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CAM Protocols: Questions & Answers

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The CAM Protocols: Questions & Answers provides responses to questions submitted to MassDEP on the implementation of the revised CAM Protocols, effective July 1, 2010. Questions on the CAM protocols may be sent to BWSC.CAM@state.ma.us

APH, Reporting Limit, Calibration

APH Questions

Can the detection limits for compounds listed in the APH method be at the same detection limit or does concentration have to jump from one compound to the other? If we meet or are below the detection limit listed in the method at one constant concentration, is that satisfactory?

The APH method does not require that the reporting limit (RL) for each APH compound be the same. The only requirements regarding RLs are as follows: (1) all RLs must be $\leq$ the CAM RLs listed in Section 1.1.1 of WSC-CAM-IX A (the APH CAM Protocol), (2) all RLs must be based on the lowest standard used in the initial calibration, and (3) all RLs must be $\leq$ the regulatory criteria.

What is the linear range to calibrate from? From the attachments within the APH Method (December 2009) it looks like it's from 0.5 ppb to 150 ppb. Would we use one set of curves or several sets for initial calibration?

The APH method does not require a specific linear range for calibration. As per Section 9.4.3 of the December 2009 APH method, the tables provided in the method are recommended range and target analyte calibration standard concentrations. It is up to each laboratory to determine the calibration range concentrations. The only requirements regarding the initial calibration are as follows: (1) the RL must be based on the lowest concentration standard used in the initial calibration and (2) a minimum of five different standards must be used (six standards if non-linear regression is used).

We have inquired about obtaining a standard for the APH Method. We have run into different standards being offered by different companies. One standard has all compounds at the same concentration (1ppm). The other standard varies concentration for each compound. Do you have any recommendations for the standard?

MassDEP has no recommendations as to which standard the laboratory uses.

If we follow CLP and CAT B QA/QC and reporting, will that meet the APH method requirements?

CLP and Category B deliverables include all raw data. Reporting requirements for the APH method do not require these full deliverables. If these full deliverables were provided, this would satisfy most of the requirements for the APH method. However, there are other parameters in the APH method that are not part of the routine CLP methods that also need to be provided (i.e., media certification results, canister vacuums, flow controller RPDs). It is highly recommended that you review the CAM Protocol, WSC-CAM-IX A , for reporting requirements when using this method.

APH, Significant Modification

If our laboratory uses an alternative analytical column for APH would we be able to answer "Yes" to Question E on the MassDEP Analytical Protocol Certification Form for Presumptive Certainty? [July 2010]

If you are considering using an alternate column and you meet the requirements of 6.3.2 of the APH method for demonstrating equivalency, then the use of the alternate column would not be considered a significant modification and you would answer "Yes" to Question E on the MassDEP Analytical Protocol Certification Form. No additional documentation would be needed as part of the lab report. You would, however, need to keep documentation of the equivalency demonstration on file so that it could be made available upon request.

Calibration, %RSD, MassDEP Analytical Protocol Certification Form

Regarding GC/MS Initial Calibration: The Quality Control Requirements and Performance Standards table for method 8260 states: For an initial calibration if %RSD > 20%, linear or non-linear regression must be used. However, under the required corrective action column, it states that if =<10% of compounds exceed the criteria, recalibration is not required as long as % RSD < 40 or r > 0.98. Does this mean that for =<10% of the compounds, an average RF can be used as long as it is not > 40% and this is included in the narrative? What would the answer to Question H on the Protocol Certification Form be in that case? [July 2010]

Ideally, if the %RSD is >20%, the lab should immediately be prompted to use linear or non-linear regression. If for some reason linear or non-linear regression cannot be performed, then the average response factor can be used as long as (1) the %RSD of the compound of interest is not greater than 40 and (2) the %RSDs do not exceed 20 and the correlation coefficients are not <0.99 for greater than 10% of the target compounds. The answer to Question H would be "No" since the %RSD of the compound of interest is outside of the acceptance criteria.

CAM Protocol Reference

In reviewing the required laboratory report information specified in Table VII A-1 (page 12) of WSC-CAM-VIIA, we noted a requirement to report a "CAM Protocol Reference" with sample results in our reports. Could you please clarify what the Department's expectations are with respect to this requirement? [July 2010]

The CAM Protocol reference is the CAM Protocol number. For example, if doing VOCs by GC/MS under the CAM, the CAM Protocol reference would be WSC-CAM-II A.

Chain of Custody, MassDEP Analytical Protocol Certification Form

Section 2.2.1 of WSC-CAM VIIA states that the chain-of-custody (COC) "must include the following information, if applicable for the samples submitted for analysis" and provides a list of required information. If the COC does not have time of collection or preservation type listed or something else on the list is missing, is it Question A or D on the MassDEP Analytical Protocol Certification Form that would be answered "No"? [July 2010]

The COC is part of the documentation that is required to be in the laboratory report, as shown on Table VIIA-1 of WSC-CAM-VIIA. Section 2.2.1 of WSC-CAM-VIIA states what is required to be on this COC in order to obtain Presumptive Certainty. Since Question A deals with sample integrity and Question D deals with laboratory reporting requirements, the missing information on the COC would cause Question D to be answered "No". The information that is missing on the COC must be listed in the laboratory narrative.

Chain of Custody, MassDEP Analytical Protocol Certification Form

The CAM says that a discrepancy between the COC and Sample IDs constitutes a "NO" answer to Question A on the MassDEP Analytical Protocol Certification Form (see 2.4.1.1 Clarification Examples). Often we encounter situations where a client will ask to modify a Sample ID from what was written on the COC. Should a client requested change, or an ambiguity which is resolved by client correspondence, be necessarily treated as a NO answer? [July 2010]

If the discrepancy between the COC and sample containers is resolved or if the client asks that a sample ID be modified, the answer to Question A should be YES, but the supporting documentation must be provided in the data package.

