This document contains Appendix D from the 2004 Princess Cruise Lines Island Princess Data Report. Appendix D contains data review narratives and other issues. The report and all the appendices for this sampling event can be downloaded from
http://www.epa.gov/owow/oceans/cruise_ships/island.html

Island Princess

2004 Analytical Results

Appendix D

March 2006

Appendix D

DATA REVIEW NARRATIVES AND OTHER ISSUES

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6505

Data Validation Report For BOD_5 Samples

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

February 9, 2005

BOD_5 Method 405.1

Completeness

During Sampling Episode 6505, all 32 samples (excluding QC samples) that were identified in the Sampling and Analysis Plan for the Island Princess (Sampling Episode 6505) were collected for analysis of 5-day Biochemical Oxygen Demand (BOD_5) by EPA Method 405.1. Sample numbers ranged between 65591 and 65753. Sampling completeness for this episode was 100% (all planned samples were collected).

The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete BOD_5 data for all submitted samples. A list of the samples collected and analyzed during Sampling Episode 6505 is provided in Table 1.

Table 1. BOD_5 Samples Collected During Sampling Episode 6505

Sample Numbers	Sample Point Description
65651, 65655, 65659, 65663, 65667	Treatment System Influent
65691, 65695, 65699, 65703, 65707, 65711, 65715, 65727	Treatment System Effluent
65631, 65635, 65639, 65643, 65647	Accommodations
65591, 65595, 65599, 65603, 65607	Galley
65611, 65615, 65619, 65623, 65627	Laundry
65731	Galley Overboard
65733	Laundry Overboard
65737	Food Pulper Overboard
65753	Source Water

According to the Quality Assurance Project Plan (QAPP) developed for the Rulemaking Support for Large Cruise Ships in Alaska Waters, sampling completeness is the number of valid samples collected relative to the number of samples planned for collection; analytical completeness is the number of valid sample measurements relative to the number of valid samples collected; and overall completeness is the number of valid sample measurements relative to the number of samples planned for collection. For the cruise ship sampling program a minimum goal of 90% completeness for sampling and analytical completeness has been established, and a minimum goal of 81% for overall completeness (determined by multiplying sampling and analytical completeness goals) has been established.

As a result of a shipping delay, 6 samples collected for BOD_5 analysis arrived at the laboratory five days following collection. According to Method 405.1, BOD_5 samples should be

analyzed within 48 hours following collection. Although the BOD_5 samples were analyzed upon receipt at the laboratory, the results are not considered valid. Therefore, for Sampling Episode 6505 both laboratory completeness and overall completeness for BOD_5 is 81%.

Holding Times

Method 405.1 requires that all BOD_5 samples be analyzed within 48 hours following collection. Analysis of traffic reports and laboratory data sheets indicates 6 of the 32 BOD_5 samples were analyzed outside the 48 hour hold time window. Table 2 shows the sample numbers, the total hold time from collection to analysis, and the measured BOD_5 result for the six samples analyzed past the method-specified holding time.

Table 2. BOD_5 Samples Exceeding Hold Times

Sample Number	Sample Description	Sample Hold Time	Method Hold Time	BOD_5 Result
65647	Accommodations Wastewater	133 hours	48 hours	112 mg/L
65707	Treatment System Effluent	134 hours	48 hours	<2 mg/L
65607	Galley Wastewater	134.5 hours	48 hours	1,630 mg/L
65727	Treatment System Effluent	134.2 hours	48 hours	<2 mg/L
65667	Treatment System Influent	133.6 hours	48 hours	281 mg/L
65627	Laundry Wastewater	134.5 hours	48 hours	102 mg/L

Because the holding time was exceeded by nearly 3 days (approximately 86 hours) for the six samples shown in Table 2, this BOD_5 data are not considered valid and should not be used in analyses for the cruise ship rulemaking. Accordingly, these results will be excluded from the analytical database.

Calibration

The calibration was performed with method blanks and glucose spiked blanks to verify seed effectiveness and analytical technique. Method blanks consist of potable water passed through an activated carbon bed to remove residual organic compounds. During Sampling Episode 6505, a total of six method blanks were prepared and analyzed for BOD_5. Five of the six method blanks had BOD_5 concentrations less than 2 mg/L. One method blank had a measured BOD_5 concentration of 3 mg/L. ERG reviewed the BOD_5 results associated with the elevated blank to determine the impact of the blank on the sample results. All of the associated

sample results were either nondetect or were greater than 10 times the blank result, indicating that the presence of BOD_5 in the blank did not adversely affect the data.

To verify seed effectiveness and analytical technique, method blanks were spiked with a sufficient amount of glucose to yield a theoretical BOD_5 concentration of 200 mg/L. Spiked method blanks are then analyzed for BOD_5, and results of the analysis, reported as percent recovery, are compared to the recovery limits for Method 405.1. Table 3 shows the results of the spiked samples.

Table 3. Analysis of BOD_5 Recovery Data for Spiked Method Blanks

Sample	Spike Result	Spike Level	Recovery	Recovery Limits
Method Blank	181 mg/L	200 mg/L	90.5%	60% - 140 %
Method Blank	167 mg/L	200 mg/L	83.5%	60% - 140%
Method Blank	169 mg/L	200 mg/L	84.5%	60% - 140%
Method Blank	153 mg/L	200 mg/L	76.5%	60% - 140%
Method Blank	157 mg/L	200 mg/L	78.5%	60% - 140%
Method Blank	151 mg/L	200 mg/L	75.5%	60% - 140%
Method Blank	166 mg/L	200 mg/L	83.0%	60% - 140%
Method Blank	183 mg/L	200 mg/L	91.5%	60% - 140%
Method Blank	210 mg/L	200 mg/L	105%	60% - 140%
Method Blank	153 mg/L	200 mg/L	76.5%	60% - 140%
Method Blank	154 mg/L	200 mg/L	77.0%	60% - 140%

Results of the spiked method blank samples indicate all recoveries are within the method/QAPP specified targets.

Precision Analysis

Reproducibility for BOD_5 is measured as relative percent difference (RPD) between duplicate samples. Laboratory duplicate samples measure the precision of the method and analyst by comparing the results of two separate analyses on the same wastewater sample. Field duplicate samples measure the precision of the field sampling method by comparing the BOD_5 results for split wastewater samples prepared in the field. The QAPP for the Cruse Ship Rulemaking provides RPD targets for all laboratory duplicate samples and field duplicate samples as less than 20% and 30%, respectively.

Table 4 shows the RPD results for laboratory duplicate samples and method blank spiked samples. The RPDs shown in Table 4 indicate the five method blank spiked duplicate samples are within the RPD target. For samples 65691 and 65695, the RPDs cannot be calculated because the results were reported as less than the detection limit. The BOD_5 results obtained from these samples are expected, since each was collected from treatment system effluent. Although actual RPDs could not be calculated, the results do indicate that laboratory precision is acceptable.

Table 4. Relative Percent Difference Between Laboratory Duplicate Samples

Sample No.	BOD_5 Result	Duplicate BOD_5 Result	RPD	RPD Target
Spiked Method Blank	181 mg/L	167 mg/L	8.0%	<20%
Spiked Method Blank	169 mg/L	153 mg/L	9.9%	<20%
Spiked Method Blank	157 mg/L	151 mg/L	3.9%	<20%
Spiked Method Blank	166 mg/L	183 mg/L	9.7%	<20%
Spiked Method Blank	153 mg/L	154 mg/L	0.7%	<20%
65691	<2 mg/L	<2 mg/L	NA	<20%
65695	<2 mg/L	<2 mg/L	NA	<20%

RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
NA: RPD can not be calculated since one or both results is less than the analytical detection limit.

Table 5 shows the RPD results for field duplicate samples. (Note that one set of field duplicate samples (samples 65707and 65727) were among those samples that were analyzed outside the 48-hour holding time and are consequently not included in Table 5.) Measured BOD_5 concentrations in each of the field duplicate samples is less than the laboratory detection limit of 2 mg/L; therefore, the RPDs cannot be calculated. The BOD_5 results obtained from these samples are expected since each was collected from treatment system effluent. Although actual RPDs could not be calculated, the results do indicate that laboratory and field precision is acceptable.

Table 5. Relative Percent Difference Between Field Duplicate Samples

Sample No.	BOD_5 Result	Sample No.	BOD_5 Result	RPD	RPD Target
65691	< 2 mg/L	65711	< 2 mg/L	NA	<30%
65695	< 2 mg/L	65715	< 2 mg/L	NA	<30%

RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
NA: RPD can not be calculated since one for both results is less than detection (2 mg/L)

Data Quality Assessment

This data validation assessment indicates the BOD_5 data collected during Sampling Episode 6505 can be used for the large cruise ship rulemaking effort, with the exception of those samples that were analyzed outside the holding time of 48 hours.

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: February 3, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Sara Clark, Quality Assurance Chemist
Sample Control Center

SUBJECT: Data Review Narrative for Classical Analyses for the Alaskan Cruise Ship Industry, Episode 6505

OVERVIEW

Under EPA Contract Number 68-C-03-068, Analytical Laboratory Services, Inc. (ALSI) submitted classical wet chemistry data for 36 samples in Episode 6505. Table 1 provides a listing of samples, matrices, descriptions, sampling dates, and the required analytes.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analytes

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65591	Aqueous	SP1, Galley wastewater	08/29/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65595	Aqueous	SP1, Galley wastewater	08/30/04	
65599	Aqueous	SP1, Galley wastewater	08/31/04	
65603	Aqueous	SP1, Galley wastewater	08/31/04 (a), 09/01/04 (b)	
65607	Aqueous	SP1, Galley wastewater	09/02/04	
65611	Aqueous	SP2, Laundry wastewater	08/29/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide
65615	Aqueous	SP2, Laundry wastewater	08/30/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65619	Aqueous	SP2, Laundry wastewater	08/31/04	
65623	Aqueous	SP2, Laundry wastewater	08/31/04 (a), 09/01/04 (b)	
65627	Aqueous	SP2, Laundry wastewater	09/02/04	
65631	Aqueous	SP3, Accommodations wastewater	08/29/04	
65635	Aqueous	SP3, Accommodations wastewater	08/30/04	
65639	Aqueous	SP3, Accommodations wastewater	08/31/04	

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analytes

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65643	Aqueous	SP3, Accommodations wastewater	08/31/04 (a), 09/01/04 (b)	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65647	Aqueous	SP3, Accommodations wastewater	09/02/04	
65651	Aqueous	SP4, Influent to wastewater treatment	08/29/04	
65655	Aqueous	SP4, Influent to wastewater treatment	08/30/04	
65659	Aqueous	SP4, Influent to wastewater treatment	08/31/04	
65663	Aqueous	SP4, Influent to wastewater treatment	08/31/04 (a), 09/01/04 (b)	
65667	Aqueous	SP4, Influent to wastewater treatment	09/02/04	
65691	Aqueous	SP6, Effluent from wastewater treatment	08/29/04	
65695	Aqueous	SP6, Effluent from wastewater treatment	08/30/04	
65699	Aqueous	SP6, Effluent from wastewater treatment	08/31/04	
65703	Aqueous	SP6, Effluent from wastewater treatment	08/31/04 (a), 09/01/04 (b)	
65707	Aqueous	SP6, Effluent from wastewater treatment	09/02/04	
65711	Aqueous	SP7, Effluent from wastewater treatment	08/29/04	total cyanide
65715	Aqueous	SP7, Effluent from wastewater treatment	08/30/04	total cyanide
65719	Aqueous	SP7, Effluent from wastewater treatment	08/31/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide
65723	Aqueous	SP7, Effluent from wastewater treatment	09/01/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC
65727	Aqueous	SP7, Effluent from wastewater treatment	09/02/04	
65731	Aqueous	SP8, Galley wastewater	08/26/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analytes

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65733	Aqueous	SP9, Laundry wastewater	08/26/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65737	Aqueous	SP10, Food pulper	08/26/04	
65741	Solid	SP11, Screening solids	08/30/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, total solids, TOC, total cyanide
65745	Aqueous	SP12, Biosludge wastewater	08/26/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide
65753	Aqueous	SP14, Source water	08/31/04	ammonia-N, COD, nitrate/nitrite, total phosphorus, TKN, TOC, total cyanide

(a) Sampling date for HEM/SGT HEM
(b) Sampling date for remaining analytes

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004) and with the specifications listed in the contract. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary table (Table 2).

SUMMARY

All samples were successfully analyzed within the contract-specified holding times for all classical wet chemistry parameters specified in the sampling and analysis plan. The calibration and continuing calibration standards were successfully analyzed. Laboratory blanks were performed for each analysis, and there was no contamination detected above the laboratory reporting limits. The QC samples, including the ongoing precision and recovery (OPR) sample and matrix spike/matrix spike duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses was acceptable, with the exception of the data issues described below.

