Responses by Dr. Robert Lewis, EPA (lewis.bob-dr@epa.gov) to questions and comments regarding Method TO-13A, 10/3/00 :

The following of questions and comments were received recently by e-mail from a user of TO-13A. He points out a number of errors and inconsistencies in the method, which we have attempted to correct in our responses below.

Please be advised that the TO methods are meant only for guidance. There in no for the user to follow these methods verbatim. ISO 12884 and ASTM 6209 are the standard methods for PAH in ambient air, prepared by EPA through its organizational membership in the census standards organizations. These standard methods have received wide scrutiny and are largely free of errors. They are performance based and rather than mandate specific equipment and supplies, which quickly become outdated, they allow the user wide discretion. Use of ASTM and ISO standards in lieu of EPA methods is consistent with Public Law 104-113, which mandates that federal agencies use private consensus standards organizations whenever possible to develop standardized methods.

Comments and questions followed by responses (in italics):

1) Sec 9.1.1 – Whatman QMA-4 seems to be the wrong part number (or description) for this filter. It should probably be just Whatman QMA filters.

The supplier or manufacturer does not matter as long as the specifications are met. ASTM 6209-98 calls for "filters, 102-mm micro-quartz-fibre, binderless, acid-washed." ISO 12884 calls for the same type filer with the proviso that they have "a filtration efficiency of 99.99% mass fraction or better for particles below 0.5 mm" Both standards offer the comment that "Glass- or quartz-fibre filters coated or impregnated with polytetrafluoroethylene have been used for collection of particle-associated PAH)." However, they state that the user must "Validate the performance of these filters before use if used in lieu of those specified."

2) Sec 10.2.4 - When using the small (1/4") PUF plugs that hold the XAD-2 resin, and the PUFs are being cleaned for re-use is it acceptable to use acetone or methylene chloride as the solvent for the cleanup?

PUF should be cleaned up with acetone before its first use only. There is no need to clean the PUF again with acetone after the initial cleanup. In fact, you probably don't need to extract it with acetone at all if you use commercially precleaned PUF from a good quality supplier. However, we can't vouch for that. The acetone is used only for initial cleanup to remove manufacturing contaminants [see Lewis et al., Anal. Chem. 49:1668-1672 (1977)] Thereafter, if the PUF is to be reused it should be fine if the extracting solvent (e.g., ether/hexane, cyclohexane, or toluene) is used to clean it up before reuse. Commercially pre-cleaned PUF should also be

extracted before use with the solvent system you will be using for analysis. Never use methylene chloride (dichloromethane) to cleanup or extract PUF.

3) Sec 10.2.6 states to use 200 g. of XAD-2 per sleeve. Method TO-13 stated that about 55 g. (2@) should be used. That seems more appropriate.

The original TO-13 was correct. See previous comments dated 5/15/00.

4) Sec 10.3.2 and 12.2.1 **B** When using the XAD-2 option, should the small PUF used to hold the XAD-2 in the sleeve also be extracted with the resin and filter using methylene chloride?

No, PUF should never be extracted with methylene chloride. Dichloromethane (DCM) partially dissolves PUF (dissolves lower molecular weight PUF polymers, called oligimers). These will leave a gummy residue in your extract that will badly interfere with your analyses. We have heard of users pre-extracting PUF with DCM to clean it up, but we have serious concerns about such a practice as we have never investigated it. If you are using DCM to extract your XAD-2 cartridge (sleeve), then you should use stainless steel screens to retain the resin in the cartridge. If you are using 10% diethyl/n-hexane, cyclohexane, or toluene to extract the XAD cartridge, then PUF retainers are OK. The cartridge should be extracted intact, but only after the outside of the glass is carefully rinsed with solvent.

5) Sec 10.3.6 **B** When concentrating the ether/hexane used to extract the PUF, concentrating at 50 deg. C seems low considering that the BP of hexane is 70 deg. C.

Obviously the temperature of the bath has to be high enough to boil the solvent. With a Kuderna Danish concentrator, as called for here, solvent must be boiled vigorously. Therefore, the water bath temperature must be well above the boiling point of the solvent. KD heating mantles may also be used. Rotary evaporators may be used instead of KDs if care is taken to prevent the solvent from going to dryness. (Note that the temperature specified in 12.2.2.1 is likewise too low.)

6) Sec 10.3.7 **B** Should the final volume of the extract be 1 ml. rather than the 5 mls. listed considering that the limit for other PAH=s in Sec 10.3.8 is < 200 ng total/cartridge.

Yes, 1 mL or less.

7) Sec 12.1.3 - Recommend changing storage temperature to 4 deg. C $\pm$2 deg. C. for consistency with other parts of the method.

The minimum storage temperature should be no higher than 4 deg.

8) Sec 12.2.1.1 **B** The first sentence instructs the analyst to put the extraction surrogates in the extraction solvent, and the same paragraph several sentences later instructs the analyst to put the surrogates in the center of the PUF. I suspect that the second sentence is correct.