EPH, Extraction

Is the SPE extraction process allowed for the EPH method?

The CAM Protocol for EPH allows for the use of SPE for extraction of aqueous samples for EPH.

EPH, Extraction, Preservation

The EPH method states to preserve water samples at time of collection with acid to a pH <2 and to chill to less than 4C. The method contains an example for extraction of a water sample by separatory funnel at pH< 2. The method also states that continuous liquid-liquid extraction (CLLE) is allowed and typically this extraction method is performed at neutral pH for BN SVOC methods. Do we follow the method and make the sample's pH< 2 or should we follow typical CLLE SVOC procedures and make the sample neutral pH. [July 2010]

According to Table 1 in each of the SW-846 extraction procedures (3510C for separatory funnel extraction and 3520C for continuous liquid-liquid extraction), the samples must be extracted at a pH <2 for SVOCs.

EPH, Required Deliverable, GC/MS

On page 27 Table IV B-4 of WSC CAM-IV B (MASS DEP EPH), GC/MS QC Parameters is listed as a required deliverable if the GC/MS technology is employed during analysis. Is it correct to assume this indicates that the DFTPP tune report and the DDT breakdown are required deliverables? Are the GC/MS QC Deliverables defined? [July 2010]

GC/MS QC Deliverables are defined. As listed in Table IV B-4 of the CAM Protocol for EPH, the required analytical deliverables for GC/MS QC parameters are referenced back to the CAM 8270D protocol, WSC-CAM-II B , Table II B-1. Table II B-1 shows which deliverables are required under the column called "Required Deliverable." In general, if GC/MS is used for EPH, the required deliverables by GC/MS will also be required for EPH in addition to the other EPH-specific deliverables. Therefore, the assumption that the DFTPP tune report and DDT breakdown are required deliverables is incorrect as Table II B-1 clearly states these are not required. Please note that GC/MS analysis is only allowed if fractionation of the sample extract has been performed.

EPH, Solvents, Significant Modification

Section 11.3.1.1.3 of the EPH method lists the following significant modification: The use of solvents other than those recommended in this method or approved extraction methods listed in Table 4. Would it be considered a significant modification if the lab uses the solvents recommended in the method (extraction using methylene chloride, solvent exchange in hexane, silica gel cleanup [fractionation] of hexane extract using hexane followed by methylene chloride, concentration of the final aromatic sample extract in methylene chloride), but uses methylene chloride instead of hexane in the final concentration step of the aliphatic extract? After silica gel cleanup, the aliphatic extract in hexane would undergo a solvent exchange in methylene chloride prior to concentration. The laboratory is interested in running the EPH method via GC/MS after fractionation, but is concerned about putting two different solvents on the system and potential adverse effects from the hexane on the column. [July 2010]

The use of methylene chloride in the final concentration step of the aliphatic extract should not adversely affect the recoveries of the aliphatics since the sample was extracted and fractionated using the correct solvents. Since the modification is only affecting the final concentration step and not the actual extraction method, this is not considered a significant modification to the method.

EPH, VPH, Laboratory Certification

Our lab is currently certified in MA for 600 series and 200 series methods. Can we obtain certification for the SW-846 methods and the EPH and VPH methods? [July 2010]

Certification for SW-846 methods and the EPH and VPH methods is not currently offered in Massachusetts. Compliance with the published CAM protocols as documented by the laboratory MassDEP Analytical Protocol Certification Form that accompanies the results promotes analytical data quality for analyses conducted on samples collected from disposal sites under the Massachusetts Contingency Plan.

EPH, VPH, Method Blanks

Regarding EPH/VPH Method Blanks: The Required Performance Standard for Method Blanks indicate that EPH/VPH "hydrocarbon ranges must be =< 10% of the most stringent applicable MCP standard..." What MCP standard (e.g. GW-1/S-1 standard) should be used for this purpose? For example, would an aqueous EPH blank aromatic range need to be =<10% of the GW-1 standard? This would be below the CAM RL and the CAM does not allow the lab to report below the RL for GC methods. [July 2010]

As shown in the table below, the laboratory is correct in stating that 10% of the most stringent MCP standard would be below the CAM RL for select hydrocarbon ranges. The Final CAM Protocols for EPH and VPH now state that the hydrocarbon ranges must be ≤ 10% of the most stringent applicable MCP standard for solid samples and ≤ 50% of the most stringent applicable MCP standard for aqueous samples.

Hydrocarbon Range (matrix)	Most Stringent MCP Standard	10% Most Stringent MCP Standard	CAM RL
C5-C8 Aliphatics (soil)	100 mg/kg	10 mg/kg	5-10 mg/kg
C5-C8 Aliphatics (water)	300 ug/L	30 ug/L	100-150 ug/L
C9-C12 Aliphatics (soil)	1000 mg/kg	100 mg/kg	5-10 mg/kg
C9-C12 Aliphatics (water)	700 ug/L	70 ug/L	100-150 ug/L
C9-C10 Aromatics (soil)	100 mg/kg	10 mg/kg	5-10 mg/kg
C9-C10 Aromatics (water)	200 ug/L	20 ug/L	100-150 ug/L

Hydrocarbon Range (matrix)	Most Stringent MCP Standard	10% Most Stringent MCP Standard	CAM RL
C9-C18 Aliphatics (soil)	1000 mg/kg	100 mg/kg	20 mg/kg
C9-C18 Aliphatics (water)	700 ug/L	70 ug/L	100 ug/L
C19-C36 Aliphatics (soil)	3000 mg/kg	300 mg/kg	20 mg/kg
C19-C36 Aliphatics (water)	14,000 ug/L	1400 ug/L	100 ug/L
C11-C22 Aromatics (soil)	1000 mg/kg	100 mg/kg	20 mg/kg
C11-C22 Aromatics (water)	200 ug/L	20 ug/L	100 ug/L