DATA ISSUES: ALKALINITY

A duplicate analysis was performed on sample 65741. The relative percent difference (RPD) between the results for the original sample and the duplicate was outside the acceptance limit established for the project. Therefore, SCC considers the alkalinity data for sample 65741 to be an estimated value.

DATA ISSUES: SULFATE

A matrix spike and matrix spike duplicate were prepared for sample 65741. The spike recoveries were below the acceptance limits established for the project. The recovery for the laboratory control sample associated with the analysis was acceptable, indicating a probable matrix interference affecting the MS/MSD analyses. Therefore, SCC considers the sulfate data for sample 65741 to be a minimum value.

DATA ISSUES: TKN

A matrix spike and matrix spike duplicate were prepared for sample 65741. The spike recoveries were below the acceptance limits established for the project. The recovery for the laboratory control sample associated with the analysis was acceptable, indicating a probable matrix interference affecting the MS/MSD analyses. Therefore, SCC considers the TKN data for sample 65741 to be a minimum value.

The TKN result (27.6 mg/L) for sample 65691was less than the corresponding ammonia-N result (27.9 mg/L). This situation is theoretically impossible, given that the ammonia-N is a subset of TKN. However the difference in the two results (0.3 mg/L) was within the measurement variability of either method. Therefore, SCC considers the TKN data in this sample to be of acceptable quality.

DATA ISSUES: TOTAL PHOSPHORUS

Matrix spike and matrix spike duplicate (MS/MSD) samples were prepared for samples 65719, 65723, 65727, 65731 and 65741. The MS/MSD percent recoveries could not be accurately measured because the samples were spiked at a level significantly lower than the analyte levels detected in the original samples. Because the amount of analyte spiked into the samples did not contribute significantly to the sample result, the MS/MSD samples were treated as sets of duplicate analyses. However, none of the relative percent difference (RPD) values met the specified criteria. Therefore, SCC considers the data for these samples to be estimated values. These cases are detailed in Table 2.

DATA ISSUES: NITRATE/NITRITE

A matrix spike and matrix spike duplicate was prepared for sample 65741. The spike recoveries were below the acceptance limits established for the project. The recovery in the laboratory control sample associated with the analysis was acceptable, indicating a probable matrix interference affecting the MS/MSD analyses. Therefore, SCC considers the nitrate/nitrite data for sample 65741 to be a minimum value.

AVAILABLE CYANIDE GREATER THAN TOTAL CYANIDE

For all samples in this episode, SCC evaluated total cyanide results against available cyanide results, and found that available cyanide was detected in samples 65603, 65659, 65731 and 65745, while total cyanide were not detected in these samples or detected at a lower amount. In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. However, for these samples, it is important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the available cyanide determination was performed by a different laboratory. In addition, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results. Therefore, it may not be possible to identify problems that would invalidate one cyanide fraction or the other.

The data for total cyanide samples in Episode 6505 were delivered in five separate data packages, each with its own associated QC sample results. Six pairs of MS/MSD samples were prepared for total

cyanide analyses in Episode 6505 on samples 65603 (galley wastewater), 65635 (accommodations wastewater), 65711 (an effluent), 65715 (an effluent), 65719 (an effluent), and 65741 (screening solids).

The data for a seventh pair of MS/MSD samples were delivered in the data package with the results for samples 65731 (galley wastewater) and 65745 (biosolids). However, because of limitations on the sample volume that was provided to the laboratory, the MS/MSD samples were prepared from a non-EPA sample of indeterminate origin and therefore are not useful in evaluating the performance of the total cyanide method on cruise ship samples.

Three of the MS/MSD pairs for aqueous samples and the one MS/MSD pair for the solid samples had acceptable recoveries of total cyanide. None of the samples used to prepare MS/MSD aliquots were samples where the available cyanide results exceeded the total cyanide results.

The MS/MSD results for sample 65603 (galley wastewater) showed recoveries of 59% in both aliquots, which is below the acceptance limits, and suggests a potential low bias in the total cyanide result for that sample. The available cyanide result of 2.2 µg/L is below the detection limit for the total cyanide analysis. Therefore, SCC recommends qualifying the total cyanide result as a minimum value and accepting the available cyanide result as reported.

Although MS/MSD samples were prepared from sample 65741 (screening solids) and met the acceptance criteria, there are no MS/MSD results for the biosolids matrix in this episode. This limits SCC's ability to evaluate the potential effects of the sample matrix for sample 65745 (biosolids), where the available cyanide results are almost 40% higher than the total cyanide results. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65745 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65731 is a galley wastewater. The only MS/MSD results for galley wastewater in this episode are for sample 65603, where the recoveries were below the acceptance criteria. Given the potential for low bias in this matrix, SCC recommends qualifying the total cyanide result as a minimum value. SCC recommends including both cyanide results for sample 65731 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65659 is an influent sample and MS/MSD aliquots are not prepared for influents, as discussed earlier. Total cyanide was reported as not detected and the available cyanide was reported at 6 times the total cyanide detection limit. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65659 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6505, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

TECHNICAL NOTES:

Silica Gel Treated - Hexane Extractable Material (SGT-HEM)

Samples 65691, 65695, 65699, 65703 and 65707 were not analyzed for SGT-HEM because the HEM results were non-detects. At EPA's request, SCC created SGT-HEM records in the database, but the results for SGT-HEM are reported as NA, with the SCC qualifier "not analyzed due to non-detect HEM result."

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's Data Review Team Leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC
Michael Walsh, CSC
Pornkeo Chinyavong, CSC

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Classicals

Industry: Alaska Cruise Ship **Reviewer:** Sara Clark

Sample	Analyte	Action	Reason	SCC Qual	Level
65741	alkalinity	Estimated value	RPD between sample and its duplicate exceeded criteria	NA	2640 mg/kg
65741	sulfate	Minimum value	Matrix interference	NA	3910 mg/kg
65741	TKN	Minimum value	Matrix interference	NA	5150 mg/kg
65719	total phosphorus	Estimated value	RPD between MS/MSD exceed criteria	NA	8.1 mg/L
65723					7.1 mg/L
65727					8.6 mg/L
65731					19.4 mg/L
65741					2760 mg/kg
65741	nitrate/nitrite	Minimum value	Matrix interference	NA	4.0 mg/kg
65603	total cyanide	Minimum value	Low MS/MSD recoveries	NA	ND
65659	total cyanide	Minimum value	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.	IRR	ND
65731					ND
65745					11 µg/L

IRR = Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose
ND = Non-detect at the laboratory's reporting limit. See the level in the database.
NA = Not applicable

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: March 31, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Jody Donnelly, Quality Assurance Chemist JMD
Sample Control Center

SUBJECT: Data Review Narrative for Dioxin/Furan Analysis for the Alaskan Cruise Ship Industry, Episode 6505

OVERVIEW

Under CSC Purchase Order 637415SSD, Axys Analytical Services submitted data for the analysis of dioxins and furans by EPA Method 1613B for one solid sample in Episode 6505. Table 1 provides a list of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifier, Description, Sampling Date, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6505	65749	Solid	SP13, Incinerator ash	08/30/04	1613B

These data have been reviewed in accordance with SCC's Data Review Guidelines for Dioxin/Furan Analysis by Method 1613B (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

The sample was successfully extracted and analyzed for the target analytes in EPA Method 1613B within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for the analysis detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable.

Reporting Limits

The sample was extracted using approximately 5 grams instead of the method-specified 10 grams. As a result, the minimum levels (MLs) provided in the database for sample 65749 increased by approximately a factor of 2. The laboratory's past experience with ash samples shows that they tend to have significant matrix interference, which is why the sample size was reduced. Because the laboratory calibrated their instrument to 5 times lower than the lowest calibration standard specified in Method 1613B, the difference in sample size has no impact on the quality of the data. The MLs provided in the database for these samples reflect the smaller sample size.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

One analyte in sample 65749 was qualified by SCC with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit but above the method detection limit. This analyte is annotated as such in the database and is detailed in Table 2.

If you have any questions regarding the analysis of this sample or the review of these data, please contact me, by telephone at (703) 461-2203 or by facsimile at (703) 461-8056.

Attachment

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Method 1613B

Industry: Alaskan Cruise Ship **Reviewer:** J. Donnelly

Sample	Analyte	Action	Reason	SCC Qual	Level (ng/kg)
65749	1,2,3,7,8,9-HxCDF	Estimated value	Analyte detected below laboratory's reporting limit but above method detection limit	J	7.30

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: January 19, 2004

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Dioxin/Furan Analysis for the Alaskan Cruise Ship Industry, Episode 6505

OVERVIEW

Under EPA Purchase Order EP-C-04-047, Axys Analytical Services submitted data for the analysis of dioxins and furans by EPA Method 1613B for one aqueous sample in Episode 6505. Table 1 provides a list of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifier, Description, Sampling Date, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6505	65611	Aqueous	SP2, Laundry Wastewater	8/29/04	1613B

These data have been reviewed in accordance with SCC's Data Review Guidelines for Dioxin/furan Analysis by Method 1613B (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

All samples were successfully extracted and analyzed for the target analytes in EPA Method 1613B within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for the analysis detected no contamination above the laboratory's reporting limits. Instead of using the method-specified clean up procedure, all samples were processed by an automated clean up procedure that employs the Fluid Management System Inc., *"Power-Prep™ System,"* using standard chromatographic clean up columns. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable. None of the dioxins/furans were detected in sample in this episode.

Reporting Limits

The sample was extracted using less than the method-specified 1000-mL aliquot, due to volume constraints. This variation in sample size increased the minimum levels (MLs) for sample 65611 by 16%. The MLs provided in the database for this sample reflect the smaller sample volume.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

If you have any questions regarding the analysis of this sample or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6505

Data Validation Report For Microbiological Analyses

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

February 8, 2005

Enterococci by MPN Method ASTM D6503-99
Fecal Coliform by MF SM 9222D
***E. Coli* by MPN Enzyme Substrate SM 9223B**

Completeness

During Sampling Episode 6505, a total of 87 samples (excluding QC samples) were collected for analysis of enterococci, fecal coliform, and *E. coli* by the methods listed above. Sample numbers ranged between 65591 and 65767. One grab sample (Sample No. 65612) was not collected on Sampling Day 1 at Sampling Point 2 (Laundry Wastewater Characterization) due to lack of wastewater generation at this sampling point, resulting in a sampling completeness of nearly 99%. The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete microbiological data for all submitted samples. A list of the samples collected and analyzed during Sampling Episode 6505 is provided in Table 1.

Table 1. List of Samples and Required Microbiological Analyses for Sampling Episode 6505

Sample Numbers	Sample Point Description
65591, 65592, 65595, 65596, 65599, 65600, 65603, 65604, 65607, 65608	Galley Wastewater
65611, 65615, 65616, 65619, 65620, 65623, 65624, 65627, 65628	Laundry Wastewater
65631, 65632, 65635, 65636, 65639, 65640, 65643, 65644, 65647, 65648	Accommodations Wastewater
65651, 65652, 65653, 65655, 65656, 65657, 65659, 65660, 65661, 65663, 65664, 65665, 65667, 65668, 65669	Treatment System Influent
65671, 65672, 65673, 65675, 65676, 65677, 65679, 65680, 65681, 65683, 65684, 65685, 65687, 65688, 65689	Influent to UV Disinfection
65691,65692, 65693, 65695, 65696, 65697, 65699, 65700, 65701, 65703, 65704, 65705, 65707, 65708, 65709, 65711, 65715, 65719, 65723, 65762, 65763, 65765, 65766, 65767	Treatment System Effluent
65731	Galley Wastewater Discharge
65733	Laundry Wastewater Discharge
65737	Food Pulper Wastewater Discharge
65753	Source Water

According to the Quality Assurance Project Plan (QAPP) developed for the Rulemaking Support for Large Cruise Ships in Alaska Waters, sampling completeness is the number of valid samples collected relative to the number of samples planned for collection; analytical completeness is the number of valid sample measurements relative to the number of valid samples collected; and overall completeness is the number of valid sample measurements relative to the number of samples planned for collection. For the cruise ship sampling program a minimum goal of 90% completeness for sampling and analytical completeness has been established, and a minimum goal of 81% for overall completeness (determined by multiplying sampling and analytical completeness goals) has been established. For Episode 6505, sampling completeness is 99%, analytical completeness is 97%, and the overall completeness is 96%.

Holding Times

The QAPP developed for the cruise ship rulemaking requires all microbiological samples be analyzed within 6 hours following collection. Due to the ship's schedule, samples 65731, 65733, and 65737 were collected 1.5 days prior to the start of the sampling episode. Because the onboard microbiologicals laboratory was not yet operating at the time of sample collection, these samples were not analyzed within the 6-hour holding time. Table 2 provides information regarding these samples.

