July 14, 2008

TO: Fred Butterfield
Ted Russell

FR: Peter McMurry

RE: Comments regarding measurement methods for particulate lead in atmospheric aerosols.

1. Comments on Draft Federal Reference Method (FRM) for Lead in Pb-PM_{10}

What are your comments on the use of the low-volume PM_{l0c} FRM sampler as the Pb-PM_{10} FRM sampler ?

I think it is a good idea. This sampler is readily available, is familiar to monitoring agencies, and has been well-tested. Furthermore, the Pb samples would be sampled in the same way as PM_{10} mass, so the fraction of mass that is Pb would be well defined.

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

Chemical analysis is not my primary area of expertise. Therefore, the views expressed here represent my synthesis of comments from today's telephone conversation.

I think very compelling arguments were made to use an extraction method such as ICP-MS rather than XRF as the FRM analysis method. These include the (1) the confidence that Pb can be effectively extracted with efficiencies that approach 100%, (2) the availability of NIST traceable standards for liquid solutions of Pb that can be used to calibrate analytical instruments used to analyze dissolved extracts and the corresponding lack of such standards for deposited Pb, (3) the availability of instruments, such as ICP-MS in states and the corresponding unavailability of XRF instruments, (4) the sensitivity of XRF to spatial distributions of deposits on filters, which are unlikely to be uniform (especially for coarse particles) and the corresponding insensitivity of extraction methods to such nonuniformities, (5) the use of proprietary software for analyzing XRF data, which shields the public from a clear understanding of how concentrations of lead are determined, and (6) the superior sensitivity of methods such as ICP-MS. I question whether XRF would meet the accuracy and precision goals required for a standard.

Because XRF is inexpensive and nondestructive, I think it makes sense to use it 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 will defer to other members on the committee on this.

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

Again, I will defer to those members of the committee who are more knowledgeable than I on this topic. I was left with the sense there are compelling arguments for using another analytical method as the FRM.

Are there any method interferences that we have not considered?

Not to my knowledge.

2. Thoughts on proposed Pb-TSP FEM.

I do not support the adoption of a design-based sampler for Pb-TSP unless its performance is first reasonably well understood. My reasons are outlined below.

It was pointed out in our telephone conference call that this is the approach that was originally used for TSP. I agree. That decision was made in an earlier era, when we'd had much less experience with aerosol sampling. After several decades of progress it would be inadvisable to endorse a method that we believe likely to fail.

I am especially concerned about the dependence of sampling efficiencies on wind speed. Local obstacles that cause updrafts or downdrafts are also likely to affect efficiencies. Such effects need to be studied. Repeatability for side-by-side measurements might not provide meaningful information on true sampling precision if these effects are significant.

I would only use "TSP" for measurements made using the Hi-Vol. Extending that terminology to a different instrument would add ambiguity to an already ambiguous concept. TSP is what the Hi-Vol collects, and is not related in any straightforward way to mass concentrations of particles in the atmosphere. "TSP" measured using a different sampler would be subject to different measurement errors. If we were to adopt a design-based lo-vol sampler, at the very least we should give it another designation, such as TSP2 (T2 for short).

I would not deploy a new low volume coarse particle Pb sampler until it has been characterized. I agree that there are inherent difficulties in working with coarse particles that make such work difficult. If laboratory evaluations are impractical, other approaches (such as computational modeling) should be considered.

If a case can be made that coarse particles ought to be measured (Phil Hopke has made persuasive arguments that they should be), then an effort should be made to devise measurement methods that provide meaningful data.