

APPENDIX C.4

CHROMIUM VI ANALYTICAL RESULTS AND DATA VALIDATION REPORTS



TETRA TECH NUS, INC.

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RACI-EPA-4237

Contract No. 68-W6-0045

December 4, 2002

Mr. Joseph LeMay, P. E.
U. S. Environmental Protection Agency
1 Congress Street, Suite 1100 (HBO)
Boston, Massachusetts 02114-2203

Subject: Hexavalent Chromium in Sediments
Industri-plex Site, Remedial Investigation/Feasibility Study
RAC I W.A. No. 116-RICO-0107

Dear Mr. LeMay:

In response to your request, Tetra Tech NUS, Inc. (TtNUS) has further evaluated the presence of hexavalent chromium in sediment samples collected from wetlands at Wells G & H and the Halls Brook Holding Area (HBHA).

On January 9, 2002, TtNUS issued a letter to your office responding to comments provided to you by the EPA's New England Regional Laboratory (NERL) regarding analytical methods and results for sediment samples analyzed for hexavalent chromium (Cr+6) under Case 0194H, SDG D02645. These samples were collected to support the Industri-plex Site Remedial Investigation/Feasibility (RI/FS) for Operable Unit 2 (OU-2).

As detailed in the response letter, it was TtNUS' opinion that due to the limitations of SW-846 colorimetric Method 7196A, the ion chromatography Method 7199 would be a better analytical alternative to overcome possible matrix interferences when measuring hexavalent chromium in anoxic sediment samples. Further, the presence of hexavalent chromium in the wetland sediments was also in question due to the reducing conditions observed in the sediments.

To provide additional information, EPA requested that TtNUS re-sample areas where previous analytical results indicated elevated concentrations of total chromium. On October 8, 2002, TtNUS collected six additional sediment samples from areas within the Wells G & H wetland and the HBHA. These samples were analyzed for sulfides, pH, ORP, total metals and hexavalent chromium using the alternative ion chromatography Method 7199.

The analytical results were presented in data validation reports submitted to your office on November 20 and 21st, 2002 (see attached). The following table summarizes the concentrations of total chromium and hexavalent chromium detected in these samples.

	<i>WH-02</i>	<i>WG-10</i>	<i>WS-08</i>	<i>CB03-06</i>	<i>CB03-10</i>	<i>WW-06</i>
Total Cr (mg/kg)	930	249	244	755	253	13,400
Cr+6 (mg/kg)	ND	ND	ND	ND	ND	17.3



TETRA TECH NUS, INC.

Mr. Joseph LeMay, P. E.
U. S. Environmental Protection Agency
December 4, 2002
Page 2 of 2

The data supports TtNUS' opinion that it is unlikely that hexavalent chromium exists in wetland sediments where elevated sulfide concentrations and reducing conditions are present. Hexavalent chromium was only present at very low concentrations in sample WW-06 that contained a total chromium concentration of 13,400 mg/kg.

Similar reducing conditions (based on ORP, sulfide, and pH values) have been generally observed through all areas of the wetlands that have been previously sampled. Currently, there is not enough data to develop a statistical correlation between total chromium and hexavalent chromium. However, it is reasonable to assume that based on the geochemistry of the wetland sediments, hexavalent chromium may only be present in areas with elevated total chromium concentrations, but would exist at very low concentrations. Consequently, it would be unreasonably conservative to assume that all of the total chromium is in the hexavalent form when using the data for risk assessment purposes.

If you have any questions or should require additional information, please call me 978-658-7899.

Very truly yours,

A handwritten signature in black ink, appearing to read 'G. Bullard'.

Gordon H. Bullard
Project Manager

PMO - Handwritten initials in a circle.

GHB:rp

Enclosures

c: H. Horahan (EPA) w/o enc.
G. Gardner/A. Ostrofsky (TtNUS) w/o enc.
L. Guzman (TtNUS) w/enc.
File N4123-1.0 w/enc.



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RAC1-EPA-4226

Contract No. 68-W6-0045

November 20, 2002

Ms. Christine Clark
Regional Sample Control Coordinator
U.S. EPA New England Regional Laboratory
Office of Environmental Measurement and Evaluation
11 Technology Drive
North Chelmsford, Massachusetts 01863-2431

Subject: Tier III Inorganic Data Validation, W.A. No. 116-RICO-0107
DAS Case 0331H, SDG D08379-IA
Southwest Research Institute
Industri-Plex Site, Woburn, Massachusetts

Hexavalent Chromium/Total Sulfide:
7/Sediments/ D08379, D08380, D08381, D08382, D08383, D08384,
D08385
(Field Duplicate Pair: D08383/D08384)

Dear Ms. Clark:

Tetratech NUS, Inc. (TtNUS) performed a Tier III data validation for the hexavalent chromium and total sulfide data for DAS Case 0331H, SDG D08379-IA, from sediment samples collected by TtNUS at the Industri-Plex site. The hexavalent chromium analysis was performed by the SW-846 Methods 3060A/7199. The sulfide analysis was performed by Methods 9030B/9034. These methods were required by TtNUS Technical Specification S02-RAC1-240. Modifications and special technical requirements were issued in order to compensate for the low percent solids of the samples. The Tier III data validation was performed as required in the April, 2002 Quality Assurance Project Plan. The data were validated according to the Region I, EPA-NE Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses, modified February 1989.

The data were evaluated based on the following parameters:

- Data Completeness
- Holding Times
- * • Calibration Verification
- * • Field and Laboratory Blank Analyses
- Matrix Spike Recoveries
- * • Laboratory Control Sample Results
- * • Laboratory Duplicate Results
- * • Field Duplicate Precision
- * • Detection Limits
- * • Sample Quantitation

* - All quality control criteria were met for this parameter.

Table I summarizes the validation recommendations, which were based on the following information:

Data Completeness

The laboratory was contacted on November 7, 2002, about a missing Form DC-2 (CSF Inventory Sheet) and some errors in the SDG Narrative. The Form DC-2, some additional shipping documents, and a revised Narrative were received on November 20, 2002.

The laboratory was also contacted on November 7, 2002, about the hexavalent chromium ion chromatography calibration curve, which did not fit the reported results. The laboratory responded on November 11, 2002, that it had used a linear curve but had inadvertently submitted a quadratic curve. The response included the linear equation. The revised linear curve printout was received on November 20, 2002.