Table 2. Microbiological Sample Exceeding Hold Times

Sample Number	Microbiological	Sample Hold Time	Method Hold Time	Result
65731	Fecal Coliform	24 hours	6 hours	8,600,000 CFU/100mL
65731	Enterococci	24 hours	6 hours	<100 MPN/100mL
65731	*E. Coli*	24 hours	6 hours	816,000 MPN/100mL
65733	Fecal Coliform	24 hours	6 hours	110,000 CFU/100mL
65733	Enterococci	24 hours	6 hours	>2,420 MPN/100mL
65733	*E. Coli*	24 hours	6 hours	>2,420 MPN/100mL
65737	Fecal Coliform	24 hours	6 hours	2,800 CFU/100mL
65737	Enterococci	24 hours	6 hours	<10,000 MPN/100mL
65737	*E. Coli*	24 hours	6 hours	<10,000 MPN/100mL

These samples were analyzed approximately 24 hours after collection. Since the holding time for these samples were exceeded by approximately 18 hours, the data from these samples are not considered valid and will not be used for the cruise ship rulemaking. Accordingly, results for these samples will be excluded from the analytical database.

Detection Limits

Some microbiological results were reported by Analytica Alaska as "greater than" a specified value (e.g., >24,200,000 MPN/100 mL). These results are qualified in the analytical database by a ">" flag and are listed in Table 3. This qualifier indicates the samples were not diluted sufficiently (i.e., the measured concentrations exceed the range of dilutions). The reported results in the database are the upper limit of the measurement range, and the ">" flag indicates that the actual concentrations are some level greater than the reported upper limit. Although the results are valid, data users should consider this data qualification in using the data.

Table 3. Microbiological Sample Results with ">" Qualifier

Analysis	Sample Numbers
Enterococci	65595, 65623, 65627, 65632, 65635, 65639, 65651, 65733
E. Coli	65651, 65652, 65663, 65733

During onboard analysis, one enterococci and *E. coli* sample (Sample No. 65737) was overly diluted to a level which generated a non-detect (ND) results, but with a detection limit much greater than typically expected. Typically, the detection limit for enterococci and *E. coli* is 1 MPN/100 ml. For this sample, the detection limits for enterococci and *E. coli* are 10,000 MPN/100 mls. Although the results from this sample are valid, their use for engineering analysis is limited.

Calculation of Fecal Coliform Density

Fecal coliform density should be computed from sample quantities that produced membrane filtration counts within the desired range of 20 to 60 fecal coliform colonies. This was not always possible for many cruise vessel samples for various reasons. First, many samples, such as wastewater treatment effluent samples, had low concentrations of microbiological contaminants, and the occurrence of fecal coliform colonies was minimal. In these cases, as specified by the method, the analyst counted all fecal coliform colonies, disregarding the lower limit of 20.

Second, most samples (other than wastewater treatment effluent) required a series of sample dilutions to obtain between 20 and 60 colony forming units per filter pad. In most cases, the analyst obtained a result within this range using one of the prepared dilutions. However, in a few instances, no single filter generated a result within the desired range (i.e., two results within the desired range, two results either above or below the desired range, one result above and one result below the desired range, etc). In these cases, as specified by the method, the analyst totaled the counts on the two filters and reported the result as a number per 100 mL. Table 4 lists the fecal coliform samples for Sampling Episode 6505 that did not yield a single result within the desired range, and for which the analyst computed the number of colony forming units

based on a calculation of the results from multiple plates. Calculations for these samples are provided in the Cruise Ship Rulemaking Record.

Table 4. Fecal Coliform Samples For Which Multiple Plates Were Used to Compute CFU/ 100 mL

Sample Number	Sample Description
65596	Galley Wastewater
65604	Galley Wastewater
65636	Accommodations Wastewater
65652	Influent to Treatment
65657	Influent to Treatment

In summary, calculation of fecal coliform density was performed as specified by the method, and the reported results are valid.

Laboratory QC Measures

QC measures for microbiologicals include positive and negative controls, media sterility checks, dilution water sterility checks, sample bottle blanks, membrane filter preparation blanks, and verification of incubator temperatures. The following describes the results of each of these QC checks used during Sampling Episode 6505. (The actual QC results are contained in Analytica Alaska's laboratory report, which is provided in the Cruise Ship Rulemaking Record.)

Positive and Negative Controls

Positive and negative controls are known cultures that are analyzed exactly like the field samples, and will produce an expected positive or negative result for a given type of medium. For Sampling Episode 6505, one medium-specific positive and negative control was analyzed for each medium lot used. Results of the positive and negative controls indicate the media used by the field laboratory for Sampling Episode 6505 produced expected results.

Media Sterility Checks

Media are checked for sterility by incubating the media at the appropriate temperature without sample and observed for growth. For Sampling Episode 6505, one medium sterility check was performed for each medium lot used. The media sterility check verified the media used by the field laboratory had not been contaminated with any of the microorganisms being analyzed for this work.

Dilution Water Sterility Checks

Dilution water is analyzed exactly like a field sample and observed for growth of fecal coliform, *E. coli*, and enterococci to verify the water is not contaminated with these organisms prior to use. For Sampling Episode 6505, one sample dilution blank was analyzed for each lot of dilution water used. Results of dilution water blank analysis verified the water had not been contaminated with any of the microorganisms being analyzed for this work.

Sample Bottle Blank

A sample bottle blank was analyzed for each bottle lot used during Sampling Episode 6505 to determine adequate bottle sterilization prior to use by the sampling crew. Results of the sample bottle blank (dilution water poured into the sample bottle and analyzed) verified the sample bottles had not been contaminated with any of the microorganisms being analyzed for this work.

Membrane Filter Preparation Blank

Membrane filter blanks were analyzed at the beginning of each set of filtered samples to document adequate sterilization of membrane filtration equipment. Membrane blanks verified that the equipment used for filtration during Sampling Episode 6505 had not been contaminated with any of the microorganisms being analyzed for this work.

Incubator Temperature

Incubator temperatures were monitored in the onboard laboratory to verify that prepared microbiological samples were being incubated at the correct temperatures. Review of the laboratories incubator log sheets generated during Sampling Episode 6505 verified the temperature was measured and recorded twice daily, no less than four hours apart, and the temperature checks were ± 0.5°C apart.

Precision Analysis

Reproducibility for the microbiological analyses is measured as relative percent difference (RPD) between duplicate samples. The QAPP for the Cruse Ship Rulemaking presents the target RPD for all laboratory and field duplicate samples as less than 20% and 30%, respectively. During Sampling Episode 6505, additional 100-ml sample volumes were collected for a number of grab samples with the intent that the laboratory would prepare a single composite and then analyze duplicate samples from the composite to evaluate laboratory precision (i.e., laboratory duplicates). The laboratory did not prepare a composite, but instead analyzed each of the 100-ml sample volumes individually. Because a composite was not prepared, laboratory precision could not be evaluated. The results obtained from analysis of these individual sample volumes are field duplicates, not laboratory duplicates, and because they were collected as laboratory duplicates, the original sample and the duplicate sample have the

same sample number. In order to differentiate the original from the duplicate, ERG assigned new SCC numbers (65762, 65763, 65765, 65766, and 65767) to the duplicate samples.

During Sampling Episode 6505, four additional sets of intended field duplicate samples (i.e., different sample numbers) were also collected and analyzed by each of the three microbiological methods. These field duplicate samples were prepared to determine the precision of the field sampling equipment. Duplicate sample data for the samples described above, along with the four intended field duplicate samples, are provided for *E. coli*, fecal coliform, and enterococci in Tables 5, 6 and 7.

Table 5. *E. Coli* Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65691	65711	ND	ND	NA	<30%
65695	65715	ND	ND	NA	<30%
65699	65719	ND	ND	NA	<30%
65703	65723	ND	ND	NA	<30%
65703	65762*	ND	1 MPN/100 mL	NA	<30%
65711	65766*	ND	ND	NA	<30%
65715	65763*	ND	ND	NA	<30%
65719	65765*	ND	ND	NA	<30%
65723	65767*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 MPN/100 mL.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

Table 6. Fecal Coliform Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65691	65711	ND	ND	NA	<30%
65695	65715	ND	ND	NA	<30%
65699	65719	ND	ND	NA	<30%
65703	65723	ND	ND	NA	<30%
65703	65762*	ND	ND	NA	<30%
65711	65766*	ND	ND	NA	<30%

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65715	65763*	ND	ND	NA	<30%
65719	65765*	ND	ND	NA	<30%
65723	65767*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 2 CFU/100ml.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

Table 7. Enterococci Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65691	65711	ND	ND	NA	<30%
65695	65715	ND	ND	NA	<30%
65699	65719	ND	ND	NA	<30%
65703	65723	ND	ND	NA	<30%
65703	65762*	ND	ND	NA	<30%
65711	65766*	ND	ND	NA	<30%
65715	65763*	ND	ND	NA	<30%
65719	65765*	ND	ND	NA	<30%
65723	65767*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 MPN/100 mL.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

The data provided in Tables 5, 6, and 7 show that all of the field duplicate samples analyzed by the laboratory had measured values less than detection. The RPDs for these samples could not be calculated because one or both of the duplicate sample results was less than the laboratory reporting limit. Although the RPD for these samples cannot be calculated, the microbiological analysis precision is acceptable for this program and the reported microbiological results are valid.

Data Quality Assessment

This data validation assessment indicates all the microbiological data collected during Sampling Episode 6505 can be used for the large cruise ship rulemaking effort, with the

exception of results for samples 65731, 65733, and 65737, which were analyzed outside the 6-hour holding time.

Data users should consider limitations of sample results derived from overly high or low sample dilution as they use the data.

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: February 4, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Erin Salo, Quality Assurance Chemist
Sample Control Center

SUBJECT: Data Review Narrative for Total and Dissolved Metals Analyses for the Alaskan Cruise Ship Industry, Episode 6505

OVERVIEW

Under EPA contract number 68-C-03-045, Southwest Research Institute submitted data for the analysis of total and dissolved metals by EPA Methods 200.7, 200.8, 245.1, and 245.5 in Episode 6505. The 34 aqueous samples and 2 solid samples in this episode were analyzed for 24 metals by Method 200.7 (ICP-AES) and selenium and thallium by Method 200.8 (ICP-MS). Mercury analyses of the aqueous samples were performed by Method 245.1, and by Method 245.5 for the solid samples. Table 1 provides a list of samples, matrices, descriptions, sampling dates, and the required analytical methods.

All 34 aqueous samples were analyzed for total and dissolved metals. The two solid samples were analyzed for total metals. The laboratory added the suffixes "D" and "T" to the sample numbers on the hard copy results to differentiate the analyses for dissolved metals and total metals, respectively. These suffixes are also used in this data review narrative. However, the sample numbers in the database will not contain these suffixes. Consistent with current EAD protocols, the total and dissolved metals distinctions are provided in the "procedure" field of the database.

The laboratory prepared matrix spike/matrix spike duplicate (MS/MSD) samples for the three aqueous effluent samples marked as "QC" on the traffic reports. In addition, the laboratory prepared an extra aqueous effluent sample MS/MSD for total and dissolved metals and a solid sample for MS/MSD for total metals.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65591	Aqueous	SP-1, Galley	8/29/2004	200.7, 200.8, and 245.1
65595	Aqueous	SP-1, Galley	8/30/2004	
65599	Aqueous	SP-1, Galley	8/31/2004	
65603	Aqueous	SP-1, Galley	9/1/2004	
65607	Aqueous	SP-1, Galley	9/2/2004	
65611	Aqueous	SP-2, Laundry	8/29/2004	
65615	Aqueous	SP-2, Laundry	8/30/2004	
65619	Aqueous	SP-2, Laundry	8/31/2004	
65623	Aqueous	SP-2, Laundry	9/1/2004	

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65627	Aqueous	SP-2, Laundry	9/2/2004	200.7, 200.8, and 245.1
65631	Aqueous	SP-3, Accommodations	8/29/2004	
65635	Aqueous	SP-3, Accommodations	8/30/2004	
65639	Aqueous	SP-3, Accommodations	8/31/2004	
65643	Aqueous	SP-3, Accommodations	9/1/2004	
65647	Aqueous	SP-3, Accommodations	9/2/2004	
65651	Aqueous	SP-4, Influent to wastewater treatment	8/29/2004	
65655	Aqueous	SP-4, Influent to wastewater treatment	8/30/2004	
65659	Aqueous	SP-4, Influent to wastewater treatment	8/31/2004	
65663	Aqueous	SP-4, Influent to wastewater treatment	9/1/2004	
65667	Aqueous	SP-4, Influent to wastewater treatment	9/2/2004	
65691	Aqueous	SP-6, Final effluent	8/29/2004	
65695	Aqueous	SP-6, Final effluent	8/30/2004	
65699	Aqueous	SP-6, Final effluent	8/31/2004	
65703	Aqueous	SP-6, Final effluent	9/1/2004	
65707	Aqueous	SP-6, Final effluent	9/2/2004	
65711	Aqueous	SP-7, Final effluent	8/29/2004	
65715	Aqueous	SP-7, Final effluent	8/30/2004	
65719	Aqueous	SP-7, Final effluent	8/31/2004	
65723	Aqueous	SP-7, Final effluent	9/1/2004	
65731	Aqueous	SP-8, Galley water discharge	8/26/2004	
65733	Aqueous	SP-9, Laundry overboard	8/26/2004	
65737	Aqueous	SP-10, Food pulper discharge	8/26/2004	
65741	Solid	SP-11, Screening solids	8/31/2004	200.7, 200.8, and 245.5
65745	Aqueous	SP-12, Waste biosludge	8/26/2004	200.7, 200.8, and 245.1
65749	Solid	SP-13, Incinerator ash	8/31/2004	200.7, 200.8, and 245.5
65753	Aqueous	SP-14, Source water	8/30/2004	200.7, 200.8, and 245.1
65761	Aqueous	Equipment blank	8/24/2004	

These data have been reviewed in accordance with SCC's Data Review Guidelines for Metals Analyses (November 2004) and with the specifications listed in EPA Methods 200.7 (Rev. 5), 200.9 (Rev. 2.2), 245.1 (03/83), and 245.5 (03/83). All data are of acceptable quality with the qualifiers described below and detailed in the data review summary table (Table 2).