Field QC, GW-1, Drinking Water Samples

When analyzing for VOCs/VPH in a GW-1 area, is it necessary to have both a trip blank and a field duplicate if the well is a groundwater monitoring well and not a drinking water well? [July 2010]

Per section 2.5 of CAM VIIA, the minimum field QC requirements in Table VII A-3 (related to field duplicates, matrix spikes, and trip blanks) required for Presumptive Certainty apply to "drinking water samples." Drinking water samples are defined as samples obtained from a public or private water supply well. This would include samples directly from a tap or from the delivery system of a private water supply prior to the tap. This requirement does not apply to all samples from

monitoring wells in GW-1 areas. See section 2.5 of CAM VIIA (2.5 through 2.5.5) for guidance on drinking water samples.

EPH, VPH, Second Source Standards

The CAM protocols for the EPH and VPH methods require the use of second source standards for the LCS and MS/MSD where the protocols for other methods only require second source standard for the ICV run directly after calibration; all other continuing calibration verification standards may be made from the same source as calibration standards. Why is there a difference for EPH and VPH? [July 2010]

The requirement to use second source standards for the LCS and MS/MSD was retained in the EPH and VPH CAM Protocols because the associated analytical methods (MADEP-VPH-04-1.1 and MADEP-EPH-04-1.1) from May 2004 dictate these requirements. The CAM Protocols for MassDEP methods maintain consistency with the requirements listed in the corresponding analytical methods.

Herbicides, Extraction

Does the updated CAM Protocol for herbicides allow for ultrasonic extraction, pressurized fluid extraction, and/or microwave extraction (3545/3546)? [July 2010]

Section 1.3 of the revised CAM Protocol for 8151A does allow the use of ultrasonic extraction, as this is consistent with the extraction procedures detailed in Section 7.2 of SW-846 method 8151A. At this time, the use of pressurized fluid extraction and/or microwave extraction is not an option for the herbicide method.

Hexavalent Chromium, Calibration

Please confirm my understanding of the calibration requirements for hexavalent chromium in the CAM Protocol. In Table VI-B-1, the frequency of the calibration is either daily or when the daily calibration QC samples (LLCV, HLCV, CCV, or CCB) fail. The criteria for the LLCV are analysis daily if initial calibration was not performed on same day as sample analysis. The criteria for the HLCV are analysis daily if initial calibration did not contain high standard at linear calibration range or if initial calibration was not performed on same day as sample analysis.

I am interpreting the requirement, therefore, to be the following: Daily analyze LLCV, HLCV, CCV, and CCB; as long as these pass, daily calibration is not required. However, once any of the daily QCs fail, re-calibration is a must. [July 2010]

Your interpretation is correct. To clarify, however, the daily "initial" calibration is not required if the LLCV, HLCV, CCV, and CCB are within the acceptance criteria.

Hexavalent Chromium, Matrix Spike

The method for hexavalent chromium in soil (SW846 3060A/7196A) fails to list the true value expected for the insoluble matrix spike. 1. Could you explain how we determine the true value? 2. Is the acceptance range of 75 - 125% based on statistical data each laboratory develops from in-house % recoveries? [July 2010]

Section 5.6 of SW-846 Method 3060A states that the insoluble matrix spike is prepared by adding 10-20 mg of lead chromate ($PbCrO_4$) to a separate sample aliquot. The true value will be dependent upon the sample weight and final volume of the digestate. The expected recovery of the insoluble matrix spike under ideal conditions is 75-125%. The following is an example scenario of how to calculate the true value of the insoluble matrix spike:

1. The molecular weight of lead chromate is 323.22 g/mole. The percentage of chromium in this mixture is 16.08% (molecular weight chromium/molecular weight lead chromate = 51.996/323.22).
2. Assume a 2.5 gram sample is spiked with 15 mg of lead chromate and digested in 100 mL solution and brought up to 100 mL after digestion and pH adjustment.
3. If 15 mg of lead chromate is added to the sample, then this corresponds to 2.41 mg chromium added to the sample (amount lead chromate * % chromium = 15 mg * 0.1608).
4. Therefore, 2.41 mg chromium are added to the 2.5 gram sample. The true value of the spike is then calculated by converting this to mg/kg: 2.41 mg / 2.5 g * 1000 g/1 kg = 964 mg/kg.

Section 1.1.2 of the CAM Protocol states that laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table VI B-1. Laboratories are not necessarily required to develop in-house recoveries from statistical data, but are certainly encouraged to do this in order to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

Hexavalent Chromium, pH, ORP

Is the laboratory required to report pH and ORP when doing hexavalent chromium analysis of aqueous samples? [July 2010]

The laboratory is not required to measure pH and ORP when doing hexavalent chromium analyses of aqueous samples.

Key Words: Hexavalent Chromium, pH, ORP

With respect to the solid hexavalent chromium analysis under the revised CAM protocols, is this up to the data user to request ORP and pH measurements or is the laboratory supposed to automatically analyze for these parameters? We are seeing the request for matrix spikes resulting in low recoveries, especially for the insoluble matrix spikes. We are having to perform pH and ORP to determine if a reducing condition exists. [July 2010]

The analyses of pH and ORP for solid matrices are required when performing the hexavalent chromium analyses; these results will be needed when the data user is performing a data usability assessment. Importantly, these analyses need to be conducted within 24 hours of sampling. Ultimately, it is the responsibility of the data user to ensure that all proper steps were completed, including this action, if needed. That being said, given the 24 hour holding period, it may be advisable for laboratory personnel to be proactive with clients in alerting them to this requirement, whenever plans are being made to test solid samples for hexavalent chromium, or total chromium, if testing for hexavalent chromium is contingent upon total chromium results.