Holding Times

Hexavalent Chromium

The hexavalent chromium samples were digested within the 7-day holding time. However, according to the Technical Specification, the digestates were to be analyzed within 2 hours of digestion. The laboratory indicated in the SDG Narrative that this was not possible because the filtration process took about 6 hours due to the sample matrix. The analysis of the samples was completed in about 9 hours.

Although the required holding time for analysis was exceeded, professional judgement was used to take no action for this parameter. According to Method 3060A, Section 6.4, hexavalent chromium "has also been shown to be stable in the alkaline digestate for up to 168 hours after extraction from soil."

Sulfide, pH, and ORP

The holding times were met for sulfide, pH, and ORP.

Matrix Spike Recoveries

Hexavalent Chromium

The recoveries for the low-level soluble hexavalent chromium matrix spike and matrix spike duplicate (MS/MSD) analysis, and for the high-level insoluble MS/MSD analysis of sample D08380 were 0 percent. Professional judgement was used not to qualify the data for this parameter since the percent recoveries for the soluble and insoluble hexavalent chromium LCS are within criteria, and the oxidation/reduction potential (ORP) and pH values indicate matrix reducing characteristics for sample D08380. In addition, as indicated by the laboratory in the Narrative, the samples contained high amounts of organic matter and sulfide. The combined and interacting influences of ORP, pH, and reducing agents (organic acids, iron II, and sulfides)

may have reduced the hexavalent chromium spikes (Section 8.5.1 of Method 3060A). As per the above reference, if the ORP (Eh) and pH of the sample fall within the reducing area, as illustrated in Figure 2 of Method 3060A (enclosed), low matrix spike recoveries are expected for these samples.

Sulfide

The recoveries for the sulfide matrix spike and matrix spike duplicate analysis of sample D08379 were below the 75 percent recovery criterion. The positive sulfide results are estimated (J) in all samples. The results may be biased low.

Post Digestion Spike Recoveries

As required by the technical specification, the laboratory performed a post-digestion spike for each hexavalent chromium sample. The results were all within the 85-115 QC criteria. Therefore, no Method of Standard Additions was required.

The good recoveries of the post-digestion spikes in the presence of reducing compounds may be due to the high pH of the Method following the digestion. According to Method 7199, Section 3.1.2, "Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. However, at a pH of 6.5 or greater, CrO_4^{2-} , which is less reactive than the HCrO_4^- , is the predominant species." The high pH of the digestate before the diphenylcarbazide is added may slow the reduction reaction, allowing the Cr(VI) to react with the diphenylcarbazide to form the color complex before the Cr(VI) is reduced.

Laboratory Control Sample Results

Hexavalent Chromium

The laboratory control sample (LCS) results were within limits for soluble and insoluble hexavalent chromium. A trivalent chromium LCS was also analyzed for hexavalent chromium to ascertain whether the hexavalent chromium results could be biased high due to oxidation of trivalent chromium to the hexavalent form caused by the alkaline digestion method. (See Method 3060A, Section 3.3.) The recovery of hexavalent chromium from the trivalent chromium LCS was 0 percent. Therefore, there does not appear to be an oxidation effect caused by the digestion method.

Sulfide

The sulfide LCS results were within limits.

Sample Quantitation

Hexavalent Chromium

The percent solids were below 30 percent for all of the sediment samples, and below 10 percent for two samples. The laboratory compensated for the low percent solids by increasing the amount of sample analyzed. Method 3060A requires 2.5 g of field-moist sample. The laboratory used sample weights of about 20 g; however, due to the dark color, all samples were

diluted 10x. Professional judgement was used not to qualify the sediment sample results based on the low percent solids of the samples because of two main reasons: (a) the sensitivities (MDL) of the alkaline digestion/ion chromatography procedures are much lower than the required quantitation limit, and (b) the water from the sludge sample evaporates during the first minutes of the alkaline digestion and does not interfere with the analysis.

Sulfide

The laboratory compensated for the low percent solids by using the maximum amount of moist solid sample allowable in Method 9030B (50 g), but the required quantitation limit of 2 mg/kg was not achieved. Professional judgement was used not to qualify the sulfide data based on the low percent solids since all of the sulfide results were well above the required quantitation limit. In addition, Method 9030B specifies analyzing an amount of sample that contains 0.2 to 50 mg of sulfide. The amounts of sulfide contained in the sample aliquots were within this range for all of the samples.

Overall Assessment of the Data

Hexavalent Chromium

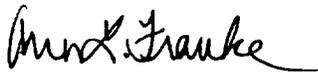
The hexavalent chromium data are accepted without qualification.

Sulfide, pH, ORP

The positive sulfide results are qualified as estimated (J) in all samples due to the low MS/MSD recoveries. The results may be biased low.

The pH and ORP data are accepted without qualification.

Sincerely,



Ann L. Franke
Data Validator



Lucy Guzman
RAC I Lead Chemist

PMO - @

Ms. Christine Clark
November 20, 2002
Page 5

Tables: Table I: Recommendation Summary Tables
 Eh/pH Diagram (Figure 2 from Method 3060A)
 Data Summary Tables

Enclosures: Data Validation Worksheets
 Communication/Phone Logs
 Field Notes
 Technical Specification No. S02-RAC1-240
 CSF Audit (DC-2 Form)
 DQO Summary Form

c: J. LeMay (EPA) w/o enc.
 G. Bullard (TtNUS) w/o enc.
 File N4123-2.6 w/ enc.