Following SCC's initial review of the data, EPA inquired about modifying the reporting convention used for metals to address EPA's need to compare sample results to the water quality criteria for Alaskan

coastal waters. The current EAD metals contracts specify that the laboratory report results down to the minimum level (ML) for each analyte. By examining both the hard copy raw data and the laboratory's electronic submission, SCC determined that results between the ML and the method detection limit (MDL) were available for all of the metals. After consultation with EPA, SCC modified the reported results such that any analytes not detected in the sample were reported as a non-detect at the laboratory's MDL rather than at the ML. As a result, there are also some analytes that are reported as detected between the ML and the laboratory's MDL. These results are flagged "J" in the database. This change also means that the hard copy data reported by the laboratory may not match the results in the database for values in the database between the MDL and ML of the analyte. This change also necessitated an additional review of all of the blank results to ensure that the low-level results reported in samples were not simply artifacts of the blanks.

SUMMARY

All 36 samples were successfully analyzed within the method-specified holding times. The initial precision and recovery (IPR) analyses and the method detection limit (MDL) study were performed and met the acceptance criteria. The minimum level standard for calcium was spiked at 500 µg/L instead of at 50 µg/L. However, SCC does not believe that this affects the data, since the calibration curves, calibration standards, and calibration blanks met all other QC requirements.

Calibration curves, calibration standards, and calibration blanks were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory's reporting limits, with the exceptions noted below and detailed in Table 2. QC samples, including laboratory control sample (LCS), matrix spike (MS) sample, matrix duplicate (MSD) sample, and laboratory serial dilution sample demonstrated that laboratory performance for these analyses was acceptable, with the exception of the issues described below.

Multiple Qualifiers

Some of the analytical results were affected by multiple qualifiers. In cases where these qualifiers suggest different biases, SCC considers the data to be estimated values. The effect of each QC failure and its associated qualifier is described in the data review narrative. Where multiple qualifiers occur, the cumulative effects of the associated qualifiers are documented in the attached Table 2.

DATA ISSUES

Blanks

Several elements were detected in the preparation blanks and some of the continuing calibration blanks (CCBs) associated with the samples in this episode at concentrations greater than the respective MDLs, but less than the method-specified MLs. (Note: This is a function of the change in reporting limits requested by EPA after the fact and not an issue of laboratory performance.) The data quality is affected as follows:

- Sample Results Less than Five Times Blank Results: When the sample result is less than five times the blank result, there are no means by which to ascertain whether or not the presence of the analyte may be attributed to contamination. Therefore, SCC recommends that the data be reported in the database as a non-detect at the MDLs, adjusted for sample size, dilution, and matrices. These instances are detailed in the attached data review summary table.

- Sample Results Greater than Five Times but Less than Ten Times Blank Results: SCC considers these results to be of acceptable quality, but they may be maximum values. These instances are detailed in the attached data review summary table.

- Sample Results Greater than Ten Times Blank Results or Analyte Not Detected in Sample: SCC does not consider the presence of the analyte in the blank to adversely affect the data in cases where the sample results are greater than ten times the associated blank results or where the analyte is not detected in associated samples. Because SCC considers such data to be acceptable without qualification, these cases do not merit further detail.

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Tin (Sn) and iron (Fe) were recovered below the method-specified criteria in the MS and MSD for sample 65591T. Therefore, SCC considers the Sn and Fe results in this sample to be of acceptable quality, but may be minimum values.

Barium (Ba), nickel (Ni), and antimony (Sb) were recovered below the method-specified criteria in the MS and MSD for solid sample 65749. Therefore, SCC considers the Ba, Ni, and Sb results in this sample to be of acceptable quality, but they may be minimum values.

Silver (Ag) was recovered above the method-specified criteria in the MS for solid sample 65749. Therefore, SCC considers the Ag result in this sample to be of acceptable quality, but it may be a maximum value.

Tin (Sn) was recovered above the method-specified criteria in the MSD and the relative percent difference (RPD) between the MS and MSD was outside the method-specified criteria for solid sample 65749. Therefore, SCC considers the Sn result in this sample to be an estimated value.

The RPD between the MS and MSD for copper (Cu), manganese (Mn), titanium (Ti), and zinc (Zn) were outside the method-specified criteria for solid sample 65749. Therefore, SCC considers the Cu, Mn, Ti, and Zn results in this sample to be estimated values.

Serial Dilutions

For silver (Ag) in solid sample 65749, the percent difference (%D) between the original analysis and the dilution exceeded the method-specified criteria. Therefore, SCC considers the sample result for Ag in sample 65749 to be an estimated value.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's Data Review Team Leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachment

cc: Marla Smith, EPA
Beverly Randolph, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodie King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** E. Salo

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65591	Fe	Minimum value	MS and MSD recovery below method-specified criteria	NA	813 µg/L
Total 65591	Sn	Minimum value	MS and MSD recovery below method-specified criteria	NA	13 µg/L
Solid 65749	Ba	Minimum value	MS and MSD recovery below method-specified criteria	NA	381 mg/kg
Solid 65749	Ni	Minimum value	MS and MSD recovery below method-specified criteria	NA	37.1 mg/kg
Solid 65749	Sb	Estimated value	MS and MSD recovery below method-specified criteria; sample result > 5x and <10x blank result	NA	7.5 mg/kg
Solid 65749	Ag	Estimated value	MS recovery above method-specified criteria and %D for serial dilution exceeded criteria	NA	9.7 mg/kg
Solid 65749	Sn	Estimated value	MSD recovery and RPD between MS/MSD above method-specified criteria	NA	58.4 mg/kg
Solid 65749	Cu, Mn, Ti, Zn	Estimated value	RPD between MS/MSD above method-specified criteria	NA	See database report
Dissolved 65615, 65619, 65691, 65695, 65699, 65715, 65719	Al	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65599, 65611, 65651, 65655, 65659	Al	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Total 65711, 65753, 65703, 65707, 65723	Al	Report in database as non-detect	Sample result < 5x blank result	NA	ND

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** E. Salo

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65627	Al	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Dissolved 65655	As	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Total 65603, 65703, 65707, 65651	As	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Solid 65741	As	Report in database as non-detect	Sample result < 5x blank result	NA	
Solid 65749	As	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Dissolved 65737, 65753, 65603, 65607, 65623, 65627, 65643, 65647, 65663, 65667, 65723, 65761, 65591, 65595, 65611, 65615, 65619, 65631, 65635, 65639, 65731, 65733	B	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65711, 65703, 65707, 65599, 65655, 65659, 65691, 65695, 65699, 65715, 65719	B	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Solid 65741	B	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Solid 65749	B	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Total 65623, 65627, 65753, 65761, 65591, 65595, 65611, 65615, 65619, 65631, 65635, 65639, 65733, 65731	B	Report in database as non-detect	Sample result < 5x blank result	NA	ND

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** E. Salo

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65643, 65607, 65599, 65659, 65691, 65695, 65699, 65715, 65651, 65655	B	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Dissolved 65643, 65753, 65647, 65631	Ba	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65663, 65703, 65707, 65723, 65623, 65635, 65639, 65619, 65655, 65659	Ba	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Total 65753	Ba	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Total 65711, 65707, 65723, 65703	Ba	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Dissolved 65711, 65737, 65753, 65603, 65607, 65623, 65627, 65643, 65647, 65663, 65667, 65703, 65707, 65723, 65631, 65635, 65639, 65651, 65655, 65659, 65695, 65699, 65715, 65719, 65731, 65733	Be	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Solid 65741	Be	Report in database as non-detect	Sample result < 5x blank result	NA	ND

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** E. Salo

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65711, 65737, 65753, 65603, 65607, 65623, 65627, 65643, 65647, 65663, 65667, 65703, 65707, 65723, 65619, 65635, 65639, 65659, 65691, 65695, 65699, 65715, 65733, 65731, 65591, 65595, 65599, 65611, 65615	Be	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved/Total 65761	Ca	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65699, 65715, 65631, 65635, 65639, 65655, 65691, 65695, 65731, 65733	Co	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65651, 65659	Co	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Total 65761, 65591, 65595, 65611, 65659, 65699, 65715, 65651, 65655	Co	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65737, 65703, 65723, 65719	Cu	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Total 65711, 65703, 65723	Cu	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** E. Salo

Sample	Analyte	Action	Reason	SCC Qual	Level
Dissolved 65611, 65615, 65619, 65631, 65635, 65639, 65651, 65655, 65659, 65691, 65695, 65699, 65715, 65719, 65733	Fe	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65595, 65599, 65731	Fe	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Total 65753	Mn	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65623, 65651, 65715, 65719	Mo	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Total 65737, 65663, 65667, 65703, 65595, 65599, 65659, 65651, 65655	Mo	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Solid 65741	Mo	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved/Total 65761	Na	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Solid 65741	Pb	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Solid 65741	Sb	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Total 65615, 65619, 65635, 65639, 65733, 65731	Se	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Total 65611	Se	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Solid 65741	Sn	Report in database as non-detect	Sample result < 5x blank result	NA	ND

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** E. Salo

Sample	Analyte	Action	Reason	SCC Qual	Level
Dissolved 65595, 65611, 65615, 65619, 65631, 65635, 65639, 65731, 65733	Ti	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65591	Ti	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Total 65737, 65643, 65611, 65651	Ti	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Total 65603, 65663, 65667, 65595, 65615, 65631, 65639, 65659, 65655, 65745	Ti	Maximum value	Sample result > 5x and < 10x blank result	NA	See database report
Total 65761, 65651, 65655, 65659, 65595, 65599	Tl	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65651, 65659, 65691, 65695, 65699, 65715	V	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Total 65591, 65599, 65619, 65635, 65691, 65695, 65715, 65733, 65595	V	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Dissolved 65623	Y	Report in database as non-detect	Sample result < 5x blank result	NA	ND
Total 65737	Y	Report in database as non-detect	Sample result < 5x blank result	NA	ND

NA = Not applicable
ND = Not detected

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: February 2, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Organics Analyses for the Alaskan Cruise Ship Industry, Episode 6505

OVERVIEW

Under EPA Contract Number 68-C-03-033, Pacific Analytical, Inc. (PAI) submitted data for the analysis of volatile organics by Method 624 and semivolatile organics by Method 625 in Episode 6505. Table 1 provides a list of samples, sample descriptions, sampling dates, matrices, and the required analytical methods. This episode included one solid sample and 34 aqueous samples for Method 624 analysis, and two solid samples and 34 aqueous samples for Method 625 analysis. The package included data for four sets of matrix spike and matrix spike duplicate (MS/MSD) samples analyzed for each method.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65591	Aqueous	SP-1 Galley wastewater	8/29/04	624, 625
65595	Aqueous	SP-1 Galley wastewater	8/29/04[a], 8/30/04[b]	624, 625
65599	Aqueous	SP-1 Galley wastewater	8/30/04[a], 8/31/04[b]	624, 625
65603	Aqueous	SP-1 Galley wastewater	9/01/04	624, 625
65607	Aqueous	SP-1 Galley wastewater	9/01/04[a], 09/02/04[b]	624, 625
65611	Aqueous	SP-2 Laundry	8/29/04	624, 625
65615	Aqueous	SP-2 Laundry	8/30/04	624, 625
65619	Aqueous	SP-2 Laundry	8/30/04[a], 8/31/04[b]	624, 625
65623	Aqueous	SP-2 Laundry	9/01/04	624, 625
65627	Aqueous	SP-2 Laundry	9/01/04	624, 625
65631	Aqueous	SP-3 Accommodations	8/29/04	624, 625
65635	Aqueous	SP-3 Accommodations	8/30/04	624, 625
65639	Aqueous	SP-3 Accommodations	8/30/04[a], 8/31/04[b]	624, 625
65643	Aqueous	SP-3 Accommodations	9/01/04	624, 625
65647	Aqueous	SP-3 Accommodations	9/01/04[a], 9/02/04[b]	624, 625