The recovery (extraction) surrogates should be spiked to the top of the sorbent bed after placement in the Soxhlet extractor. If PUF is used, the PUF plug should be removed from the glass cartridge before placing it in the Soxhlet extractor. The filter should be folded in quarters and placed in the Soxhlet first. The step in 12.2.1.1 calling for running the Soxhlet empty for 2 hrs. is not necessary. The glassware can be cleaned and solvent rinsed before assembly and use.

9) Sec 12.2.2.3 says to use a micro Snyder column with the nitrogen blowdown. Typically a micro Snyder is not used with the nitrogen blowdown, but rather is used when boiling solvent off.

It is unclear what the author means here by an Aopen micro-Snyder attachment.@ What he was attempting to describe is the final concentration by nitrogen blow-down. Typically the Snyder column is not used here (in fact, it would be impossible to use it here as the nitrogen jet must be lowered into the mouth of the KD tube). Perhaps the Aopen micro-Snyder attachment@ is a Amodified@ Snyder column that is basically an open tube. In any event, I see not purpose for it.

10) Sec 12.2.2.4 and 12.2.2.6 instruct the analyst to rinse the concentrator tube with hexane, and bring back to final volume with hexane. This is after adding 5 mls of cyclohexane in Sec 12.2.2.2. Is this correct, or should cyclohexane be used (especially if doing silica gel cleanup).

The rinse solvent in 12.2.2.2 should be hexane, not cyclohexane.

11) Sec 12.3.2 and Sec 12.3.3 indicate that 10% diethyl ether should be used. What is the other 90%?

The author carelessly omitted hexane here. It is obviously 10% diethyl ether/90% n-hexane.

12) Sec 12.3.3 indicates that a slurry should be prepared to transfer the silica gel to the Pasteur pipet. It is difficult to transfer a slurry to a small diameter opening on the pipet. Would it be acceptable to add the dry silica gel to the pipet, and then rinse it with solvent? Also, 10 g. seems like too much silica gel for a 6@ disposable pasteur pipet. That is the amount specified in Method 3630C for 250 mm x 10 mm id column. If the mass of silica gel is wrong, should the volume of elution solvents be changed?

A Pasteur pipette should not have been specified here. Obviously, one would not hold 10 g. of silica gel. Incidentally, this step is not necessary for most ambient air samples. Here is what ASTM 6209 says:

A13.2.1 Column preparation: Extract silica gel (10.1.9), type 60, in the Soxhlet extractor (9.2.1) with dichloromethane (10.1.5) for 6 h (minimum rate, 3 cycles/h) and then activate by heating in a foil-covered glass container for 16 h at 150°C.

13.2.2 Pack a small piece of glass wool into the bottom of a glass chromatography column of 15- to 25-mL capacity (for example, by 11.5-mm i.d. x 160-mm long) and slurry 10 g of activated silica gel (10.1.9) into the column with pentane (10.1.8). Tap the column gently as the slurry is settling to ensure proper packing. Finally, add 1 g of anhydrous Na_2SO_4 (10.1.10) to the top of the silica gel. Prior to use, rinse the column with pentane (10.1.8) at 1 mL/min for 1 h to remove any trace of contaminants. Preelute with 40 mL of pentane (10.1.8) and discard the eluate.

Note: Cleanup procedures may not be needed for relatively clean matrix samples.

13.3 Column chromatography:

13.3.1 While the pentane preelutant covers the top of the column, transfer 1 mL of sample extract in n-hexane (10.1.7) to the column, and wash with 2 mL of n-hexane to complete the transfer. Allow it to elute through the column. Immediately prior to exposure of the Na_2SO_4 (10.1.10) layer to the air, add 25 mL of pentane (10.1.8) and continue the elution. Discard the pentane eluate.

13.3.1.1 If dichloromethane (10.1.5) is used for extraction of the sample, solvent exchange it with n-hexane (10.1.7). This may be accomplished by diluting the extract at least 2-fold with hexane and concentrating to 1 mL at 30°C under a purified nitrogen stream. The dilution and concentration process should be repeated at least twice. Alternatively, a micro KD concentrator fitted with a micro-Snyder column by be used for concentration.

13.3.1.2 The pentane fraction contains the aliphatic hydrocarbons collected on the filter/adsorbent combination. If desired, this fraction may be analyzed for specific aliphatic organics. Elute the column at 2 mL/min with 25 mL of dichloromethane (10.1.5) in pentane (10.1.8) (4:6 V/V) and collected in a 50 mL K-D (9.2.2) flask equipped with a 5-mL concentrator tube for concentration to less than 5 mL. Concentrate the concentrate to 1 mL or less under a gentle stream of nitrogen (10.1.3.2) as previously described.

13.3.1.3 An additional elution of the column with 25 mL of methanol will elute polar (oxygenated and nitrated) PAH. This fraction may be analyzed for specific polar PAH.@

13) Sec 12.3.5 indicates that A10% diethyl ether in pentane (4:6 v/v)@ should be used. Which is correct?

