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14 Jun 1995

California Environmental Protection Agency
Department of Toxic Substances Control, Region 2
Attn: Ms. Mary Rose Cassa
700 Heinz Avenue, Suite 200
Berkeley, CA 94710

Subj: ALTERNATIVE METHODS FOR PAH ANALYSIS
REMEDIAL INVESTIGATION/FEASIBILITY STUDY (RI/FS)
NAVAL STATION, TREASURE ISLAND

Dear Ms. Cassa:

The regulatory agencies have voiced concern that the normal contract laboratory program (CLP) method quantitation limits are not as low as the Environmental Protection Agency (EPA) Region IX preliminary remediation goals (PRG) and the National Oceanic and Atmospheric Administration (NOAA) effects range-low (ER-L) values. The primary concern is the quantitation limits for polynuclear aromatic hydrocarbons (PAH). While PAHs were not the only compounds of concern, they are the largest group of analytes for which the quantitation limits currently do not meet regulatory criteria. The purpose of this letter is to compare the methods for PAH analysis and to present the Navy's recommendation.

Method 8310 has been recommended for the analysis of PAHs, instead of the CLP semivolatile organic analysis (SVOA), also referred to as method 8270. Method 8310 uses high performance liquid chromatography (HPLC) in conjunction with an ultraviolet detector for the analysis of 16 PAHs. The CLP SVOA method uses gas chromatography/mass spectrometry (GC/MS) for analysis of the 16 PAHs and 45 other semivolatile analytes. A third possibility is a modified CLP SVOA method which uses selective ion monitoring (SIM) GC/MS and can achieve lower quantitation limits than the normal CLP method. In general, this method is used primarily to detect the 16 PAHs, but some laboratories can expand the total list to 30 analytes. When the list is expanded, a normal GC/MS method is generally used and the lower detection limits are achieved by eliminating the gel-permeation chromatography (GPC) cleanup.

The Navy is willing to consider using alternative methods in order to reach lower quantitation limits, provided such methods are available and meet the project data requirements. However, there are advantages and disadvantages to using any analytical method. Relying on a method without carefully considering the disadvantages may compromise the quality and usefulness of the data gathered.

Several factors are important to consider when selecting the appropriate method for an analysis:

- The method should provide information at a reasonable cost to the project. The modified CLP SVOA method is comparable in cost if only PAHs are analyzed, but is most costly if all 30 analytes are requested.

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- The method should provide quantitative results for all suspected analytes of concern. If PAHs are of potential concern, then any of the three methods would be acceptable. If other semivolatile analytes are of potential concern, then the CLP SVOA method may be most appropriate.

- The quantitation limits provided by the method should be equal to or lower than the criteria to which the data will be compared. The quantitation limits achievable by method 8310 and the modified CLP SVOA better meet the PRG and ER-L criteria for PAHs than the regular CLP SVOA. However, even with the low detection limit methodology, certain ER-L criteria will still not be met. A high moisture content will also affect quantitation limits.

- The method should not be susceptible to problems from matrix interferences. Such interferences can cause false positives or increased detection limits. Matrix interferences include target and nontarget compounds to which the detector is sensitive in the same way it is sensitive to the compounds being analyzed. For example, high concentrations of petroleum hydrocarbons are a matrix interference during the analysis of PAHs and other semivolatile compounds. Analysis of sediment and tissue samples is very susceptible to matrix interferences because of the organic material in the samples.

- The method should not rely on an excessive amount of sample "cleanup" intended to reduce matrix interferences. This may cause more false negatives because the sample cleanup may remove the analytes of interest. Method 8310 relies significantly on sample cleanup to reduce matrix interferences.

- The identification technique used by the method should enable definitive analyte identification. Method 8310 has a greater possibility for false positives because it relies on retention time and ultraviolet absorption to identify analytes. More definitive identification is possible using retention time in conjunction with MS or SIM.

A comparative analysis of the analytical methods is enclosed. Enclosure (1) compares the PRG and ER-L values to the detection limits of the alternative methods proposed for the analysis of remedial investigation samples. Enclosure (2) lists the advantages, disadvantages, and costs associated with each method.

The Navy proposes using the modified CLP SVOA method for the analysis of PAHs in sediment and tissue samples collected during the ecological investigation. PAHs were the only semivolatile analytes detected during the initial ecological investigation. Therefore, PAHs will be of primary concern to the ecological assessment, which is evaluating primarily the aquatic habitat surrounding Treasure Island. The lower detection limits achievable by this method are equal to or lower than the ER-L criteria for all but two PAHs. This is a significant improvement over the detection limits for the normal CLP SVOA method which did not meet ER-L criteria for 8 of the 16 PAHs.

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On the other hand, the Navy proposes using the normal CLP SVOA method for the analysis of soil samples at terrestrial sites. At these sites, human health criteria are of primary concern, and PRGs will be used to evaluate the data. There are only two PAHs, benzo(a)pyrene and dibenzo(a,h) anthracene, for which the quantitation limits of the proposed method do not meet the PRGs. The costs associated with changing the analytical methodology for these two analytes is not justified. It would also be problematic for the human health risk assessment to perform data analysis on two data sets with quantitation limits that are significantly different.