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65651	Aqueous	SP- 4 Influent	8/29/04	624, 625
65655	Aqueous	SP-4 Influent	8/30/04	624, 625
65659	Aqueous	SP-4 Influent	8/30/04[a], 8/31/04[b]	624, 625
65663	Aqueous	SP-4 Influent	9/01/04	624, 625
65667	Aqueous	SP-4 Influent	9/01/04	624, 625
65691	Aqueous	SP-6 Effluent	8/29/04	624, 625
65695	Aqueous	SP-6 Effluent	8/30/04	624, 625
65699	Aqueous	SP-6 Effluent	8/30/04[a], 8/31/04[b]	624, 625
65703	Aqueous	SP-6 Effluent	9/01/04	624, 625
65707	Aqueous	SP-6 Effluent	9/02/04	624, 625
65711	Aqueous	SP-7 Effluent	8/29/04	624, 625
65715	Aqueous	SP-7 Effluent	8/30/04	624, 625
65719	Aqueous	SP-7 Effluent	8/30/04[a], 8/31/04[b]	624, 625
65731	Aqueous	SP-8 Galley wastewater	8/27/04	624, 625
65733	Aqueous	SP-9 Laundry	8/27/04	624, 625
65737	Aqueous	SP-10 Food pulper	8/26/04	624, 625
65741	Solid	SP-11 Screening solids	8/30/04[a], 8/31/04[b]	624, 625
65745	Aqueous	SP-12 Biosludge	8/26/04	624, 625*
65749	Solid	SP-13 Incinerator ash	8/30/04	625
65753	Aqueous	SP-14 Source water	8/30/04	624, 625
65757	Aqueous	Trip blank	9/01/04	624
65760	Aqueous	SP-10 Food pulper	9/03/04	625
65761	Aqueous	Equipment blank	8/24/04	625

[a] Collection date for volatiles
[b] Collection date for semivolatiles
* Sample was received at the laboratory broken, no semivolatiles analysis for this sample

These data have been reviewed in accordance with SCC's Data Review Guidelines for Volatile and Semivolatile Analyses By Methods 624 and 625 (November 2004) and according to the specifications in the methods. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are

considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary tables (Table 2 and 3).

SUMMARY

All samples were successfully analyzed for the target analytes according to EPA Methods 624 and 625, with the exception of sample 65745. The volume of sample 65745 for semivolatile analysis was broken upon receipt at the laboratory. Method 624 samples were prepared and analyzed within holding times. Method 625 samples were extracted and analyzed within the method-specified holding times, and GPC clean-up procedures were performed on all samples. All calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery samples (OPR) and MS/MSD samples, as well as surrogate and internal standard recoveries, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below.

DATA ISSUES: METHOD 624

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples

MS/MSD samples were prepared for samples 65715, 65719, and 65731, and solid sample 65741. One analyte, 2-chloroethylvinyl ether, was not recovered in any of these MS/MSD samples. Although Method 624 does not provide QC limits for MS/MSD recoveries, the lack of recoveries in the MS/MSDs indicate potential difficulties in the analysis of this compound in samples. Therefore, SCC recommends that the results for 2-chloroethylvinyl ether be excluded from the database. Please note that SCC did not initiate reanalysis of the affected samples because the holding time had expired by more than 45 days. These cases are detailed in Table 2.

For solid sample 65741, toluene is not recovered in the MS sample, but had acceptable recovery in the MSD sample. Therefore, SCC considers the toluene result in solid sample 65741 to be an estimated value (see Table 2).

DATA ISSUES: METHOD 625

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

MS/MSD samples were prepared for samples 65711, 65715, 65719, and solid sample 65749. For sample 65719, hexachlorocyclopentadiene was not recovered in the MS/MSD. Hexachlorocyclopentadiene recoveries were at acceptable level for other MS/MSD samples. For solid sample 65749, benzidine was not recovered in the MS/MSD. Benzidine recoveries were at acceptable levels for other MS/MSD samples. Although Method 625 does not provide QC limits for the recoveries, the lack of recoveries in the MS/MSDs indicate potential difficulties in the extraction of these compounds in samples. Therefore, SCC recommends that the hexachlorocyclopentadiene result in sample 65719, and benzidine result in sample 65749 be excluded from the database. These cases are detailed in Table 3.

TECHNICAL NOTES:

Reporting Limits

The reporting limits for this project are the same limits required for Methods 1624 and 1625, and are based on the lowest initial calibration (ICAL) standard, adjusted for actual sample size and final extract volume. Some sample results in this episode were reported by the laboratory with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit. In keeping with current EAD practices, and to maintain consistency in the database, all "J" flagged data will be reported in the database as non-detects at the minimum levels (MLs) as specified in Method 1624 and 1625, as required for this project.

The acid fractions for samples 65591, 65595, 65599, 65619, 65631, 65635, 65639, 65651, 65659, 65695, 65699, 65711, 65719, and 65749 were lost due to extraction apparatus failures during extraction. The acid fractions for these samples were re-extracted and analyzed within holding time. However, several samples were re-extracted using less than the 1000-mL volume specified by the method because of the limited volume of the remaining samples. This variation in sample size increased the MLs for these samples by as much as 64%. The MLs provided in the database for the acid fractions of these samples reflect the smaller sample volumes.

For Method 624, the laboratory increased the QC sample spiking concentration, the concentration of the lowest calibration standard, and the ML for 2-chloroethylvinyl ether by a factor of five because of problems with instrument sensitivity. The ML provided in the database for this analyte was increased by factor of five for all samples.

Broken Sample

Both 1-L bottles of sample 65745 for semivolatile analysis were received at the laboratory broken. Therefore, no data are included in the database for the analysis of semivolatile organics by Method 625 for sample 65745.

If you have any questions regarding the analyses of these samples or the review of these data, please contact me by telephone at (703) 461-2346, or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table for Method 624

Episode: 6505 **Analysis:** Method 624

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Samples	Analyte	Action	Reason	SCC Qual	Level
65715, 65719, 65731, 65741	2-chloroethylvinyl ether	Exclude from database	Not recovered in the MS/MSD	Exclude	NA
65741	toluene	Estimated value	Not recovered in the MS, but acceptable MSD recovery	NA	136 µg/L

Table 3
Data Review Summary Table for Method 625

Episode: 6505 **Analysis:** Method 625

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Samples	Analyte(s)	Action	Reason	SCC Qual	Level
65719	hexachlorocyclopentadiene	Exclude from database	Not recovered in the MS/MSD	Exclude	NA
65749	benzidine	Exclude from database	Not recovered in the MS/MSD	Exclude	NA

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: January 19, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for PCB Congener Analyses for the Alaskan Cruise Ship Industry, Episode 6505

OVERVIEW

Under EPA Purchase Order EP-C-04-047, Axys Analytical Services submitted data for the analysis of chlorinated biphenyl congeners by EPA Method 1668A for one sample in Episode 6505. Table 1 provides a list of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifier, Description, Sampling Date, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6505	65451	Aqueous	SP4, Influent Wastewater	8/29/04	1668A

These data have been reviewed in accordance with SCC's Data Review Guidelines for Chlorinated Biphenyl Analysis By Method 1668, Revision A (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with this sample. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

The sample was successfully extracted and analyzed for the target analytes in EPA Method 1668A within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks associated with this sample detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable, with the clarification provided below.

Reporting Limits

The sample was extracted using a 887-mL aliquot, rather than the method-specified 1000-mL aliquot, due to volume constraints. This variation in sample size increased the MLs for sample 65651 by 13%. The MLs provided in the database for this sample reflect the smaller sample volume.

If you have any questions regarding the analyses of this sample or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: January 10, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Pesticide Analyses for the Alaskan Cruise Ship Industry, Episode 6505

OVERVIEW

Under EPA Purchase Order EP-C-04-046, Pacific Analytical, Inc. (PAI) submitted data for the analysis of organohalide pesticides by EPA Method 1656A and organophosphorus pesticides by EPA Method 1657A for two samples in Episode 6505. Table 1 provides a list of samples, matrices, description, and the required analytical methods.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Method
65599	Aqueous	SP1, Galley wastewater	8/30/04	1656A, 1657A
65659	Aqueous	SP4, Influent to wastewater	8/30/04	1656A, 1657A

These data have been reviewed in accordance with SCC's Data Review Guidelines for Pesticide Analyses (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary tables (Tables 2A and 2B).

SUMMARY

All samples were successfully extracted and analyzed for the target analytes in EPA Methods 1656A and 1657A within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory's reporting limits. All organohalide pesticides samples were processed through gel permeation chromatography (GPC), Florisil, and sulfur removal cleanups. All organophosphorus pesticides samples were processed through GPC and carbon column cleanup. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below. No matrix spike/matrix spike duplicate (MS/MSD) samples were required for this episode.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Reporting Limits

The laboratory's reporting limits are based on the lowest calibration points specified in the methods, adjusted for dilution, rather than the minimum levels (MLs) listed in the methods. In most cases, the laboratory's reporting limits are lower than the method-specified MLs.

Some sample results in this episode were reported by the laboratory with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit. In keeping with current EAD practices, and to maintain consistency, all "J" flagged data will be reported in the database as non-detects at the laboratory's reporting limits.

Multiple Qualifiers

Some analytical results were affected by multiple qualifiers. In cases where these qualifiers suggest different biases, SCC considers the data to be estimated values. The effect of each QC failure and its associated qualifier are described in this data review narrative. Where multiple QC failures occur, the cumulative effects of the associated qualifiers are documented in the Tables 2A and 2B.

DATA ISSUES: METHOD 1656A

Preparation Blank

Dacthal and terbuthylazine were detected in the preparation blank at 0.012 µg/L and 2.42 µg/L, respectively, which were below the laboratory's reporting limits. Dacthal was not detected in either sample in this episode, and terbuthylazine was not detected in sample 65599. Therefore, SCC believes that the data quality was not affected.

For sample 65659, the terbuthylazine result is less than five times the blank result. When the sample result is less than five times the blank results, there are no means by which to ascertain whether or not the presence of the analyte may be attributed to contamination. Therefore, SCC recommends that the terbuthylazine result of 5.38 µg/L in sample 65659 be reported in the database as a non-detect at the laboratory's reporting limit (see Table 2A).

Surrogate Recoveries

For sample 65599, all surrogate recoveries on both columns are below the method-specified criteria. Therefore, SCC considers all organohalide pesticides data in this sample to be minimum values (see Table 2A).

For sample 65659, the surrogate recoveries for decachlorobiphenyl on both columns are below the method-specified criteria. However, the other two surrogate recoveries are within the method-specified criteria, indicating that the extraction efficiency is in control. Therefore, SCC believes that the data quality for these samples is not affected by the low recovery of one surrogate.

Ongoing Precision and Recovery (OPR)

Metribuzin, dichlone, norflurazon, and carbophenothion were recovered below the method-specified criteria in the OPRs associated with samples 65599 and 65659. Therefore, SCC considers the non-detects data for these analytes in these samples to be minimum values (see Table 2A).

Sample Results

According to the method, the computed result for a target analyte detected on the primary column analysis must be confirmed and agree within a factor of two with the result computed for that analyte on the confirmation column. For sample 65599, the dieldrin result of 0.365 µg/L from the primary column differed by more than the method-specified factor of two from the confirmation column result of 0.128 µg/L. The peak resolution was poor on the primary column, which indicates a potential positive interference.

Due to matrix interferences in sample 65659, the chromatograms from both primary and secondary columns show that the simazine and dicofol peaks, although distinct, are not completely resolved from other closely eluting compounds on one of the two columns. Because other compounds elute within 20 seconds, and non-target multicomponent peaks surround the simazine and dicofol peaks on secondary column, the identification and quantification for these analytes are suspect. Also, the methoxychlor and endrin aldehyde results from the primary column differed by more than the method-specified factor of two from the results for the confirmation column.