**INDUSTRI-PLEX SITE
DAS Case 0331H, SDG D08379-IA**

Table I - Recommendation Summary for the Sediment Samples

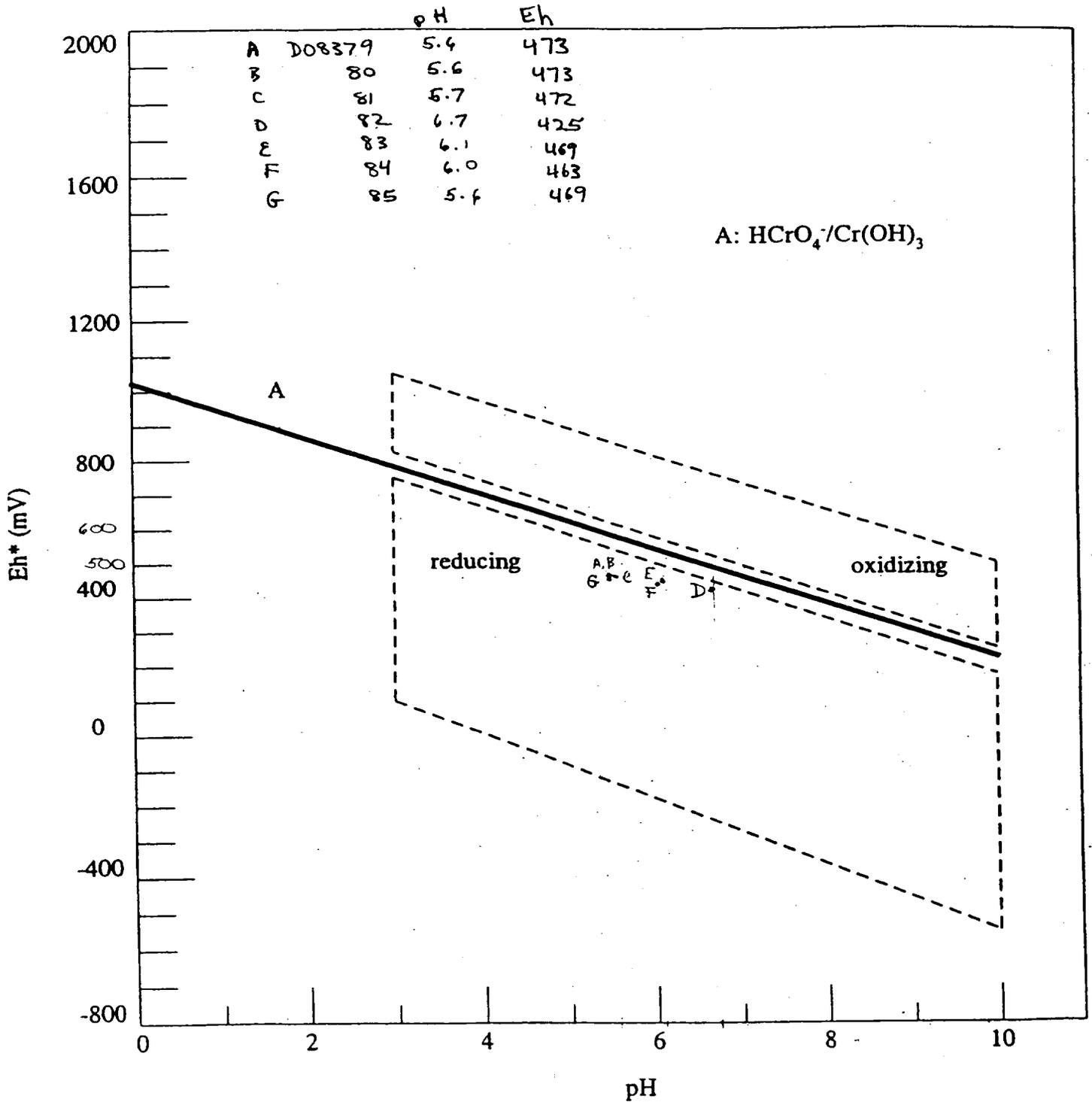
Hexavalent Chromium	A
Total Sulfide	J ¹
ORP	A
pH	A

A - Accept the data.

J¹ - Estimate (J) positive results in all samples due to low matrix spike and matrix spike duplicate recoveries. Results may be biased low.

FIGURE 2
Eh/pH PHASE DIAGRAM

The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

Soil Wet Chemistry Analysis
 Site: Industri-Plex
 Case: 0331H; SDG: D08379-IA

EPA Sample Number	D08379	D08380	D08381	D08382	D08383
Station Location	IPSD-WH02-100802	IPSD-WG10-100802	IPSD-WS08-100802	IPSD-CB0306-100802	IPSD-CB0310-100802
Date Sampled	10/8/2002	10/8/2002	10/8/2002	10/8/2002	10/8/2002
Date Extracted					
Date Analyzed					
Dilution Factor	10	10	10	10	10
Percent Solids	11.5	13.0	7.69	5.83	13.7
QC Identifier	None	None	None	None	Field Dup. IPSD-CB0310-100802
Chromium VI (mg/kg)	0.859 U	0.777 U	1.51 U	1.98 U	0.830 U
Sulfide (mg/kg)	153 J	49.0 J	340 J	10100 J	554 J
pH (S.U.)	5.65	5.63	5.68	6.72	6.10
Redox Potential (Eh)(mV)	473	473	472	425	469

U - Not detected; UJ - Detection limit approximate; J - Quantitation approximate
 Note: Dilution Factor applies only to Chromium VI analysis

Soil Wet Chemistry Analysis
 Site: Industri-Plex
 Case: 0331H; SDG: D08379-IA

EPA Sample Number	D08384	D08385
Station Location	IPSD-DP01-100802	IPSD-WW06-100802
Date Sampled	10/8/2002	10/8/2002
Date Extracted		
Date Analyzed		
Dilution Factor	10	10
Percent Solids	13.5	11.2
QC Identifier	Field Dup. IPSD-CB0310-100802	None
Chromium VI (mg/kg)	0.817 U	17.3
Sulfide (mg/kg)	530 J	262 J
pH (S.U.)	6.050	5.57
Redox Potential (Eh)(mV)	463	469

U - Not detected; UJ - Detection limit approximate; J - Quantitation approximate
 Note: Dilution Factor applies only to Chromium VI analysis



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RAC1-EPA-4227

Contract No. 68-W6-0045

November 21, 2002

Ms. Christine Clark
Regional Sample Control Coordinator
U.S. EPA New England Regional Laboratory
Office of Environmental Measurement and Evaluation
11 Technology Drive
North Chelmsford, Massachusetts 01863-2431

Subject: Tier III Inorganic Data Validation, W.A. No. 116-RICO-0107
DAS Case 0331H, SDG D08379-IB
Southwest Research Institute
Industri-Plex Site, Woburn, Massachusetts

Total Metals:
7/Sediments/ D08379, D08380, D08381, D08382, D08383, D08384,
D08385
(Field Duplicate Pair: D08383/D08384)

Dear Ms. Clark:

Tetrattech NUS, Inc. (TtNUS) performed a Tier III data validation for the total metals analytical data for DAS Case 0331H, SDG D08379-IB, from sediment samples collected by TtNUS at the Industri-Plex site. The samples were digested and analyzed according to the EPA SW-846 Methods 3050B/6010B, modified to increase the sample size to compensate for the low percent solids of the samples. The Tier III data validation was performed as required in the April, 2002 Quality Assurance Project Plan. The data were validated according to the Region I, EPA-NE Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses, modified February 1989.