This is a very serious error. The solvent mixture should be 40% dichloromethane/60% pentane (i.e., 4:6) (See ASTM 6209, Section 13.3.1.2 above).

14) Sec 13.1.3 indicates that a 50 ng/ul solution of DFTPP should be used to tune the instrument, and Sec. 8.3.1 specifies a 2 ul injection . I suspect that since Sec 13.3.3 indicates that 50 ng total should be used, this section should also read 50 ng.

We do not understand this provision of TO-13A. Most GC/MS systems are tuned by allowing a small amount of calibration gas to enter the ion source through a valve system that operates independently of the GC system. The tuning procedure is typically done automatically by the operating software and is an iterative process that can take several minutes to complete. Alternatively, the instrument can be tuned manually, which would most likely take longer. The transient time of a GC peak of DFTPP would be much too short to allow for this iterative tuning process. What is probably meant here is that the injection of DFTPP can be used to check the tune of the instrument. We would tune the GC/MS according to the manufacturer's recommended procedures, and if desired, check this tune with an injection of DFTPP.

15) Sec. 13.2.1.8 **B** It seems that there several compounds assigned to the IS Acenapthene-d10 that should be assigned to Perylene-d12. They are benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene, Dibenz(a,h)anthracene and benzo(g,h,i)perylene. This change would be consistent with sec 13.4.5 that indicates that the IS closest to the RT of the analyte should be used.

Benzo(ghi)perylene, dibenz(ah)anthracene, indeno(123-cd)pyrene, perylene, benzo(b)fluoranthene, and coronene can be assigned to perylene-d12. See ASTM 6209 or ISO 12884 for correct assignments.

16) Sec 13.2.2.1 and Table 4 indicate that the IS concentration to be used is 0.5 ng/ul (1 total ng) while Sec 14.4.3 indicates that 2 ng/ul (4 total ng) should be used. Which is correct?

We *would recommend trying to keep the concentrations of the IS near what you expect in your field samples, regardless of what is recommended in TO-13A. Of course, the concentration of the IS should be several times higher than the minimum detection limits. We usually run our IS at 1 ng/µL, but*

could probably run at 0.5 ng/µL as well. A concentration of 2 ng/µL is probably too high for analyzing sample extracts from ambient air.

According to ASTM 6209 and ISO 12884, typical IS concentrations for ambient air are 1 ng/µL for the lighter PAHs and 0.1 ng/µL for the heavier PAHs.

17) Sec 13.3.2 **B** Suggest changing transfer line temperature to a range like 250 **B** 300 deg. C.

We usually run our transfer line at 280 deg. C. If we run much lower than that, we lose some sensitivity on the higher boiling PAHs. The recommended transfer line temperature in ASTM 6209 and ISO 12884 is 275-300 deg. C.

18) Sec 13.3.4.5 **B** Remove the sentence **A**For all other target compounds, the values for % RSD must be less than or equal to 30 percent**@**. All compounds specified in Table 7 have RSD limits specified.

Table 7 specifies 30% maximum RSD for all analytes. Perhaps there is some redundancy.

19) Sec 13.4.5 indicates that the continuing calibration standard is used to calculate the sample concentration, while Sec 13.3.4.2 and the equation listed in Sec 13.4.6.1 indicate that the initial calibration should be used. I suspect that Sec 13.4.5 should be revised.

Yes, this appears to be an inconsistency in the method.

20) Sec 13.4.8 **B** The last sentence seems to imply that samples can be accepted with compounds up to 20% above the calibration range. This disagrees with Sec 13.4.7.1

We agree. You should use the criterion set forth in Sec 13.4.7.1

21) Sec 14.2.1 **B** The definition in this section of a process blank seems to me to be either a Laboratory method blank, or the cartridge certification sample and therefore are already defined.

The blank here is indeed a laboratory matrix blank.

22) Sec 8.2.2 indicates that a glass tube furnace should be used for activating the silica gel used for cleanup. Other EPA methods(e.g. Method 3630C) on which this cleanup seems to be based do not indicate this as a requirement. Suggest that this section be removed or modified.

See ASTM 6209, Section 13.2.1 (above).

23) Table 3 **B** The criterion for Ion 442 (40% of Mass 198) seems incorrect. Most methods have this ion with a criteria of 40 to 100% of Mass 198. Suggest revising Table 3.

The broader criterion is probably acceptable here also.

24) Sec 12.2.1 calls for charging the Soxhlet apparatus with the extraction solvent and refluxing for two hours prior to setting up samples. The solvent is then removed, and a fresh charge of solvent is used to extract the samples. With the current emphasis on waste minimization I believe that it would be appropriate to rinse the apparatus with solvent prior to extracting samples rather than cleaning the apparatus with such a large volume of solvent.

We agree. This was answered previously in comments regarding 12.2.1.1 (see above).

25) Section 10.2.5 calls for cleaning the XAD-2 resin twice prior to use. With the availability of pre-cleaned resin, and the emphasis on waste minimization, is this actually necessary?

Once is certainly enough with today's source of XAD-2.