After discussions with SCC, EPA authorized the analysis of samples 65599 and 65659 by a GC/MS method utilizing selected ion monitoring (SIM) to determine if the target analytes, in fact, were present in the samples, or if the original GC/ECD results were false positives. The results of the GC/MS SIM analyses were reviewed by SCC and we determined that most of the pesticides could not be confirmed, except for simazine in sample 65659. Simazine was detected by GC/MS at 0.957 µg/L in sample 65659, and that result was included in the database.

DATA ISSUES: METHOD 1657A

Ongoing Precision and Recovery (OPR)

Two OPR samples were analyzed for this episode. Methamidophos was not recovered in OPR1, and was recovered below the method-specified criteria in OPR2. Therefore, SCC considers the non-detect data for methamidophos in all samples to be minimum values (see Table 2B).

If you have any questions regarding the analyses of these samples or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments:

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2A
Data Review Summary Table

Episode: 6505 **Analysis:** 1656A

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65659	terbuthylazine	Report in the database as non-detect	Sample result < 5x blank result	NA	ND
65659	metribuzin, dichlone, norflurazon, carbophenothion	Minimum values	Low OPR recoveries	NA	ND
65659	simazine	Result report from GC/MS confirmation analysis	Peak interference in GC/ECD analysis	NA	0.957 µg/L
65599	All target analytes listed in 1656A, except as noted below	Minimum values	Low surrogate recoveries	NA	ND
65599	metribuzin, dichlone, norflurazon, carbophenothion	Minimum values	Low surrogate recoveries; low OPR recoveries	NA	ND

ND = Non-detect at the laboratory's reporting limit. See level in database.
NA = Not applicable

Table 2B
Data Review Summary Table

Episode: 6505 **Analysis:** 1657A

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65599, 65659	methamidophos	Minimum value	No OPR recovery on first attempt, and low recovery on second attempt	NA	ND

ND = Non-detect at the laboratory's reporting limit. See level in database.
NA = Not applicable

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6505

Data Validation Report For Settleable Solids Samples

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

February 8, 2005

Settleable Solids Method 160.5

Completeness

During Sampling Episode 6505, all 33 samples (excluding QC samples) that were identified in the Sampling and Analysis Plan for the Island Princess (Sampling Episode 6505) were collected for analysis of Settleable Solids (SS) by EPA Method 160.5. Sample numbers ranged between 65591 and 65753. Sampling completeness for this episode was 100% (all planned samples were collected).

The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete SS data for all submitted samples. A list of the samples collected and analyzed during Sampling Episode 6505 are provided in Table 1.

Table 1. SS Samples Collected During Sampling Episode 6505

Sample Numbers	Sample Point Description
65651, 65655, 65659, 65663, 65667	Treatment System Influent
65691, 65695, 65699, 65703, 65707, 65727, 65711, 65715	Treatment System Effluent
65631, 65635, 65639, 65643, 65647	Accommodations
65591, 65595, 65599, 65603, 65607	Galley
65611, 65615, 65619, 65623, 65627	Laundry
65731	Galley Overboard
65733	Laundry Overboard
65737	Food Pulper Overboard
65753, 65764	Source Water

According to the Quality Assurance Project Plan (QAPP) developed for the Rulemaking Support for Large Cruise Ships in Alaska Waters, sampling completeness is the number of valid samples collected relative to the number of samples planned for collection; analytical completeness is the number of valid sample measurements relative to the number of valid samples collected; and overall completeness is the number of valid sample measurements relative to the number of samples planned for collection. For the cruise ship sampling program a minimum goal of 90% completeness for sampling and analytical completeness has been established, and a minimum goal of 81% for overall completeness (determined by multiplying sampling and analytical completeness goals) has been established.

As a result of a shipping delay, 6 samples collected for SS analysis arrived at the laboratory five days following collection. According to Method 160.5, samples should be analyzed within 48 hours following collection. Although the SS samples were analyzed upon receipt at the laboratory, the results are not considered valid. Therefore, for Sampling Episode 6505 both laboratory completeness and overall completeness for SS is 81%.

Holding Times

Method 160.5 requires SS samples be analyzed within 48 hours following collection. Analysis of traffic reports and laboratory data sheets indicates 6 of the 32 SS samples were analyzed outside the 48 hour hold time window. Table 2 provides information on the samples analyzed outside the method-specified holding time.

Table 2. SS Samples Exceeding Hold Times

Sample Number	Sample Description	Sample Hold Time	Method Hold Time	SS Result
65647	Accommodations Wastewater	129 hours	48 hours	1.1 ml/L
65707	Treatment System Effluent	129 hours	48 hours	<0.1 ml/L
65607	Galley Wastewater	129 hours	48 hours	1.8 ml/L
65727	Treatment System Effluent	129 hours	48 hours	<0.1 ml/L
65667	Treatment System Influent	129 hours	48 hours	24 ml/L
65627	Laundry Wastewater	129 hours	48 hours	0.99 ml/L

Because the holding time was exceeded by more than 3 days (approximately 81 hours) for the six samples shown in Table 2, this SS data is not considered valid and should not be used in the engineering assessment for the cruise ship rulemaking. Accordingly, these results will be excluded from the analytical database.

Precision Analysis

Reproducibility for SS is measured as relative percent difference (RPD) between duplicate samples. The QAPP for the Cruse Ship Rulemaking specifies the target RPD for field duplicate samples as less than 30%. Field duplicate samples were collected for SS, and the results are shown in Table 3. The RPDs shown in Table 3 could not be calculated since one or both of the field duplicate sample results were less than the laboratory reported detection limit.

Although the RPD for these samples cannot be calculated, SS analysis precision is acceptable for this program, and the reported SS results are valid.

Table 3. Relative Percent Difference Between Field Duplicate Samples

Sample No.	SS Result	Sample No	SS Result	RPD	RPD Target
65691	<0.1 ml/L	65711	<0.1 ml/L	NA	<30%
65695	<0.1 ml/L	65715	<0.1 ml/L	NA	<30%
65753	<0.1 ml/L	65764	<0.1 ml/L	NA	<30%

NA: RPD cannot be calculated since one or both of the sample results is less than the detection limit.
RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.

Data Quality Assessment

This data validation assessment indicates the SS data collected during Sampling Episode 6505 can be used for the large cruise ship rulemaking effort, with the exception of those samples that were analyzed outside the holding time of 48 hours.

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: February 3, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Sara Clark, Quality Assurance Chemist
Sample Control Center

SUBJECT: Data Review Narrative for Available Cyanide Analyses by Method OIA-1677 for the Alaska Cruise Ship Industry, Episode 6505

OVERVIEW

Under EPA Purchase Order EP-C-04-048, Bayer Material Science LLC, submitted data for the analysis of available cyanide by EPA Method OIA-1677 for 33 samples in Episode 6505. Table 1 provides a listing of samples, matrices, descriptions, and sampling dates. Available cyanide was the only analysis performed by Bayer for these samples.

Table 1 - Sample Identifiers, Matrices, Descriptions, and Sampling Dates

EPA Sample #	Matrix	Sample Description	Sampling Date
65591	Aqueous	SP1, Galley wastewater	08/29/04
65595	Aqueous	SP1, Galley wastewater	08/30/04
65599	Aqueous	SP1, Galley wastewater	08/31/04
65603	Aqueous	SP1, Galley wastewater	09/01/04
65607	Aqueous	SP1, Galley wastewater	09/02/04
65615	Aqueous	SP2, Laundry wastewater	08/30/04
65619	Aqueous	SP2, Laundry wastewater	08/31/04
65623	Aqueous	SP2, Laundry wastewater	09/01/04
65627	Aqueous	SP2, Laundry wastewater	09/02/04
65631	Aqueous	SP3, Accommodations wastewater	08/29/04
65635	Aqueous	SP3, Accommodations wastewater	08/30/04
65639	Aqueous	SP3, Accommodations wastewater	08/31/04
65643	Aqueous	SP3, Accommodations wastewater	09/01/04
65647	Aqueous	SP3, Accommodations wastewater	09/02/04
65651	Aqueous	SP4, Influent to wastewater treatment	08/29/04
65655	Aqueous	SP4, Influent to wastewater treatment	08/30/04
65659	Aqueous	SP4, Influent to wastewater treatment	08/31/04
65663	Aqueous	SP4, Influent to wastewater treatment	09/01/04
65667	Aqueous	SP4, Influent to wastewater treatment	09/02/04

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

EPA Sample #	Matrix	Sample Description	Sampling Date
65691	Aqueous	SP6, Effluent from wastewater treatment	08/29/04
65695	Aqueous	SP6, Effluent from wastewater treatment	08/30/04
65699	Aqueous	SP6, Effluent from wastewater treatment	08/31/04
65703	Aqueous	SP6, Effluent from wastewater treatment	09/01/04
65707	Aqueous	SP6, Effluent from wastewater treatment	09/02/04
65711	Aqueous	SP7, Effluent from wastewater treatment	08/29/04
65715	Aqueous	SP7, Effluent from wastewater treatment	08/30/04
65719	Aqueous	SP7, Effluent from wastewater treatment	08/31/04
65731	Aqueous	SP8, Galley wastewater	08/26/04
65733	Aqueous	SP9, Laundry wastewater	08/26/04
65737	Aqueous	SP10, Food pulper	08/26/04
65741	Solid	SP11, Screening solids	08/30/04
65745	Aqueous	SP12, Biosludge wastewater	08/26/04
65753	Aqueous	SP14, Source water	08/31/04

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004), and with the specifications listed in the analytical requirements summary for this episode. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary table (Table 2).

SUMMARY

All samples were successfully analyzed within the method-specified holding times for available cyanide. Initial precision and recovery samples (IPRs) were successfully performed prior to sample analysis. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks were performed and there was no contamination detected above the laboratory's reporting limits. The QC samples, including the ongoing and precision recovery (OPR) sample and matrix spike/matrix spike duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses was acceptable, with the exception of the data issues described below.

DATA ISSUES

Available Cyanide Greater than Total Cyanide

For all samples in this episode, SCC evaluated total cyanide results against available cyanide results, and found that available cyanide was detected in samples 65603, 65659, 65731, and 65745, while total cyanide were not detected in these samples or detected at a lower amount. In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. However, for these samples, it is important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the available cyanide determination was performed by a different laboratory. In addition, the overall homogeneity of the waste

stream being sampled can have a significant effect on the cyanide results. Therefore, it may not be possible to identify problems that would invalidate one cyanide fraction or the other.

In sample 65603 (galley wastewater), the available cyanide result of 2.2 µg/L is below the detection limit for the total cyanide analysis. Therefore, SCC recommends accepting the available cyanide result as reported.

Although MS/MSD samples were prepared from sample 65741 (screening solids) and met the acceptance criteria, there are no MS/MSD results for the biosolids matrix in this episode. This limits SCC's ability to evaluate the potential effects of the sample matrix for sample 65745 (biosolids), where the available cyanide results are almost 40% higher than the total cyanide results. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65745 in the database, but flagging them to indicate the irreconcilable differences.

The available cyanide result in sample 65731 (galley wastewater) was 12.9 µg/L and and total cyanide was a non-detect at 5 µg/L. SCC recommends including both cyanide results for sample 65731 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65659 is an influent sample and MS/MSD aliquots are not prepared for influents, as discussed earlier. Total cyanide was reported as not detected and the available cyanide was reported at 6 times the total cyanide detection limit. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65659 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6505, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Please note that the samples were analyzed for total cyanide by Analytical Laboratory Services, Inc. A separate narrative has been prepared for the total cyanide analysis.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's Data Review Team Leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC
Pornkeo Chinyavong, CSC

Table 2
Data Review Summary Table

Episode: 6505 **Analysis:** Available Cyanide

Industry: Alaska Cruise Ship **Reviewer:** S. Clark

Sample	Analyte	Action	Reason	SCC Qual	Level
65745	Available cyanide	—	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose	IRR	NA
65731					
65659					
65603		Minimum value	Result for available cyanide greater than total cyanide, low MS/MSD recoveries	NA	2.2 µg/L

NA = Not applicable
IRR = Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: January 18, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty
Senior Scientist

SUBJECT: Issues Associated with Results for Total Cyanide versus Available Cyanide for Episodes 6503, 6504, 6505, and 6506

The purpose of this memorandum is to provide a general discussion of the analysis of various forms of cyanide in aqueous samples, describe the cyanide analyses conducted as part of EPA's investigation of discharges from Alaskan cruise ships, and provide recommendations regarding specific results from Sampling Episodes 6503, 6504, 6505, and 6506.

Forms of Cyanide

Cyanide is an inorganic moiety composed of one carbon atom and one nitrogen atom that is most often found as an anion with a charge of -1. The cyanide anion can bond with various metals or other elements to form a wide range of cyanide compounds. The simplest form of cyanide is hydrogen cyanide, HCN, which readily dissociates into H^+ and CN^- in water. HCN is known as "free cyanide" and is the most toxic form of cyanide. Most forms of cyanide are toxic, with their toxicities depending on their ability to release free cyanide.