The data were evaluated based on the following parameters:

- Data Completeness
- * • Holding Times
- Calibration Verification
- * • Field and Laboratory Blank Analyses
- ICP Interference Check Sample Results
- * • Matrix Spike Recoveries
- * • Laboratory Control Sample Results
- Laboratory Duplicate Results
- * • Field Duplicate Precision
- NA • Furnace Atomic Absorption Results
- * • ICP Serial Dilution Results
- * • Detection Limits

- Sample Quantitation
- NA • Performance Evaluation Sample Results

* - All quality control criteria were met for this parameter.

Table I summarizes the validation recommendations, which were based on the following information:

Data Completeness

These sediment samples were collected for hexavalent chromium analysis; however, EPA requested this additional total metals analysis after receiving the hexavalent chromium results. Only ICP metals were requested (no mercury). Total metals analysis is not listed in the chain-of-custody form. A performance evaluation (PE) sample was not included for these samples.

The laboratory was contacted on November 7, 2002, about a missing Form DC-2 (CSF Inventory Sheet). The Form DC-2 and some additional shipping documents were received on November 20, 2002.

The laboratory was contacted on November 20, 2002, about the reason for the low sample weight of sample D08379. The laboratory responded on November 20, 2002, that there was insufficient sample remaining after the wet chemistry analysis of this sample.

Calibration Verification

The percent recoveries for selenium and thallium were outside the 80-120 percent quality control (QC) criteria in the CRDL standard analysis. The positive selenium results less than 3x CRDL are qualified as estimated (J) due to a high recovery. The results may be biased high. The positive thallium result less than 3x CRDL in sample D08384, and the non-detected thallium results in the remaining samples are estimated (J, UJ) due to high and low recoveries. The bias in these results is uncertain.

ICP Interference Check Sample Results

Positive results for thallium was detected in the ICSA solution at absolute levels greater than 2x IDL when this metal was not supposed to be present in the solution. These results may be due to ICP interference if the concentration of aluminum, calcium, iron, and magnesium in any field sample is $\geq 50\%$ of the ICS solution concentration. The estimated ICP interference for each affected metal in the field sample is calculated, and the following actions are taken:

- If the calculated interference is positive, estimate (J) positive results and accept non-detected results for the affected metals. Reject (R) positive results if the reported concentration is due entirely ($\geq 80\%$) to the ICP interference.
- If the calculated interference is negative, estimate (J, UJ) positive and non-detected results for the affected metals.

- If the calculated interference is less than 1% of the sample concentration reported for the affected metal, the ICP interference is considered negligible and no action is taken.

The sample listed in the table below had iron at a level greater than 50% of its respective level in the ICSA solution. Therefore, the following action was taken:

Sample	Affected Metal	Sample Concentration (µg/L)	Sample Concentration, Interferent (µg/L) - Fe	Estimated Interference (µg/L)	Action
D08384	Thallium	23.0*	146200*	71.6	Reject

* - Both thallium and iron were reported from a 5 times dilution analysis. These values are the diluted results before adjustment for the dilution factor.

The positive thallium result is rejected (R) in sample D08384 since the reported concentration might be due entirely to the positive iron ICP interference.

Chromium was reported at concentration greater than 10 mg/L in sample D08385. The estimated ICP interference of chromium on arsenic is greater than 10 percent of the reported arsenic concentration in this sample, and also is greater than 2x CRDL of arsenic. The positive arsenic result in sample D08385 is estimated (J) due to positive chromium ICP interference. The result may be biased high.

Laboratory Duplicate Results

The absolute difference (RPD) for thallium was greater than the 2x CRDL QC criterion for sediment samples in the laboratory duplicate analysis of sample D08382. The non-detected thallium results are estimated (UJ) in the sediment samples due to poor laboratory duplicate precision. The bias is undetermined. The positive thallium result in D08384 was previously rejected, and no further action is needed.

Sample Quantitation

The percent solids of all of the samples were below 30 percent. For all samples except D08379, the laboratory adequately compensated for the low percent solids by increasing the amount of sample analyzed. Therefore, no action is taken.

For sample D08379, the amount of sample analyzed was less than one gram due to the small amount of sample remaining after the wet chemistry analysis. The laboratory compensated for the low percent solids by decreasing the final volume used. However, the amount of sample analyzed may have not been representative of the sample location. Professional judgement was used to estimate (J) all positive results and reject (R) all non-detected results in sample D08379 due to the small amount of sample analyzed.

Overall Assessment of the Data

The positive selenium results less than 3x CRDL are qualified as estimated (J), and the non-detected thallium results are estimated (UJ) due to poor linearity near the CRDL. The selenium results may be biased high. The bias of the thallium results is uncertain.

The positive thallium result is rejected (R) in sample D08384 since the reported concentration might be due entirely to positive iron ICP interference.

The positive arsenic result in sample D08385 is estimated (J) due to positive chromium ICP interference. The result may be biased high.

The non-detected thallium results are estimated (UJ) due to poor laboratory duplicate precision. The bias is undetermined.

All positive metals results are estimated (J), and the non-detected results for beryllium, silver, and thallium are rejected (R), in sample D08379 because the small amount of sample analyzed may have not been representative.

Sincerely,



Ann L. Franke
Data Validator



Lucy Guzman
RAC I Lead Chemist

PMO - 

Tables: Table I: Recommendation Summary Tables
Data Summary Tables

Enclosures: Data Validation Worksheets
Communication/Phone Logs
Field Notes (in Case 0331H, SDG D08379-IA)
CSF Audit (DC-2 Form)
DQO Summary Form

c: J. LeMay (EPA) w/o enc.
G. Bullard (TtNUS) w/o enc.
File N4123-2.6 w/ enc.

