be also given to coordination with the evolving NAATS metals sampling program which generally (but not always) utilizes PM_{10c} samplers combined with ICP-MS analyses (at most but not all sites), and which would benefit from greater internal consistency.

Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?

The precision, bias and MDL of the XRF method should be adequate for a Pb NAAQS in the currently proposed range of 0.1 to 0.3 µg/m^3, although a PM_{10} sampling method is not recommended if the level is greater than or equal to 0.2 µg/m^3. The XRF precision, bias and MDL could pose problems for a NAAQS set at the lower end of the EPA staff-recommended range of 0.02, and may result in uncertainties in spatial patterns and temporal trends at population-oriented monitoring sites where levels are likely to fall well below the proposed NAAQS range. The indicated XRF PM_{10} Pb MDL of 0.001 µg/m^3 would be only 1% of the lower bound level of the proposed NAAQS and unlikely to have a significant influence on compliance determinations. I also think its likely that this MDL could be further reduced. For example the current MDL for $PM_{2.5}$ Pb in the IMPROVE network is closer to 0.0001 µg/m^3.

Current Pb precision comparisons are limited to concentrations above 10% of the current NAAQS (i.e. 0.15 µg/m^3). This limit will need to be lowered to reflect the hopefully much lower level of the currently revised NAAQS. Also, since it generally appears likely that the Administrator may select a level (and form) of the standard which are less stringent than are warranted by the Agency's Risk/Exposure Assessment and Staff Paper, some consideration should be given to collection of accurate and precise data at levels below and possibly well below the level of the NAAQS selected in this review cycle.

Are there any method interferences that we have not considered?

None that I'm aware of – related to XRF analysis of Pb on PM_{10C} filters. However, it should be recognized that XRF is not very well suited for analysis of fiberglass TSP or hi-volume Quartz PM_{10} filters. ICP-MS would be a better choice for an FRM analytical method that could be used across all potential filter types, and would provide a better basis for comparative sampling to develop better information on Pb particle size distributions, sources etc. – especially in the event that TSP (and/or hi-vol PM_{10}) are retained (or specified as FEM).

Other minor comments on Pb PM_{10} FRM:

p. 3, para 1, line 6: The hyphenated "24-hour sample" is correct here, but all other instances of the number "24" in this document are also (incorrectly) attached by hyphen to the words that follow. These include "24-hours" in line 3 and "24-cubic meters" in line 5 of this paragraph and 2 instances of "24-m^3" in 2nd and 3rd paragraphs on page 5.

p. 6, para 1: You present optimal (150 µg/cm^2) and minimal (15 µg/cm^2) PM_{10} mass loading levels (roughly 75 and 7.5 µg/m^3 respectively) for XRF Pb quantification, but also indicate potential distortion with "unusually heavy deposits". Why not also provide the PM_{10} mass level that would be considered unusually heavy (i.e. an upper bound to go along with the ideal and minimal loading levels). Also, unless mass measurements are

required, how will it be known whether the filter loading is above, below or within the range where distortion-free measurements are expected?

p. 6, para 2, line 3: You could add "S/P" to this list of XRF interferences.

p. 7, para 2, line 6: This effect is "especially significant and more complex for PM_{10} measurements…" than for what?

p. 8, section 6.1.2, last line: Just for curiosity, what is the basis for your selection of this blank Pb limit of 4.8 ng/cm^2? This (x 11.86 cm^2 of exposed filter / 24 m^3 of air sampled) would yield an implied ambient Pb concentration of 0.002 µg/m^3 - or about twice the indicated Pb XRF MDL - or about 1% of a standard of 0.2 µg/m^3 (are you giving us a hint about the intended level of the NAAQS?).

p. 9, section 6.2.3, line 2: What do you mean "Filters are typically archived in cold storage"? For what current analyses is this cold storage procedure "typical"? Will it be required for Pb sampling? What elements, if any, which are quantifiable by XRF do you expect to see volatized from filters if they are not kept in cold storage prior to analysis? Certainly you don't expect any loss of Pb, do you?

Comments on "Approaches for development of a low-vol TSP sampler"

Although the hi-vol TSP sampler can and does collect particles larger than 10 microns which can become ingested and contribute to Pb body burdens, and which are emitted by some Pb source categories, the fundamental problem with the current hi-vol TSP sampler is that the particle cut size characteristics are not well characterized and can be highly variable as a function of wind speed and direction. If it is considered important to include Pb contributions from particles larger than 10 microns, the Agency should devote appropriate resources toward development of a sampler which efficiently captures larger particles, but which has less variable and more clearly characterized cut size characteristics. The ability to collect multiple sequential samples between periods of sample collection would also be desirable. It is likely that such a sampler would also have value in characterizing concentration (& deposition) of other metals or aquatic nutrients, for example.

It should be clearly recognized in advance that there are practical limits to the upper particle cut sizes that can be captured (especially by low volume samplers) with reasonable precision (I would guess an upper bound of about 20 microns). It should also be easier to reduce/eliminate wind directional biases than wind speed biases. Some advance consideration – and discussion with dosimitry experts – would be useful to guide (& perhaps further justify – or not) the planned development efforts. In any event, consistency of results with the current TSP hi-vol should be considered a necessary or desirable design criterion.