In summary, The Navy proposes using the modified CLP SVOA method for the analysis of PAHs in sediment and tissue samples collected during the ecological investigation but will use the normal CLP SVOA method for the analysis of soil samples at terrestrial sites. PRC requests that the agencies review the alternatives presented and provide the Navy with input about the proposals.

If you have any questions or comments about these proposals or the comparative analysis, please call me at (415) 244-2560.

Sincerely,

Original signed by:

ERNESTO M. GALANG
Remedial Project Manager
by direction of
the Commanding Officer

Encls: (1) Table 1- Comparison For PAH Quantitation Limits With Human Health And Ecological Criteria For Soils
(2) Table 2- Comparison Of Alternate Methods To Achieve Lower PAH Quantitation Limits

Copies to:
California Regional Water Quality Control Board (Attn: Mr. Michael Bessette)
California Department of Fish and Game (Attn: Dr. Michael Martin)
U.S. Environmental Protection Agency, Region IX (Attn: Ms. Rachel Simons)
U.S. Fish & Wildlife Services (Attn: Mr. Steve Schwarzbach)
Bay Area Air Quality Management District (Attn: Mr. Julian Elliot)
Bay Conservation and Development Commission (Attn: Mr. Steve McAdam)
National Oceanic & Atmospheric Administration (Attn: Ms. Denise Klimas)

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Copies to: (cont)
NAVSTA Treasure Island (Attn: Mr. Jim Sullivan)
San Francisco Department Of Public Health (Attn: Ms. Amy Brownell)
TI RAB Community Co-chair (Attn: Mr. Brad Wong)
PRC Environmental Management, Inc. (Attn: Ms. Sharon Tobias)

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TABLE 1

COMPARISON OF PAH QUANTITATION LIMITS WITH HUMAN HEALTH AND ECOLOGICAL CRITERIA FOR SOILS

Analyte	CAS[a] No.	PRG[b] (mg/kg)	ER-L[c] (mg/kg)	Quantitation Limits (mg/kg)[d]		
				CLP SVOA (8270)	Modified CLP SVOA	Method 8310
Acenaphthene	83-32-9	360	0.016	(0.33)	(0.026)	(0.1)
Acenaphthylene	208-96-8		0.044	(0.33)	0.026	(0.4)
Anthracene	120-12-7	19	0.0853	(0.33)	0.026	0.02
Benzo(a)anthracene	56-55-3	0.61	0.261	(0.33)	0.026	0.02
Benzo(a)pyrene	50-32-8	0.061	0.43	(0.33)	0.026	0.02
Benzo(b)fluoranthene	205-99-2	0.61		0.33	0.026	0.04
Benzo(k)fluoranthene	207-08-9	6.1/0.61[e]		0.33	0.026	0.02
Benzo(g,h,i)perylene	191-24-2			0.33	0.026	0.04
Chrysene	218-01-9	24/6.1[e]	0.384	0.33	0.026	0.02
Dibenzo(a,h)anthracene	53-70-3	0.061	0.0634	(0.33)	0.026	0.02
Fluoranthene	206-44-0	2600	0.60	0.33	0.026	0.1
Fluorene	86-73-7	300	0.019	(0.33)	(0.026)	(0.2)
Indeno(1,2,3-cd)pyrene	193-39-5	0.61		0.33	0.026	0.1
Isophorone	78-59-1	470		0.33	0.026	NA
2-Methylnaphthalene	91-57-6		0.07	(0.33)	0.026	NA
Naphthalene	91-20-3	800	0.16	(0.33)	0.026	0.1
Phenanthrene	85-01-8		0.24	(0.33)	0.026	0.02
Pyrene	129-00-0	2000	0.665	0.33	0.026	0.04

Notes:

[a] CAS: Chemical Abstract Service
[b] PRG: Preliminary remediation goals for residential scenario (Region IX, EPA) February 1995
[c] ER-L: Effects Range-Low (NOAA)
[d] mg/kg: milligrams/kilogram
[e] California-modified PRG

Quantitation limits in parentheses ( ) do not meet the PRG or ER-L criteria

TABLE 2

COMPARISON OF ALTERNATE METHODS TO ACHIEVE LOWER PAH QUANTITATION LIMITS

Method	Quant. limit (mg/kg)	Disadvantages	Advantages	Cost
CLP SVOA (8270) using gas chromatography/ mass spectrometry (GC/MS)	0.33	• Detection limits above PRG and ER-L for some analytes	• Positive GC/MS identification • All SVOAs reported • Reasonable cost	• $400 (for 60 analytes)
Method 8310 using high performance liquid chromatography (HPLC)	0.02-0.4	• Matrix interference may result in false positive or dilution of sample • False negatives may result from sample cleanup methods • Tissue and sediment samples susceptible to matrix interference • Only PAHs reported	• Detection limits below PRG and ER-L for most analytes • Reasonable cost	• $250 (PAHs only)
Modified CLP SVOA--low detection limit method using GC and selective ion monitoring (SIM)	0.026	• Only PAHs reported • High cost for additional analytes	• Detection limits below PRG and ER-L for most analytes • Positive GC/MS identification • All SVOAs reported	• $400 (PAHs only) • $600 (for 30 analytes)