"Total cyanide" (or "cyanide, total") is an operationally defined term used to describe the cyanides that are measured using the total cyanide test. Total cyanide methods attempt to measure the amount of CN^- present in a sample, regardless of its oxidation state or complexation to other ions or compounds. Some complexes and organic cyanide compounds are resistant to the dissociation that occurs during the digestion/distillation step, and others are completely decomposed. Therefore, total cyanide is a method-defined parameter because the analytical conditions determine the actual analyte quantity measured.

Compounds such as metallocyanides are resistant to oxidation, with iron cyanide being one of the most resistant, and nickel, copper, and noble metal cyanides being somewhat resistant. These compounds will contribute to the measured total cyanide to some degree, but are not always completely recovered by the digestion/distillation procedure. Cyanide compounds such as thiocyanate, cobaltocyanide compounds, and cyanohydrin organic compounds are not measured at all by this procedure include because they decompose during the digestion procedure.

Two other operationally defined groups of cyanide species are "available cyanide," and "cyanide amenable to chlorination" (or "amenable cyanide"). Available cyanide generally encompasses both the free cyanide and those complexed species that are relatively easily dissociated in a weak acid solution. Amenable cyanide is the term used to describe that fraction of cyanide that can be destroyed by the common wastewater treatment procedure of chlorinating the wastewater. Some cyanides in solution will react with chlorine (Cl_2) to form cyanogen chloride (CNCl), a highly toxic gas with limited solubility. The cyanogen chloride hydrolyzes at alkaline pH to form the cyanate ion (CNO^-), which is much less toxic than the parent cyanide. Amenable cyanide encompasses the true free cyanide portion, plus additional cyanides that easily dissociate in aqueous solutions.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Analytical Methods for the Analysis of Cyanide in Aqueous Samples

Total Cyanide Methods

The seven methods approved at 40 CFR 136 for total cyanide in aqueous samples are:

- EPA Method 335.2
- EPA Method 335.3
- Standard Method 4500-CN^- D
- Standard Method 4500-CN^- E
- ASTM Method D2036-98A
- USGS Method I-3300-85
- USGS Method I-4302-85

EPA Methods 335.2 and 335.3 were employed by the two laboratories that analyzed samples from Episodes 6503, 6504, 6505, and 6506 for total cyanide. However, this general discussion applies to all seven approved methods.

All of the total cyanide methods involve digestion of the sample using concentrated sulfuric acid with magnesium ion in solution as a catalyst. (The digestion procedure is presented as the stand-alone procedure Standard Method 4500-CN^- C). The cyanide is converted to HCN gas, which is collected in a scrubber containing NaOH. This solution is then analyzed for the CN^- ion. The determinative methods use one of several techniques to measure CN^-, including titration with silver nitrate, colorimetry with an organic dye, or automated distillation-colorimetry for continuous flow analytical systems that utilizes UV oxidation of the sample to release bound cyanide.

Available Cyanide Methods

The four methods approved at 40 CFR 136 for available cyanide in aqueous samples are:

- EPA Method 335.1
- Standard Method 4500-CN^- G
- ASTM Method D2036-98B
- Method OIA-1677

Method OIA-1667 was employed for the analyses of available cyanide in Episodes 6503, 6504, 6505, and 6506. However, this general discussion applies to all four approved methods.

Although these four methods are approved at 40 CFR 136 for “available cyanide,” there are slight differences in forms of cyanide that are targeted by these methods. Generally speaking, the differences are not significant in compliance monitoring, but may be more important in other types of investigations.

The OIA-1677 procedure targets the weak acid dissociable cyanide by treating the sample with ligand-exchange reagents that release cyanide ions from the metal-cyano complexes. During the analysis, cyanide ions are converted to hydrogen cyanide (HCN) that passes through a gas diffusion membrane into an alkaline receiving solution where it is converted back to cyanide ion. The cyanide ion is monitored amperometrically, using a silver electrode.

EPA Method 335.1, SM 4500-CN^- G, and ASTM D2036-98B measure the cyanide amenable to chlorination. In these methods, two aliquots of the sample are analyzed. One aliquot is subjected to chlorination and the other aliquot is not. Both aliquots are distilled and analyzed for CN^-. The amenable

cyanide is calculated as the difference between the cyanide results from the chlorinated and nonchlorinated aliquots.

Difficulties and Interferences in the Analysis of Cyanide

A number of interferences affect cyanide determinations. Strong oxidizers, such as free chlorine, will destroy the "amenable" portion of cyanide. Sulfide present in the sample will oxidize cyanide into thiocyanate, which is not measurable in the cyanide methods. The sample should be tested for sulfide at the time of sample collection, and if sulfides are found, they should be removed by precipitation with lead carbonate or cadmium nitrate. This precipitation procedure should take place before the sample is preserved with NaOH, and any insoluble sulfide that is produced should be removed by filtration. Additional steps may be needed if the sample contains sulfide *and* particulate matter that may consist of alkali metal-heavy metal-cyanide complexes.

Most interferences in the total cyanide determination are removed by the distillation step, but some are not. Nitrate and nitrite can form cyanide as a reduction product of nitrogen-containing organic compounds, and are removed by the addition of sulfamic acid during distillation. Aldehydes can form cyanohydrins, which will convert to nitrile during the digestion. Sulfides also can be produced during distillation, and will distill along with cyanide and form thiocyanate. Sulfide production can be prevented by the addition of lead carbonate to the absorber solution, and the subsequent filtration of the absorber solution before analysis. Other potential interferences include sugars that can form cyanohydrins, sulfur compounds that may release sulfide, compounds that could release or form nitrite, as well as any sample constituent that could produce one of the interferences under the conditions of the digestion.

Method OIA-1677 does not employ a digestion step. Therefore, sulfides must be removed by the precipitation procedure described above. In addition to concerns about sulfides reacting with the cyanide in the sample before it can be measured (i.e., a negative interference), sulfides also can be a positive interference in this procedure if they react with acid in the sample to produce hydrogen sulfide (HS_2). The hydrogen sulfide will cross the membrane in the gas diffusion cell and produce a signal at the silver electrode that would be measured as cyanide. As noted in the method, "polysulfides" (compounds containing more than one sulfide) can be intractable interferences.

Interpretation of Cyanide Results

In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. While this usually holds true for wastewater effluent samples, some effluents and some other sample types, such as influents, may yield results in which the free or available cyanide results exceed the total cyanide results. For example, the results for free cyanide derived using the chlorination technique can result in free cyanide concentrations greatly in excess of total cyanide concentrations. When this occurs, it is likely due to the formation of cyanide by chlorination of nitrogen-containing organic compounds in the sample. While it might be possible to determine if such nitrogen-containing organics were present in the sample, this step is neither required nor practical for laboratories performing routine cyanide analyses.

Sulfides that may be in the sample present a significant possibility for false negative results for total cyanide through the oxidization of cyanide to thiocyanate, which is not measured by the cyanide methods, as discussed above. Sulfides can be both a negative interference and a positive interference with the determination of available cyanide by Method OIA-1677, as described above.

It is also important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the amenable cyanide determination is made using

separate aliquots of a separate sample. Thus, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results.

While the results for any cyanide measurement are evaluated by SCC relative to the requirements of the methods used for the determinations, it may not be possible to identify problems that would invalidate one cyanide fraction or the other. In instances where there are one or more QC failures associated with one of the cyanide fractions, but not with the other fraction, the results for the fraction with the QC failures will be appropriately qualified.

In instances where there are no QC failures associated with either cyanide fraction, but the available cyanide results are greater than the total cyanide results by a large margin, there is no way to determine which analysis was correct. In such cases, both sets of cyanide results are suspect. For the purposes of reviewing results for EPA's Effluent Guidelines Program, when cyanide is reported as present (e.g., not a non-detect) in both fractions and there are no QC failures in either fraction, differences where the available cyanide results are more than 30% above the total cyanide results suggest that irreconcilable problems exist. The 30% difference is a consensus value used by SCC. Differences less than 30% are considered a function of the routine variability that could be present in both measurements.

When such irreconcilable problems exist with the results of paired samples analyzed for both total and available cyanide, SCC recommends that both results (total and available) be included in the database, and that both results be flagged to alert the data user to the presence of such problems.

Cyanide Methods Used for Samples from the Alaskan Cruise Ship Project

The following table lists the methods used for total and available cyanide for Episodes 6503, 6504, 6505, and 6506. Two different laboratories performed the total cyanide analyses for these four episodes, using two different methods approved at 40 CFR 136. One other laboratory analyzed the available cyanide for all four episodes using Method OIA-1677.

Episode #	Method for Total Cyanide	Method for Available Cyanide
6503	EPA Method 335.3	Method OIA-1677
6504	EPA Method 335.2	Method OIA-1677
6505	EPA Method 335.3	Method OIA-1677
6506	EPA Method 335.2	Method OIA-1677

Based on communications with the sampling contractor, the samples were tested for sulfide in the field, using a field colorimeter with a detection limit of approximately 10 µg/L. Samples testing positive for sulfides were treated in the field to minimize the interferences. Because of concerns regarding whether the treated samples were subsequently filtered in the field, the laboratories were instructed to filter any sample showing turbidity.

A review of the traffic reports (TRs) for the samples in these four episodes indicates that some of the samples in Episode 6503, the first episode in the Alaskan Cruise Ship project, were not treated with lead carbonate to remove sulfides. SCC consulted EPA and the sampling contractor and determined that the following 11 samples were not treated with lead carbonate:

65202, 65207, 65211, 65227, 65231, 65235, 65269, 65273, 65277, 65283, and 65295

In an effort to address the potential positive interference of nitrate and nitrite in the samples, the laboratories performing the total cyanide analyses were advised to increase the amount of sulfamic acid added to each sample during distillation by a factor of 2, from 2 g per sample to 4 g per sample.

Episode-specific Findings

SCC has reviewed the results for both total cyanide and available cyanide in Episodes 6503, 6504, 6505, and 6506. Episode-specific findings are detailed below.

In addition to the data qualifiers described in SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004), two additional qualifiers were developed to address the total and available cyanide results from the Alaskan Cruise Ship Project. In cases where the available cyanide results exceed those for total cyanide by more than 30% and there are not any matrix-specific quality control data such as matrix spike recoveries, the total cyanide and available cyanide results will be flagged with the "IRR" qualifier. The "SCC Reason" field in the database for such results will read "Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose."

In other instances, when SCC's review identifies multiple concerns with the results for a given sample, including those that begin with sample collection and others involving the analysis of the sample itself or any associated quality control samples, the total cyanide and available cyanide results will be flagged with the "MISCA" qualifier. The "SCC Reason" field in the database for such results will read "Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample."

Episode 6503

Three sets of matrix spike/matrix spike duplicate (MS/MSD) samples were prepared for total cyanide analysis in Episode 6503 on samples 65207 (accommodations wastewater), 65269 (an effluent), and 65273 (an effluent). The MS/MSD recoveries for the three aqueous MS/MSD pairs were below the acceptance limits:

- 22% and 21% for sample 65207,
- 30% and 33% for sample 65269, and
- 5% and 1% for sample 65273

suggesting a potential for low bias in the total cyanide results for the associated aqueous samples.

The recoveries for the laboratory control samples (LCS, OPR, or QC check sample) analyzed along with the field samples were acceptable, indicating that the laboratory's overall analytical process was in control and suggesting either problems with the distillation process or an interference present in the sample matrix. Because the focus of the EAD analytical contracts is on effluent samples and because there are no acceptance criteria for aqueous matrices other than effluents, no MS/MSD analyses were performed on samples representing influents to the treatment process.

The total cyanide result for Sample 65273 (effluent) was reported as a non-detect at 5 µg/L and available cyanide was a non-detect at 2 µg/L. An MS/MSD pair for available cyanide was prepared from this sample and had recoveries of 101% and 102% respectively, while the MS/MSD recoveries for total cyanide were 5% and 1%, as noted earlier. This suggests a significant potential for low bias in the total cyanide result. Therefore, based on the low MS/MSD recoveries for total cyanide in this sample, the total

cyanide non-detect is considered a minimum value and the available cyanide result is considered acceptable without qualification.

There were nine other samples in Episode 6503 that exhibited the pattern of total cyanide results less than the available cyanide results. Samples 65219, 65227, 65231, and 65235 are influents to treatment and, as noted above, there are no MS/MSD analyses that demonstrate the performance of either method for this matrix type. Samples 65227, 65231, and 65235 also are among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and given the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for samples 65227, 65231, and 65235 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples. Sample 65219 was treated in the field, therefore SCC recommends including both cyanide results for sample 65219 in the database, but flagging them to indicate the irreconcilable differences.