The evaluation of the pH and ORP results can also be used to eliminate the need for corrective action with low matrix spike recoveries. However, the use of this evaluation assumes that the pH and ORP analyses were performed (within 24 hours) and not after observing low matrix spike recoveries, which could be as long as 30 days after the sample was collected. Therefore, the pH and ORP analyses must not be performed to determine if a reducing condition exists after observing low matrix spike recoveries. It may be in the laboratory's best interest to always perform these analyses in order to eliminate more complex corrective actions for low matrix spike recoveries.

Hexavalent Chromium, pH, ORP, Holding Time

The holding time for pH and ORP is very short. Is it acceptable to do the pH and ORP measurements in the field or, if done in the lab after 24 hours, allow narration of this issue without losing Presumptive Certainty? [July 2010]

> The SW-846 method requirements for pH state that the sample must be analyzed as soon as possible. Therefore, the 24-hour holding time for pH and ORP has always been required in the CAM Protocol for hexavalent chromium. You do have the option to perform the pH and ORP measurements in the field if holding times will be an issue. If the pH and ORP analyses are performed outside of the 24-hour holding time, respond "No" to Question A. Please note that although there would be no Presumptive Certainty if the holding time was exceeded for pH and ORP, this does not mean that the data are unusable.

Hexavalent Chromium, ORP

The CrVI method in the CAM cites the ORP method as ASTM Method D1498-93, but the current method for ORP is D1498-98. Are either acceptable? [July 2010]

> The current ASTM method for ORP is D1498-08. Either version of the ASTM method is acceptable to use. The hexavalent chromium CAM Protocol has been updated with the most current method for ORP.

Hexavalent Chromium, Sample Container

Is there a requirement to collect soil/sediment samples for hexavalent chromium without headspace? [July 2010]

> There is no requirement for samples to be collected without headspace. The requirement is that the aliquot of soil/sediment for hexavalent chromium analysis come from an unopened container. If there is only one jar submitted, the aliquot for hexavalent chromium analysis must be removed from the jar before the other parameters. Many times, data users wait for the results of total chromium before deciding whether or not to prepare the samples for hexavalent chromium. Therefore, the requirement for an unopened container was added to the CAM protocol to ensure that the original sample is undisturbed and not compromised in any manner prior to removing an aliquot for hexavalent chromium.

Hexavalent Chromium, Sample Container, MassDEP Analytical Protocol Certification Form

We are trying to educate our clients on the need for a separate jar for hexavalent chromium. I'm not sure if we should be evaluating Question B for this requirement.

Example: CrVI is requested by a client yet no separate jar is provided and many other parameters were also requested. Should we evaluate their sample container submittal and answer this question accordingly? Obviously if we answered "No", we would narrate. If this doesn't fall under the Presumptive Certainty questions, could we simply narrate that the aliquot taken for CrVI digestion was not from a separate jar? [July 2010]

> The issue of a separate jar for the hexavalent chromium analysis would affect Question A on the MassDEP Analytical Protocol Certification Form. As stated in Table VII A-2 of WSC-CAM-VII A regarding Question A, If soil/sediment samples for hexavalent chromium are collected in the same jar as other analytical parameters and the digestion of hexavalent chromium is not conducted prior to other parameters, respond "No."

Interference, Dilution

With obvious interference present and surrogate recovery <10%, can the laboratory go directly to dilution without re-analyzing the sample undiluted? [July 2010]

The CAM Protocols state that reanalysis of a sample with obvious interference and surrogate nonconformances is not required as long as the surrogate recoveries are >10%. The CAM Protocols do not require that the sample be analyzed undiluted when obvious interference is present and surrogate recoveries are <10%; in this instance reanalysis only on dilution is required. This requirement is included in the Performance Standard table under Required Corrective Action.

MCP Analytical Services Request Form

Is use of the "MCP Analytical Services Request Form" required? Where may I find the most current form? [July 2010]

Use of the MCP Analytical Services Request Form  is optional. The intent of the form is to provide a mechanism for the data users to communicate all requirements to the laboratory regarding their samples. The form provides information to the laboratory that will ensure the samples are properly analyzed as it specifies required reporting limits, the presence of drinking water samples, and the required analyte list. It also provides reminders to the data user to ensure the proper number of QC samples are collected, samples are put on ice, properly preserved, etc.

MassDEP Analytical Protocol Certification Form, Reporting Limit

Question G on the MassDEP Analytical Protocol Certification Form reads "Were the reporting limits at or below all CAM reporting limits specified in the selected CAM protocols?" If there is an RL exception that has already been noted for a particular analysis (e.g., Chlordane for 8081), how should the laboratory answer this question - "Yes" or "No"? [July 2010]

If there is a CAM RL exception defined in the CAM Protocol and the laboratory's reporting limit agrees with the expected reporting limit for this exception as defined in the CAM Protocol, then the answer to Question G is YES.

MassDEP Analytical Protocol Certification Form, Reporting Limit

With respect to CAM Reporting Limits: Is a complete list of CAM RLs for each CAM method / analyte available to answer Question G on the Analytical Protocol Certification Form? Some CAM protocols list a range for the CAM reporting levels, but not specific values. In some cases the highest reporting level in the RL range is below the GW-1/S-1 standard. [July 2010]

The reporting limits for each analyte must fall within the CAM RL range provided in the CAM Protocol. In some instances, reporting limit ranges were provided instead of specific values, due to slight variability amongst laboratories. The reporting limits are not determined solely on MCP Method 1 standards as MCP assessment endpoints are not limited to the Method 1 standards (i.e., other considerations such as the assessment of background may be relevant).