**INDUSTRI-PLEX SITE
 DAS Case 0331H, SDG D08379-IB**

Table I - Recommendation Summary for Total Metals Sediment Samples

Aluminum	J ⁴	Magnesium	J ⁴
Antimony	J ⁴	Manganese	J ⁴
Arsenic	J ^{3,4}	Mercury	NA
Barium	J ⁴	Nickel	J ⁴
Beryllium	R ²	Potassium	J ⁴
Cadmium	J ⁴	Selenium	J ^{1,4}
Calcium	J ⁴	Silver	R ²
Chromium	J ⁴	Sodium	J ⁴
Cobalt	J ⁴	Thallium	J ² , R ^{1,2}
Copper	J ⁴	Vanadium	J ⁴
Iron	J ⁴	Zinc	J ⁴
Lead	J ⁴		

NA – Not analyzed.

- J¹- Estimate (J) the positive results <3x CRDL due to poor linearity near the CRDL. Results may be biased high.
- J²- Estimate (UJ) the non-detected results due to poor linearity near the CRDL and due to poor laboratory duplicate precision. The bias based on both parameters is uncertain.
- J³- Estimate (J) the positive result in sample D08385 due to positive chromium ICP interference. The result may be biased high.
- J⁴- Estimate (J) the positive results in sample D08379 due to the small amount of sample analyzed.
- R¹- Reject (R) the positive result in sample D08384 since the result may be due entirely to positive iron ICP interference.
- R²- Reject (R) the non-detected results in sample D08379 due to the small amount of sample analyzed.

SOIL METAL ANALYSIS BY METHOD 6010B (mg/kg)

Site: Industri-Plex

Case: 0331H; SDG: D08379-IB

EPA Sample Number	D08379	D08380	D08381	D08382	D08383
Station Location	IPSD-WH02-100802	IPSD-WG10-100802	IPSD-WS08-100802	IPSD-CB0306-100802	IPSD-CB0310-100802
Date Sampled	10/8/2002	10/8/2002	10/8/2002	10/8/2002	10/8/2002
Date Extracted					
Date Analyzed					
Dilution Factor	5	2	1	1	1
Percent Solids	11.5	13.0	7.7	5.8	13.7
QC Identifier	None	None	None	None	Field Dup. IPSD-CB0310-100802
Aluminum	30500 J	13300	4180	13800	5510
Antimony	45.3 J	13.0	2.8	6.4	2.9
Arsenic	909 J	173	64.5	497	200
Barium	200 J	102	97.9	116	71.5
Beryllium	R	1.5 U	1.2 U	1.6 U	0.72 U
Cadmium	20.1 J	5.6	6.6	28.0	22.3
Calcium	28300 J	17700	16000	13900	16300
Chromium	930 J	249	244	755	253
Cobalt	31.5 J	25.1	10.5	105	8.4
Copper	1010 J	276	186	658	186
Iron	127000 J	51500	19900	67600	22700
Lead	2470 J	649	194	454	171
Magnesium	7870 J	2650	1690	4250	2320
Manganese	657 J	1300	724	961	81.2
Nickel	70.0 J	33.8	20.8	66.6	21.6
Potassium	2660 J	570	528	1110	627
Selenium	8.8 J	4.3 J	5.1	5.0	3.7
Silver	R	1.5 U	1.2 U	1.6 U	0.72 U
Sodium	2840 J	787	1580	1620	855
Thallium	R	6.1 UJ	4.8 UJ	6.5 UJ	2.9 UJ
Vanadium	240 J	88.3	26.5	66.8	101
Zinc	3300 J	815	813	4880	1730

U - Not detected; UJ - Detection limit approximate; J - Quantitation approximate;

R - Rejected

Soil TAL Metal Analysis By Method 6010B (mg/kg)

Site: Industri-Plex

Case: 0331H; SDG: D08379-IB

EPA Sample Number	D08384	D08385	
Station Location	IPSD-DP01-100802	IPSD-WW06-100802	
Date Sampled	10/8/2002	10/8/2002	
Date Extracted			
Date Analyzed			
Dilution Factor	1	1	
Percent Solids	13.5	11.2	
QC Identifier	Field Dup. IPSD-CB0310-100802	None	
Aluminum	5130	9360	
Antimony	3.1	4.2	U
Arsenic	208	41.5	J
Barium	67.9	198	
Beryllium	0.72	0.84	U
Cadmium	22.4	5.6	
Calcium	19800	14900	
Chromium	234	13400	
Cobalt	9.6	10.8	
Copper	177	310	
Iron	21000	10500	
Lead	158	369	
Magnesium	2190	2200	
Manganese	76.7	233	
Nickel	21.5	25.8	
Potassium	599	375	
Selenium	3.8	4.3	
Silver	0.72	0.84	U
Sodium	832	561	
Thallium		3.4	UJ
Vanadium	101	79.4	
Zinc	1910	1180	

U - Not detected; UJ - Detection limit approximate; J - Quantitation approximate;
R - Rejected



TETRA TECH NUS, INC.

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RACI-EPA-3520

Contract No. 68-W6-0045

January 9, 2002

Mr. Joseph LeMay, P.E.
U.S. Environmental Protection Agency
1 Congress Street, Suite 1100 (HBO)
Boston, Massachusetts 02114-2203

Subject: Response to EPA June 13, 2001 Memorandum Re: Chromium VI Data
Industri-plex Site, Remedial Action Oversight
RAC I W.A. No. 104-RXBF-0107

Dear Mr. LeMay:

Pursuant to your request, Tetra Tech NUS, Inc. (TtNUS) is providing responses to comments provided to you by EPA's New England Regional Laboratory (NERL) regarding analytical methods and results for sediment samples analyzed for hexavalent chromium (Cr+6) under Case 0194H, SDG D02645. Samples were collected to support the Industri-plex Site Remedial Investigation/Feasibility (RI/FS) for Operable Unit 2 (OU-2).

BACKGROUND

In February 2001, TtNUS collected 30 sediment samples for total metals analysis from a wetlands located within the Industri-plex Site study area. Twenty percent of these samples were randomly selected and analyzed for Cr+6 by SW-846 Methods 3060A and 7196A in accordance with TtNUS Specification No. S01-RAC1-0152. The initial results for these samples indicated elevated concentrations of Cr+6. These results were not expected because; 1) previous sediment samples collected in similar environments within the site study area did not show the presence of Cr+6, and 2) the observed oxidation reduction potential (ORP) and pH reducing conditions for these sample matrices should have precluded the presence of Cr+6. As a result, EPA requested that TtNUS resample three areas where the highest concentrations were observed to confirm the presence of Cr+6. TtNUS re-sampled three locations in June 2001. The analytical results for the re-sampled areas indicated that Cr+6 was not detected.