The total cyanide results for Sample 65207 (accommodations wastewater) were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 15.7 µg/L. The MS/MSD recoveries for total cyanide were 21% and 22%, as noted earlier. Sample 65207 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, given the low MS/MSD recoveries for total cyanide in this sample and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65207 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65211 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Total cyanide was detected at 14 µg/L, while available cyanide was reported at 88.4 µg/L. Sample 65211 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65211 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65295 is listed as a source water sample, a matrix type that should not present significant analytical difficulties. Sulfide was not detected in this sample by the field test performed at the time of collection and therefore, this sample is among the 11 samples that were not treated with lead carbonate. Although the presence of available cyanide at 19 µg/L in the source water is unexpected, there is no analytical evidence to suggest that the available cyanide result be excluded. However, an engineering review or other information not available to SCC may lead to a different conclusion. Therefore, SCC recommends including both cyanide results for sample 65295 in the database, but flagging them to indicate the irreconcilable differences.

Episode 6503 included two sets of field duplicate samples that were sent to the laboratories blind. The two pairs were samples 65261 and 65281, and samples 65265 and 65283, all effluent samples. The total cyanide results in sample 65261 were reported as a non-detect at 5 µg/L, while available cyanide was reported as a non-detect at 2 µg/L. For sample 65281, the blind field duplicate, the total cyanide results were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 8.96 µg/L. A similar pattern occurs for the cyanide results in the other field duplicate pair. Total cyanide was reported as a non-detect at 5 µg/L in both samples 65265 and 65283, while available cyanide was detected at 5.86 µg/L in sample 65265 and as a non-detect a 2 µg/L in sample 65283.

The MS/MSD recoveries for total cyanide in effluent sample 65273 were very low (1% and 5%), and low (33% and 30%) in sample 65269, suggesting a potential negative basis that may affect the total cyanide results in samples 65261, 65281, 65265, and 65283. Therefore, SCC recommends that the total cyanide results in sample 65261 and 65281 be considered minimum values. The difference between the available cyanide results in the two field duplicate samples (e.g., a non-detect at 2 µg/L and a detect at 8.96 µg/L) cannot be explained on the basis of the MS/MSD results for available cyanide in sample 65273, which was also an effluent. Given the discrepancy between the field duplicate results for available cyanide, SCC recommends including the available cyanide results for samples 65261 and 65281 in the database, but flagging them to indicate the irreconcilable differences. SCC recommends that the total cyanide results for samples 65261 and 65281 also be flagged to indicate the irreconcilable differences, as a further precaution.

Because of the low MS/MSD recoveries in the other effluent samples, the total cyanide result for sample 65265 is considered a minimum value. The available cyanide result of 5.86 µg/L is well within 30% of the reported detection limit for total cyanide (e.g., 5 µg/L), and therefore would normally not be qualified. However, because the available cyanide result in the field duplicate of the sample, 65283 is a non-detect at 2 µg/L, SCC recommends including both the total and available cyanide results for sample 65265 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65283 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Given the very low MS/MSD recoveries for total cyanide in effluent samples in this episode, SCC recommends flagging both cyanide results for sample 65283 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples.

Episode 6504

Three sets of MS/MSD samples were prepared for total cyanide analysis in Episode 6504 on samples 65519 (an effluent), 65523 (an effluent), and 65527 (accommodations wastewater), and all showed acceptable spike recoveries. Thus, there do not appear to be pervasive problems with the recovery of total cyanide in samples from this episode.

A comparison of the total cyanide results and available cyanide results for samples 65395, 65455, 65459, 65463, 65467, and 65471 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at approximately 11 to 36 µg/L. In addition, total cyanide was reported as present in sample 65411 at 6 µg/L, while the available cyanide result was 35.7 µg/L (e.g., six time the total cyanide result).

Sample 65395 is listed as the galley wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65395 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65411 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system, and as noted above, there are no MS/MSD data that demonstrate method performance for matrices other than effluents. During the review of the data, SCC noted that the traffic report for the aliquot of Sample 65411 for total cyanide analysis indicated that the aliquot was collected at 14:00 on 8/10/04, while the traffic report for the aliquot submitted for available cyanide analysis indicated that that aliquot was collected at 3:00 PM (15:00) on 8/11/04. This concern was resolved following discussions with EPA and the sampling contractor, whose field records indicated that both aliquots were collected at the same time, and that the

one traffic report was incorrect. Having resolved the issue of the time of sample collection, but lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65411 in the database, but flagging them to indicate the irreconcilable differences.

Samples 65455, 65459, 65463, 65467, and 65471 are all influents to treatment, collected from the same sampling point on consecutive days. The results from samples 65463, 65467, and 65471 are remarkably consistent, varying by only 0.2 µg/L across all three samples. The results for samples 65455 and 65459 are similar to one another, but about twice the concentrations found in the other three samples from this sampling point. There are no MS/MSD analyses that demonstrate method performance for this matrix type, but the consistency in the results suggests that whatever matrix effects may be taking place, they are reproducible. However, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65455, 65459, 65463, 65467, and 65471 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6504, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Episode 6505

The data for total cyanide samples in Episode 6505 were delivered in five separate data packages, each with its own associated QC sample results. Six pairs of MS/MSD samples were prepared for total cyanide analyses in Episode 6505 on samples 65603 (galley wastewater), 65635 (accommodations wastewater), 65711 (an effluent), 65715 (an effluent), 65719 (an effluent), and 65741 (screening solids).

The data for a seventh pair of MS/MSD samples were delivered in the data package with the results for samples 65731 (galley wastewater) and 65745 (biosolids). However, because of limitations on the sample volume that was provided to the laboratory, the MS/MSD samples were prepared from a non-EPA sample of indeterminate origin and therefore are not useful in evaluating the performance of the total cyanide method on cruise ship samples.

Three of the MS/MSD pairs for aqueous samples and the one MS/MSD pair for the solid samples had acceptable recoveries of total cyanide. None of the samples used to prepare MS/MSD aliquots were samples where the available cyanide results exceeded the total cyanide results.

The MS/MSD results for sample 65603 (galley wastewater) showed recoveries of 59% in both aliquots, which is below the acceptance limits, and suggests a potential low bias in the total cyanide result for that sample. The available cyanide result of 2.2 µg/L is below the detection limit for the total cyanide analysis. Therefore, SCC recommends qualifying the total cyanide result as a minimum value and accepting the available cyanide result as reported.

Although MS/MSD samples were prepared from sample 65741 (screening solids) and met the acceptance criteria, there are no MS/MSD results for the biosolids matrix in this episode. This limits SCC's ability to evaluate the potential effects of the sample matrix for sample 65745 (biosolids), where the available cyanide results are almost 40% higher than the total cyanide results. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65745 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65731 is a galley wastewater. The only MS/MSD results for galley wastewater in this episode are for sample 65603, where the recoveries were below the acceptance criteria. Given the

potential for low bias in this matrix, SCC recommends qualifying the total cyanide result as a minimum value. SCC recommends including both cyanide results for sample 65731 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65659 is an influent sample and MS/MSD aliquots are not prepared for influents, as discussed earlier. Total cyanide was reported as not detected and the available cyanide was reported at 6 times the total cyanide detection limit. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65659 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6505, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Episode 6506

A comparison of the total cyanide results and available cyanide results for samples 65896, 65900, 65904, 65908, and 65912 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at levels from approximately 36 to 77 µg/L.

All five of these samples are from the same sampling point, SP 2, and represent influents to the black water and gray water treatment system. Thus, these samples are not treated effluents. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65896, 65900, 65904, 65908, and 65912 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6506, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Summary of Results from Episodes 6503, 6504, 6505, and 6506

SCC's recommendations for handling the total and available cyanide results for the Alaskan Cruise Ship project samples are summarized in the table on the following page

Note: The results in the database are reported in the units provided by the laboratories that performed the analyses. Method OIA-1677 specifies reporting results in units of micrograms per liter (µg/L), whereas the older methods (335.2 and 335.3) specify reporting results in units of milligrams per liter (mg/L). However, for ease of comparison in the table the follows, the results for total cyanide have been converted to the same units as the available cyanide results, µg/L. "ND" indicates that cyanide was not detected. In these cases, the reported detection limit is shown in parentheses.

If you have any questions about the information in this memorandum or the cyanide results in the database, please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Jodi King, ERG
Deb Falatko, ERG
Deb Miller, CSC
Michael Walsh, CSC
Pornkeo Chinyavong, CSC

Summary of SCC Recommendations for Cyanide Results in the Alaskan Cruise Ship Project

Episode	Sample #	Matrix	Total Cyanide (µg/L)	Available Cyanide (µg/L)	SCC Recommendation
6503	65207	Accommodations wastewater	ND (5)	15.7	Sample not treated with lead carbonate to remove sulfides. Low MS/MSD recoveries for total cyanide. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65211	Food pulper wastewater	14	88.4	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65219	Influent to treatment	ND (5)	10.4	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65227	Influent to treatment	ND (5)	7.54	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data for influents. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65231		ND (5)	35.4	
6503	65235		ND (5)	16	
6503	65261	Effluent from treatment	ND (5)	ND (2)	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65265		ND (5)	5.86	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65273		ND (5)	ND (2)	Total cyanide qualified as minimum value.
6503	65281		ND (5)	8.96	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65283	Effluent from treatment	ND (5)	ND (2)	Total cyanide qualified as minimum value. Sample not treated with lead carbonate to remove sulfides. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.

Episode	Sample #	Matrix	Total Cyanide (µg/L)	Available Cyanide (µg/L)	SCC Recommendation
6503	65295	Source water	ND (5)	19.1	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6504	65395	Galley wastewater	ND (5)	22.4	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6504	65411	Food pulper	6	35.7	
6504	65455	Influent to treatment	ND (5)	26.9	
6504	65459	Influent to treatment	ND (5)	29	
6504	65463	Influent to treatment	ND (5)	11.7	
6504	65467	Influent to treatment	ND (5)	11.5	
6504	65471	Influent to treatment	ND (5)	11.6	
6505	65603	Galley wastewater	ND (5)	2.2	Total cyanide qualified as minimum value
6505	65659	Influent to treatment	ND (5)	30.7	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6505	65731	Galley wastewater	ND (5)	12.9	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6505	65745	Biosolids	11	15.2	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6506	65896	Influent to treatment	ND (5)	45.5	
6506	65900	Influent to treatment	ND (5)	36.2	
6506	65904	Influent to treatment	ND (5)	75.6	
6506	65908	Influent to treatment	ND (5)	72.2	
6506	65912	Influent to treatment	ND (5)	76.5	

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: January 31, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty, Ph.D.
Senior Scientist

SUBJECT: Summary of Telephone Conversation with the Available Cyanide Laboratory

At your suggestion, I contacted the laboratory that ran the available cyanide analyses for Episodes 6503 to 6506 and asked about cross-contamination concerns, glassware washing procedures, and other aspects of the analysis that might explain the discrepancies between the total and available cyanide results. I spoke with John Sebroski, the laboratory director at Bayer Material Science on January 19, 2005. John gave me the following information:

- All of the "glassware" involved in the analysis is disposable. This includes the cups on the autosampler, the tubing on the flow injection system, etc. They do not reuse any of it, so there are no washing issues.

- The design of the flow injection instrumentation minimizes any concerns about carryover because the sample is injected into a continuous flow of solution that runs through the analyzer.

- They do run frequent blanks on the instrument, especially after QC samples such as the lab control sample (LCS or OPR). Those QC samples are run at relatively high levels, and there is no evidence of carryover or memory effects in the blanks. (I also confirmed this prior to calling him, using the data for these four episodes.)

- The OIA-1677 method has an ASTM counterpart that uses the same technique. There is a 2004 version of the ASTM standard that addresses the potential for sulfide interferences by introducing a bismuth nitrate reagent into the system to remove sulfides. John indicated that the use of the bismuth nitrate reagent could easily be accommodated using Method OIA-1677, since the instrumentation is the same as the ASTM standard.

- John indicated that sulfide problems for total cyanide are always a significant issue. He also said that the flow injection system for available cyanide can detect (and be affected by) sulfides at a much lower level than the field test methods will detect. Therefore, any sample not treated with lead carbonate in the field may well have an interference for available cyanide, even if the field test was negative for sulfides.

In summary, my conversation with Mr. Sebroski confirms much of the information SCC summarized in our lengthy discussion of the issues surrounding the total and available cyanide results for this project and generally rules out the chance that analytical concerns, such as carryover or glassware cleaning procedures, as an explanation for the observed cyanide results. Please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com, if you have any questions.

Federal Sector
Civil Systems Development Division
6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020