PAC, Holding Time

I have a question regarding the holding time for Physiologically Available Cyanide (PACN) method. The holding time requirements for Aqueous and Soil samples states: 14 days to distillation; analyze distillates within 24 hours of distillation.

Does the 24 hour analysis time line start once the distillation process is completed OR at the start time of the preparation / distillation of the samples? [July 2010]

Analysis should be performed within 24 hours of the time the distillation process is completed.

PAHs, Tailing Factor Evaluation

If we are only analyzing samples for PAHs, does the benzidine and pentachlorophenol tailing factor criteria have to be met and/or reported? [July 2010]

The evaluation of the pentachlorophenol tailing factor is performed when analyzing for the acid fraction only. Therefore, this does not need to be performed when analyzing for PAHs only. In order to check the effect of the inlet and column inertness on the base-neutral fraction, this must be performed for benzidine when analyzing for PAHs only. This is clarified in the Performance Standard Table of the CAM 8270 (IIB) Protocol.

PCBs, Extraction, TSCA

If a party is working on a site potentially contaminated by PCBs, are there any special steps that should be taken to help ensure that subsequent data will be usable under the MCP as well as TSCA, if needed? [July 2010]

If soil and/or sediment samples are analyzed for PCBs at a site, and it is anticipated that such data may be submitted to EPA as part of a TSCA review process, it would be advisable to check with appropriate personnel at EPA Region I, with respect to allowable extraction techniques. In the past, EPA Region I has required the use of the Soxhlet extraction method (SW-846 3540C or SW-846 3541), one of several extraction methods allowed under the CAM Protocol for PCBs (WSC-CAM-VA).

Preservation, Freezing, Soil

Preservation of soils by freezing is allowed to extend holding time up to 1 year, excluding VOCs, perchlorate, cyanide, and hexavalent chromium. What about pH and ORP? [July 2010]

The process of freezing and thawing the samples can change the reducing/oxidizing qualities of the original sample. Therefore, freezing soil/sediment samples to extend the holding time for pH and ORP is not allowed.

Preservation, pH, MassDEP Analytical Protocol Certification Form

If we received VOA vials that indicate that they are acid preserved, but the pH>2, is there a question on the MassDEP Analytical Protocol Certification Form that should be answered "No"? [July 2010]

Question A deals with the condition of samples upon receipt at the laboratory and should be answered "No" if the pH is outside of the method acceptance criteria. Question A reads as follows:

"Were all samples received in a condition consistent with those described on the Chain-of-Custody, properly preserved (including temperature) in the field or laboratory, and prepared/analyzed within method holding times?"

Please note that in addition to providing a "No" response, an explanation in the laboratory narrative is also required.

Reporting Limit

Why is the cyanide CAM RL been set at 0.005 - 0.010 mg/L when the lowest regulatory Limit for Cyanide under 310 CMR 40.0000 is 0.030mg/L (GW-3 standard)? [July 2010]

The reporting limit is not based strictly on the lowest MCP standard. MCP analyses also include the evaluation of other conditions, such as background concentrations. The reporting limit reflects the lowest reasonable detection level that can be consistently achieved by labs with a reasonable level of effort and diligence. Some laboratories are consistently able to report down to 0.005 mg/L and this also demonstrates the ability of the protocol to achieve the EPA National Recommended Water Quality Criteria, Freshwater CCC of 0.0054 mg/L if surface water is being evaluated.

Response Factors, Coelution

In the 8260 CAM Table II A-1, the rejection criteria for non-detected results is listed as RF <0.05. Appendix IV of the REDUA Policy (MCP Representativeness Evaluations and Data Usability Assessments Policy #WSC-07-350) states that for RRF[JD1] <0.05 (with no technical justification for RRF being lower), non-detected results for affected compounds are rejected. Would coelution be a "technical justification"? Also, in the National Functional Guidelines, there is a Table 15 for VOCs exhibiting poor response (22 analytes) for which the minimum RRFs must be $\geq$ 0.010 and 1,4-dioxane which must be $\geq$ 0.0050 (all others at 0.050) and these values are used to reject non-detects. [July 2010]

A generalized statement as to whether coelution would be a "technical justification" for a low response factor cannot be made. Typically, coelution should not affect the response of the target compounds analyzed via GC/MS as different ions can be used for identifying and quantifying the compounds in question that may be coeluting. The coelution should therefore not adversely affect the results if different ions are used for quantitation.

The reference to the response factors listed in the National Functional Guidelines in the comment is correct. However, rejection criteria in the CAM Protocols as well as Appendix IV of the REDUA guidance are based on EPA Region I data validation guidelines and not the National Functional guidelines. Please refer to the References provided in Appendix IV of REDUA. Also, the National Functional guidelines cited above were based off of the most recent Contract Laboratory Program (CLP) Statement of Work (SOW) SOM01.2 which is significantly different from the SW-846 methods on which the CAM protocols are based. The EPA Region I data validation guidelines are based on the older CLP SOW OLM03.2 which is more comparable to the SW-846 method requirements.

Significant Figures

Could you explain the basis for the CAM protocol's approach to reporting data in terms of "significant figures"? Did you consider using EPA's Contract Lap Program (CLP) approach? [July 2010]

During development of the significant figure guidance in the CAM Protocols, consideration was given to using CLP approaches. The issues with the CLP approaches are that no one approach is applicable for all methods (see summary table below), and they depend on the units used to

report the results. Many laboratories report solid results in units of mg/kg while others use ug/kg; therefore, a general approach for values <10 would not work in all scenarios. As stated in the footer of the performance standard table in each CAM protocol, the suggested number of significant figures to report does not have a mathematical basis: Reporting protocol for "significant figures" is a policy decision included for standardization and consistency for reporting of results and is not a definition of "significant" in the scientific or mathematical sense.