Based on the conflicting data and at your request, EPA's Quality Assurance Office conducted an independent review of the analytical data and data validation reports prepared by TtNUS. Enclosed, please find the TtNUS' responses to EPA's comments.

Since June 2001, TtNUS has conducted an extensive review of the data and worked very closely with Dr. Neil Pothier (Ceimic Corporation) to evaluate the analytical methods, the potential analytical interferences that are inherent with the method, the effects of strong reducing conditions within the sample matrix, potential analytical errors, and possible impacts to the sample results. This evaluation has shown that the selected analytical method has a high potential for matrix interferences that may result in false-positive results for Cr+6.

Strong reducing conditions, as observed in the site sediment sample matrix, may also have a significant impact on the matrix spike recoveries, post-digestion spike recovery, and validity of the method of standard addition (MSA). In the presence of strong reducing conditions, the Cr+6



TETRA TECH NUS, INC.

Mr. Joseph LeMay, P.E.
January 9, 2002
Page 2 of 2

spike could be reduced to trivalent chromium (CR+3) and the low spike recoveries could be incorrectly interpreted as poor analytical performance, thus rendering the data as unreliable.

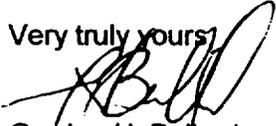
Finally, TtNUS discovered that the laboratory had made several calculation errors which led to originally reporting incorrect values for Cr+6. These errors have since been corrected and a revised data validation report was issued on December 31, 2001 (see enclosure). This revised data validation report also describes in detail and addresses several of the issues discussed by NERL, specifically low spike recoveries. The data validation report also discusses technical issues with the applicability of using SW-846 Methods 3060A and 7196A for these particular sample matrices from this site (i.e. samples with reducing conditions, high concentration of sulfides, etc.).

As stated in the revised data validation report, "For these sediment samples, there is not enough information available to determine whether the low matrix spike recovery, the low post-digestion spike recoveries, and the failed MSA are due solely to the reducing characteristics of the sediment samples or due to other matrix interference effects, potential laboratory analytical errors, or a combination of all these factors. The accuracy of the low concentration positive values and non-detected results obtained directly from the colorimetric analysis can not be determined with the analytical information available. Therefore professional judgement was used to reject the positive and non-detected results for all samples except D02673 and D02679.

Due to the limitations of SW-846 Methods 3060A and 7196A, the ion chromatography method (Method 7699) is suggested as an alternative method, to overcome possible matrix interference when measuring hexavalent chromium in anoxic sediment samples. In addition to pH, ORP, and sulfides analyses, other ancillary parameters such as total organic carbon (TOC), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) may also be useful to characterize each sample and assist in the interpretation of the quality control data outside the conventionally accepted criteria.

If you have any questions or should require additional information, please call me or Ms. Lucy Guzman at 978-658-7899.

Very truly yours,


Gordon H. Bullard
Project Manager

PMO - @

GHB:rp

Enclosures

c: H. Horahan (EPA) w/o enc.
L. Guzman (TtNUS) w/enc.
G. Gardner/A. Ostrofsky (TtNUS) w/o enc.
File N4123-1.0 w/ enc.

RESPONSES TO EPA COMMENTS
JUNE 13, 2001
EVALUATION OF THE HEXAVALENT CHROMIUM DATA

Comment 1. The Technical Specification Analysis of Soil Samples for Hexavalent Chromium and Total Sulfides, Delivery of Analytical Services by Tetra Tech NUS, Inc. dated August 2000 does not include provisions for sediment sample analysis, specifically accounting for the low percent solids in sediment samples. Region I requires the rejection of data reported for samples with percent solids which are less than 10% and estimate all positive results and reject non-detects for samples with percent solids greater than 10% and less than or equal to 30%. The Tetra Tech data validation procedures did not include this requirement.

Therefore, the Cr(VI) data for the following samples are rejected due to percent solids less than 10%: D02672, D02687.

The Cr(VI) data, which was reported as non-detected, for the following samples are rejected due to percent solids greater than 10% and less than or equal to 30%: D02673, D02679.

The Cr(VI) data, which are reported as positive results, for the following sample are estimated due to percent solids greater than 10% and less than or equal to 30%: D02649, D02650, D02697, D02718, D02722, D02727, D02729, and D02734.

Response: TtNUS does not technically agree with the application of this particular EPA Region I data validation rule to the colorimetric procedure for several reasons:

- a) Unlike CLP procedures for solids that are typically only applicable to soil samples (i.e. low moisture content), the alkaline digestion method (Method 3060A) is applicable to various matrices including high moisture content (i.e. low percent solids) samples such as sediments and sludges.
- b) The method detection limit (MDL) for Methods 3060A/7196A is much lower than the required project quantitation limit. Consequently, even if the sample has only 10 percent solids (equivalent to a 1:10 dilution) the laboratory will be able to achieve the project goal for sensitivity.
- c) The water from the sediment sample evaporates during the first minutes of the alkaline digestion process and does not interfere with the analysis.
- d) Several problems were encountered when increasing the sample aliquot to compensate for the high moisture of the sediment samples:
 - The alkaline digestate for several samples became very thick and impossible to filter.
 - The digested extract was very dark and needed to be diluted before completing the colorimetric analysis by Method 7196A.
 - The color-developed sample aliquot is measured against a non-color reagent added background sample. If the sample is dark, the background sample absorbance may be greater than the absorbance of the sample resulting in negative values.

Comment 2. The Tetra Tech NUS, Inc. data validation report did not indicate that the laboratory did not provide the bench sheets for sample digestion. The Method 3060A indicates the importance of checking the pH of the digestion solution prior to digesting the samples. The data package did include the logbook pages for performing the pH analysis of the samples, however the digestion solution was not included in these logbook pages. The logbook pages which demonstrate that the digestion heating devices were maintained at the method required 90-95°C temperature were not provided. Therefore, the digestion procedure cannot be verified.