CLP Method	**Required # Significant Figures**
OLM04.3 (older organic methods)	2 significant figures for values ≥10 and 1 significant figure for values <10
OLC03.2 (older low-level organic methods)	2 significant figures for all values
SOM01.2 (new organic methods)	2 significant figures for all values
ILM05.2 (older inorganic methods)	3 significant figures for values ≥10 and 2 significant figures for values <20
ISM01.2 (new inorganic methods)	3 significant figures for values ≥10 and 2 significant figures for values <20

Standard Reference Material, Soil, Metals

The three NIST soil Standard Reference Materials (SRMs) do not contain all 14 MCP metals, but a sediment SRM does. Can the sediment SRM be used for soil batches? Neither the soil nor sediment SRMs has certified concentrations for all 14 MCP metals. Some of the concentrations are listed as either *Reference Values or Information Values*. How should the laboratory handle those metals without certified values in the SRMs and how does the MassDEP Analytical Protocol Certification Form get answered? [July 2010]

> There are soil reference materials on the market that contain all 14 MCP metals that can be used and provide 95% confidence limits for each metal, as specified in the performance standard tables for the CAM Protocols for metals.

Standard Reference Material, Cyanide, Hexavalent Chromium, Metals

I have the following questions concerning the requirements for analyzing a Standard Reference Material (SRM) for each batch of analyses for Metals, Hexavalent Chromium and Total Cyanide in soil:
1. What are the requirements of an SRM?
2. Does the SRM have to be NIST 'Traceable'?
3. What are the accreditation requirements for the provider of the SRM? and
4. On the certificate of analyses, what is the required set of information? [July 2010]

> 1. The standard reference material (SRM) for the metals, hexavalent chromium and total cyanide CAM protocols must be a soil or sediment matrix that contains the analytes of interest at known concentrations and with 95% confidence limits.
> 2. The SRM does not have to be NIST 'Traceable'.
> 3. There are currently no accreditation requirements for the provided of the SRM.
> 4. The required set of information on the certificate of analyses is the true concentration of the analyte of interest and the control limits (95% confidence limits).

SVOCs, SW-846 References, MassDEP Analytical Protocol Certification Form

Based on the statement below from WSC-CAM-IIB, is it still acceptable to use 8270C CAM and meet Presumptive Certainty as long as the narrative/report states that 8270C was employed?

"The QC requirements and performance standards specified in Table II B-1 together with the analytical procedures described in EPA SW-846 Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), constitute the WSC-CAM-II B protocol. All protocols included in the CAM are considered "methods" published by the MassDEP pursuant to the provisions of 310 CMR 40.0017(2). Use of EPA SW-846 8270D is a "Presumptive Certainty" requirement of WSC-CAM-II B. However, it should be noted that if the laboratory utilizes the analytical procedures in SW-846 Method 8270C instead of 8270D, it is acceptable to answer "YES" to Question B on the MassDEP Analytical Protocol Certification Form since there are no analytical procedural differences between 8270C and 8270D." **[July 2010]**

> Yes, the text cited from WSC-CAM-IIB is stating that requirements of Presumptive Certainty will be met if the laboratory utilizes SW-846 method 8270C instead of 8270D. However, all requirements in the Performance Standard table (Table IIB-1) must be included in the analysis, regardless of which SW-846 method version is used. The version of the method utilized by the laboratory must be documented in the data package.

SW-846 References

I see most of the updated methods are referring to the SW846 Rev IV updates. But if you open CAM method 8260, it references 8260B pretty much throughout the document and only twice refers to 8260C (ICAL, CCs). Was this planned or did someone not do a word search on the document and replace 8260B with 8260C? [July 2010]

The SW-846 method references within WSC-CAM-IIA (8260-VOCs) were planned. All CAM protocols were based on the most recently promulgated versions of the method. SW-846 8260B is the current method on the SW-846 web site while SW-846 8260C is still listed under the "New Methods" section on this web site. However, MassDEP identified certain requirements in non-promulgated versions that would be beneficial for the CAM protocols. In the case of the 8260 protocol, the response factor requirements from SW-846 8260C were included. As with all CAM protocols, all requirements in the Performance Standard table (Table IIA-1) must be included in the analysis, regardless of which SW-846 method version is used.

TO-15, Reporting Limit

Is it meant to be an option for clients to ask for TO-15/SIM on the full MA list (39 compounds)? I am being asked for this by a client. This is a pretty long list to do by SIM. [July 2010]

CAM Reporting Limits (RLs) via the use of SIM were provided in the CAM Protocol to provide data users an option when full scan RLs would not be able to achieve the project objectives. The intention of including the SIM RLs was not so data users would request the full list (39 compounds) to be analyzed by SIM. Section 1.1.1 of the CAM Protocol states that RLs lower than the full scan RLs for target analytes may be required to satisfy project requirements. The requirement is that the RL (based on the concentration of the lowest calibration standard) for each contaminant of concern must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., MassDEP Indoor Air Threshold Values, background, etc.). Meeting MCP standards or criteria may require the use of SIM. It would be preferable for your client to tell you the project objectives and together you can determine whether full scan or SIM analysis for each target analyte will be required to achieve these objectives.

VOCs Continuing Calibration, LCS

The Volatile Organics Continuing Calibration criteria do not contain a Required Performance Standard/Corrective Action that pertains to Difficult Analytes. "%D must be <20 for each target analyte" "If <20% of compounds exceed criteria, recalibration is not required as long as %D <40."