Response: EPA is correct, the laboratory did not provide a sample digestion worksheet. TtNUS agrees that this information would be useful in evaluating the uncertainty of possible analytical error. TtNUS will require this documentation in future work.

Comment 3. The digestion pH was not optimized. The Region has found that a pH optimization procedure must be performed prior to preparing and analyzing samples for Cr(VI) determination. Several spikes containing Cr(VI), soluble and insoluble, and Cr(III) must be spiked on field samples at a range of pHs to determine the appropriate pH to recover the Cr(VI) in the matrix under investigation.

An extensive digestion pH study was previously performed on soil and sediment samples from this site. The data from this study can be found in data validation reports for Case numbers 0156H, SDG 02227, and for the soils in Case 0157H, SDG D02203.

The pH optimization procedure may not be applicable in all circumstances, especially in sample matrices exhibiting strong reducing characteristics, as observed in the site sediment samples. As demonstrated by the previous study, all of the hexavalent chromium (CR+6) spike was reduced to trivalent chromium (CR+3) and the digestion pH had no affect on the recovery of the Cr+6. Based on the previous study results, it was determined that the optimum pH for samples from this site was consistent with the pH required by Method 3060A. Furthermore, the preliminary results from the recent analysis of similar site sediment samples by ion chromatography, Method 7699, indicate that the pH required by the alkaline digestion Method 3060A is also appropriate to digest insoluble CR+6 spikes.

Comment 4. The Tetra Tech NUS, Inc. data validation report indicates that the laboratory did not perform a laboratory duplicate analysis. Sample D02645 and its duplicate were included in the analysis log on page 41/42.

Sample D02645 was analyzed in duplicate as shown in the analysis log on page 42. However, the laboratory did not perform the method of standard additions (MSA) on the laboratory duplicate.

Comment 5. The Tetra Tech NUS, Inc. technical specification does not include a spike containing Cr(III) to determine that the procedure is not converting the Cr(III) to Cr(VI). The ORP and pH results indicate a reducing atmosphere which is contrary to the number of positive results which are reported for Cr(VI). The Tetra Tech data validation does indicate that the soluble matrix spike was recovered at 1% and the insoluble matrix spike was recovered at 70% which are low recoveries. This fact indicates that the digestion procedure may not be at the

appropriate pH for adequate recovery of Cr(VI) in this particular matrix. It must be noted that the insoluble Cr(VI) was spiked at approximately 100 times the concentration of the soluble Cr(VI) spike. A seventy five percent recovery is the lower acceptance limit. All Cr(VI) data should be estimated due to the low matrix spike recoveries. It also must be considered that twelve out of seventeen sample results were determined with method of standard addition (MSA) due to poor recovery of the post digestion spike which may indicate that the digestion pH may not be appropriate. The samples with low post digestion spike recoveries and MSA results with curves which did not meet criteria were rejected. This includes samples: D02649, D02650, D02692, D02697, D02705, D02729 and D02734.

Response: Regarding the first part of this comment addressing the Cr+3 spike, the previous study that was conducted to optimize the digestion pH for samples from this site included spiking with Cr+3. The results did not indicate oxidation of the Cr+3 to Cr+6. Also, note that as further precaution against the oxidation of Cr+3, the addition of Mg ²⁺ in an alkaline buffer, is required in Method 3060A to suppress oxidation of native Cr+3 in the sample (see Method 3060A, Section 3.3).

It is TtNUS' professional opinion that the zero or very low matrix recoveries were due to the reducing sample conditions and not because of the pH used to digest the sample. The combined and interacting influences of ORP, pH, and reducing agents that may be present in the sample matrix (organic acids, iron II, and sulfides) may have reduced the hexavalent chromium spikes (see also Section 8.5.1 of Method 3060A). This phenomenon is also noted in "Chromium Speciation Analysis in Soils/Sediments - Zero Percent Matrix Spike Recoveries May Not Equal Unreliable Data" and "Hexavalent Chromium Extraction from Soils: Evaluation of an Alkaline Digestion Method" (see attached). The lower post-digestion spike recoveries may also be explained due to reducing sample characteristics whereby the post-digested Cr+6 spiked may have been reduced to Cr+3.

The soluble and insoluble spike recoveries for the laboratory control samples (LCS) were within the 80-120% recovery limits indicating that the laboratory analysis was within controls.

Comment 6. The Tetra Tech data validation report indicates that the MSA correlation coefficient result was below the quality control limit for sample D02645. The data on page 20/25 indicate that the correlation coefficient is .998 which is within the acceptance limit. Therefore, the positive result should not be estimated in sample D02645.

Response: TtNUS agrees with EPA's comment based on the originally reported data. However, it should be noted that based on further evaluation and the revised data validation report, the analytical result for this sample was rejected. Revised data tables are presented in the revised data validation report submitted on December 31, 2001.

Comment 7. The laboratory data package and the Tetra Tech NUS, Inc. data validation report indicates Cr(VI) in sample D02743 as 20.5 mg/Kg. This value could not be reproduced. According to the calculation on page 23/28 of the data package the result should be 4.64 mg/Kg.

TtNUS agrees with EPA's comment based on the originally reported data. However, it should be noted that based on further evaluation and the revised data validation report, the result for this sample was rejected. Revised data tables are presented in the revised data validation report submitted on December 31, 2001.



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RAC1-EPA-3503

Contract No. 68-W6-0045

December 31, 2001

Ms. Christine Clark
Regional Sample Control Coordinator
U.S. EPA New England Regional Laboratory
Office of Environmental Measurement and Evaluation
11 Technology Drive
North Chelmsford, Massachusetts 01863-2431

Reference: RAC1-EPA-3029 Letter, dated May 8, 2001

Subject: Resubmittal of Tier III Inorganic Data Validation, W.A. No. 116-RICO-0107
DAS Case 0194H, SDG D02645
Ceimic Corporation
Industri-Plex Site, Woburn, Massachusetts

Hexavalent Chromium, Total Sulfide:

17/Sediments/ D02645, D02649, D02650, D02672, D02673,
D02679, D02687, D02692, D02697, D02705,
D02709, D02718, D02722, D02727, D02729,
D02734, D02743
(Field Duplicate Pairs: D02649/D02650,
D02722/D02727)

Dear Ms. Clark:

This data validation resubmittal affects only the hexavalent chromium results reported in the above-referenced letter. This re-submittal does not affect the total sulfide data. The laboratory recalculated the hexavalent chromium results to correct for the background absorbance that was not subtracted in the originally submitted results.