The CCAL may also be used the LCS, which does have a wider acceptance criteria for difficult analytes and therefore at times may exceed the 40%D criteria. What should the CCAL criteria be for Difficult Analytes, less than 60%D? This would correspond to the 40-160% recovery allowance for Difficult Analytes within the LCS. [July 2010]

As you stated, there is a discrepancy in the VOC CAM Protocol WSC-CAM-II A regarding the evaluation of the continuing calibration and LCS. Since the LCS can also be used as the continuing calibration check for this protocol, the continuing calibration check should also contain an allowance for "difficult analytes." Therefore, the corrective action of the WSC-CAM-II A protocol for the continuing calibration should state that if $\leq$20% of compounds exceed the percent difference criteria, recalibration is not required as long as %D <40 (or <60 for "difficult analytes"). MassDEP has revised WSC-CAM-II A protocol accordingly to address this discrepancy.

VOCs, Continuing Calibration, Narration

It is denoted within the Volatile Organics Continuing Calibration Performance standard that all CCAL exceedences >20%D are required to be narrated. If the CCAL is considered to be within the overall method allowances, should this be required? There is concern this may lead to confusion for the average end data user when making their Data Usability Assessment. In addition, the details will be provided in the form of narration, as the CCAL is not a required deliverable. [July 2010]

If the percent difference of any compound exceeds 20, there is a requirement in the CAM Protocol to narrate the exceedance even if within the overall method allowance (<20% of target analytes exceeding criteria). It is important for the data user to be aware of these exceedances as the affected compound could be a contaminant of concern at their site; this could potentially affect the accuracy of the affected compound result, even if most of the other compounds were within criteria. MassDEP feels the additional information adds value to the data usability assessment.

VOCs, Preservation, Soil

For analysis of soil by WSC-CAM-II A (8260B),is preservation of low-level soil samples with Sodium Bisulfate still an acceptable preservation option?

My reading of the sample collection table from the protocol is that Sodium Bisulfate is still acceptable, as footnote 2 references a list of acceptable techniques in EPA Method 5035A. [July 2010]

Appendix II A-1 does infer that a variety of options are available for preservation of soil samples, as indicated by footnote #2 in the table. However, Section 1.3 of the WSC-CAM-II A (8260B) protocol does state the following: *"The use of sodium bisulfate as the low-level preservation method for solid samples with high organic matter or humic material content has been known to result in the formation of acetone and MEK at potentially significant concentrations in samples. Sodium bisulfate preservation must never be used when these conditions are either present or suspected. It should be noted that freezing (< -7OC), and not sodium bisulfate addition, is the preferred low-level preservation method for solid samples (see Appendix II A-1)."*

Therefore, as stated on the cover page of Appendix II A-1, the selection of preservation for samples analyzed for VOCs should be based on the data quality objectives of the sampling program. The technique preferred by MassDEP will be acceptable in almost all cases while other techniques such as the use of sodium bisulfate or EnCore samplers may only be applicable with certain soil types.

VPH, Calculating Range CFs

How does one calculate a Range CF in the VPH method? Which components are used? [July 2010]

CALCULATION OF RANGE CFs

Calculate the range CFs using ONLY the relevant components/peaks.
When calculating range CFs for the Aliphatic Hydrocarbons, integrate the ALIPHATIC PEAKS (only) valley-to-valley, and they divide the COLLECTIVE AREA of these ALIPHATIC PEAKS by the collective mass purged of these ALIPHATIC PEAKS (only). When calculating the range CF for C9-C10 AROMATICS, integrate the AROMATIC PEAK (1,2,4-TMB) valley-to-valley, and they divide the AREA of this peak by the mass purged. This is what MassDEP meant to be implied in the following procedures outlined in Section 11.1 of the VPH Method:

11.1.3 Using the FID chromatogram, calculate an average collective CF for the total concentration of the C5 - C8 Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 3 components (n-pentane, 2-methylpentane, 2,2,4-trimethylpentane) against the collective concentration injected.

11.1.4 Using the FID chromatogram, calculate an average collective CF for the total concentration of C9 - C12 Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 2 components (n-decane and n-butylcyclohexane) against the collective concentration injected. Alternatively, the CF for C9 - C12 Aliphatic Hydrocarbons can be calculated using the collective area response of 3 components (n-nonane, n-decane and n-butylcyclohexane).

11.1.5 Using the PID chromatogram, calculate an average collective CF for the total concentration of C9 - C10 Aromatic Hydrocarbons. This value is the value for 1,2,4-trimethylbenzene, the only aromatic standard within this range.

VPH, LCS

How do I analyze the LCS in the VPH method? [July 2010]

Analyze the LCS like a calibration standard using valley-to-valley integration of the individual peaks. The percent recoveries are evaluated using the individual peak/analyte.

Do NOT do collective "from baseline" integration of multiple peaks. If the collective from-baseline approach is taken, you will encounter problems dealing with the aromatic compounds that elute in the FID aliphatic ranges aliphatic compounds that elute in the PID C9-C10 Aromatic range, as well as noise in the baseline.

The recommended individual valley-to-valley approach is what most labs are doing in New England. This approach was what was intended, as indicated in Section 10.4.2.3 of the VPH Method, where mention is made of the potential low recovery of a single analyte in the C9-C12 Aliphatic range:

"10.4.2.3 Laboratory Control Sample - A Laboratory Control Sample is prepared by fortifying a 5 mL reagent water blank with 4 uL of the matrix spiking solution (for water samples), or by fortifying 25 mL of methanol with 1.0 mL of the matrix spiking solution (for soil/sediment samples). The spike recovery must be between 70% and 130%. Lower recoveries of n-nonane are permissible (if included in the calibration of the C9-C12 aliphatic range). If the recovery of n-nonane is <30%, note the nonconformance in the narrative."

VPH, pH, Narration

If our laboratory received VPH vials that do not meet the pH less than 2 requirement, then we should answer no to Question A. As for the explanation in the case narrative, do you need more than "The pH of the sample vials for sample _____ were greater than 2, which is above the method requirement of <2". [July 2010]

This is an appropriate narration if you also specify the actual pH.

VPH, Significant Modification

I am looking for some clarification regarding how the MassDEP views the determination of VPH ranges and targets by mass spectrometry. I realize this is considered a "significant modification" and cannot support presumptive certainty, but what exactly does that mean for an LSP? If a sample is analyzed for VPH by mass spectrometry, the laboratory would check "No" for Question D and narrate the non-conformance in the case narrative.

1) How does this affect the data from an LSP's usability standpoint and does this differ based on cleanup process analyses versus site closure analyses?
2) Is MassDEP considering accepting mass spectrometry as an acceptable modification?
3) Why does the MassDEP accept/specify mass spectrometry analysis of ranges for air methods (APH) and not soil/water (VPH)? [July 2010]

(1) The MCP specifies cleanup standards and/or requirements for ranges of aliphatic and aromatic hydrocarbon fractions, as those ranges are defined in 310 CMR 40.0006. For example:

C5 through C8 Aliphatic Hydrocarbons means the cumulative concentration of all aliphatic hydrocarbon compounds with boiling points greater than 36°C and less than 150°C, as measured by chromatographic methods approved by the Department or equivalent procedures, excluding the individual compounds listed at 310 CMR 40.0974(2).

An LSP is free to make a case that a method (e.g., GC/MS) provides data consistent with this definition. This is also addressed in the VPH method, Section 1.12, with respect to a laboratory's obligation to support the validity of procedures and methods purported to quantify "Volatile Petroleum Hydrocarbons", as that term is defined in Section 3.0 of the MassDEP VPH method:

"Laboratories who make such modifications, and or develop and utilize alternative approaches and methods, are further required to demonstrate:

That such modifications or methodologies adequately quantify the petroleum hydrocarbon target ranges, as defined in Sections 3.4 through 3.6 of this document, ensuring that any methodological uncertainties or biases are addressed in a manner that ensures protective (i.e., conservative) results and data (e.g., over, not under-quantification of the more toxic ranges);

That such modifications and/or methodologies employ and document initial and continuing Quality Assurance/ Quality Control procedures consistent with similar approaches detailed in the MADEP Compendium of Analytical Methods; and

That such methods and procedures are fully documented in a detailed Standard Operating Procedure."

The ability to use any scientifically defensible and relevant analytical method during any phase of an MCP process is allowable, as specified in 310 CMR 40.0017. However, the burden is on the LSP to demonstrate the validity of a procedure and application to the site assessment issue under evaluation. For example, one issue that would exist in a GC/MS VPH technique is the selection of quantitation ions for the collective quantification of C9-C10 Aromatic Hydrocarbons.

(2) MassDEP is considering the use of GC/MS for the analysis of VPH. This methodology is currently not finalized, but will be investigated over the course of the next year.

(3) The types and levels of hydrocarbons within an air matrix are limited by volatility constraints. An aqueous and solid matrix is more complex. However, as stated above, the use of GC/MS for VPH will be explored and validated in the future.

VPH, Significant Modification, Internal Standards

Is the use of an internal standard allowed for the VPH method? As you know, PID bulbs are prone to decrease response due to "fogging" of the lens. In our experience, using an internal standard helps with drift to reduce calibration of the instrument. Would use of an internal standard be considered a major modification of the method? [July 2010]

As stated in Section 9.4.1 of the VPH method, an internal standard calibration procedure is not recommended for this method. Therefore, no performance standards were included for internal standards in the most recently revised CAM Protocol for VPH. MassDEP would prefer that laboratories not use internal standards to compensate for potential issues with the detector. Recalibration is the preferred approach, especially due to the need to verify the accuracy of the reporting limit with the lowest initial calibration standard. This will be especially important when the detector is showing a decreased response.

Use of an internal standard in the VPH method is considered by MassDEP as a "significant modification" and would prevent the achievement of Presumptive Certainty.

VPH, Surrogates, Matrix Spikes

Section 1.4.4 of the previous version of the VPH CAM Protocol stated: *"Appropriate surrogates and full matrix spikes must be added to the methanol extract through the septum seal prior to equilibration of the sample to room temperature. All samples should be shaken for 2 minutes to assure adequate mixing prior to analysis. A 100 microliter (µL) aliquot (or other appropriate volume) of the methanol extract must then be removed and added to reagent water to provide a 5 mL "adjusted" sample volume."* Why is this not stated in the revised CAM Protocol? [July 2010]

The spiking of surrogates and matrix spikes directly into the methanol extracts is still required. This is clearly stated in Sections 9.1.3.2 and 9.1.3.3 of the VPH method. Since this is a procedural requirement, it was eliminated from the CAM protocol which is used to clarify QC requirements of each method. The addition of 100 microliters to a 5 mL adjusted sample volume is handled slightly differently in each laboratory to come up with the same dilution factor. This procedural requirement, therefore, was eliminated from the CAM protocol.

VPH, Surrogates, Soil

On page 15 of the SOP method, it states that for medium level soils 1.0mL of surrogate at 50 ppm is to be added through the septum into the methanol preserved soil sample. Would it be within the SOP to use a more concentrated surrogate standard to allow the use of less volume added to the sample? [July 2010]

It would be acceptable to use a more concentrated surrogate standard to allow the use of less volume added to the sample. If the volume of surrogate added is $\geq$100 uL, this volume must be included in the final extract volume for all calculations. The surrogate issue described above is not considered a "significant modification."