TetraTech NUS Inc. (TtNUS) performed a Tier III data validation on the re-submitted hexavalent chromium analytical data for DAS Case 0194H, SDG D02645, from sediment samples collected by TtNUS at the Industri-Plex Site. The hexavalent chromium analysis was performed by the SW-846 Methods 3060A and 7196A according to the requirements of the TtNUS technical specification S00-RACI-152. The Tier III data validation was performed as required by the June, 2000 Quality Assurance Project Plan. The data were validated according to the Region I, EPA-NE Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses, modified February 1989.

The data were evaluated based on the following parameters:

- Data Completeness
- * • Holding Times
- * • Calibration Verification
- * • Laboratory Blank Analyses

- Matrix Spike Recoveries
- Post Digestion Spike Recoveries
- * • Laboratory Duplicate Results
- * • Laboratory Control Sample Results
- * • Field Duplicate Precision
- * • Sample Quantitation Limits
- Sample Quantitation

* All quality control criteria were met for this parameter.

Note: Criteria were met for the laboratory and field duplicate results based on the direct colorimetric method. No method of standard additions (MSA) was performed for the laboratory duplicate analysis of sample D02645. Since the results were rejected due to other parameters, this issue is not discussed further.

Table I summarizes the validation recommendations which were based on the following information:

Data Completeness

This data package was originally submitted on April 17, 2001. TtNUS performed a Tier III data validation and reported the results on May 8, 2001. Due to unusually high positive results for hexavalent chromium in the sediment samples, EPA, TtNUS, and the laboratory independently further evaluated this data package. Some hexavalent results were greater than the total chromium results, and the presence of hexavalent chromium in highly anoxic sediment samples was not expected.

During the second review, TtNUS noted that the original calculation of the MSA hexavalent chromium results did not include the absorbance reading for a sample aliquot with zero standard added. Also, the MSA results were calculated without subtracting the background absorbance reading of the sample before the addition of the color reagent, diphenylcarbazide. TtNUS contacted the laboratory about these problems. The laboratory resubmitted the background-corrected results to TtNUS on August 24, 2001. However, the MSA background absorbance was only subtracted from the absorbance reading for the original sample with zero standard added and not from the standard-added samples. The laboratory recalculated the MSA values including the background-subtracted absorbance of the original sample and all the spiked sample aliquots. The laboratory resubmitted the hexavalent chromium results again on December 13, 2001.

Matrix Spike Recoveries

Hexavalent Chromium:

The recovery for the low-level soluble matrix spike analysis of sample D02625 was 0 percent and the high-level insoluble spike recovery was 66 percent, below the 75 percent quality control (QC) criterion. Professional judgement was used not to qualify the data for this parameter since the percent recovery for the soluble and insoluble hexavalent chromium LCS are within criteria and the oxidation/reduction potential (ORP) and pH indicate matrix reducing characteristics of sample D02645. The combined and interacting influences of ORP, pH, and reducing agents (organic acids, iron II, and sulfides) may have reduced the hexavalent chromium spikes (Section 8.5.1 of Method 3060A-see enclosure). As per the above reference, if the ORP (Eh) and pH of

the sample fall within the reducing area, as illustrated in Figure 2 of Method 3060A (see enclosure), low matrix spike recoveries are expected for these samples. (See also references enclosed, "Chromium Speciation Analysis in Soils/Sediments – Zero Percent Matrix Spike Recoveries May Not Equal Unreliable Data" and "Hexavalent Chromium Extraction from Soils: Evaluation of an Alkaline Digestion Method".)

The soluble hexavalent chromium spiked to the sample might have been totally reduced to the trivalent form, while only a fraction of the insoluble spike was reduced. The insoluble chromium was spiked at higher concentration than the soluble form (due to limitations in accurately weighing smaller aliquots of the insoluble chromium salt). Consequently, only a fraction of the available insoluble hexavalent chromium may have reacted with the available reducing agents in the sample aliquot. The soluble and insoluble LCS recoveries were within limits, indicating that the low matrix spike recovery for sample D02645 is probably due to a sample matrix effect and not an analytical error.

Post Digestion Spike Recoveries

Hexavalent Chromium

According to the technical specification, the laboratory was required to perform a post-digestion spike for each sample. If the percent recovery was outside the QC criteria, indicating a possible matrix interference effect, the laboratory was required to use the method of standard additions (MSA) to determine the hexavalent chromium concentration of the sample.

The laboratory performed a post-digestion spike for the samples that were collected on February 5-7, 2001. No post digestion spike (only MSA) was performed for the remaining samples collected on February 8, 9, and 12, 2001. The post digestion spike percent recovery for samples D02673 and D02679 met the 85 percent data validation QC criterion while the percent recoveries for samples D02645, D02649, D02650, and D02672 were below 85 percent. The low post digestion spike recoveries may have been caused by the presence of soluble reducing agents such as fulvic acids that reacted with the hexavalent chromium spike (Section 8.6.2 of Method 3060A).

MSA analysis using a series of standard additions was performed on all the samples except D02673 and D02679 (which met the post-digestion spike recovery criterion). As discussed in the Data Completeness section, the MSA results in the original data submittal (April 17, 2001) were not corrected for the background sample color, and the MSA calculations did not include the absorbance reading from a zero standard added sample aliquot. In the December, 2001 resubmittal, the MSA values were recalculated including the original sample (zero standard added), and the background absorbance was subtracted from the original sample as well as from all the spiked sample aliquots.

The MSA is designed to compensate for matrix interference effects and, when conditions for the method's validity are met, it is considered a more accurate basis for calculating inorganic sample results than a standard calibration curve. The MSA technique involves adding a known amount of standard to one or more aliquots of the digested sample, and plotting the curve of the absorbance versus concentration of the standard added for each of the aliquots. The MSA compensates for matrix interference that enhances or depresses the hexavalent chromium color absorbance, producing a different slope from that of the calibration standards. The hexavalent chromium concentration is then calculated from the MSA curve. The validity of the hexavalent chromium result, however, depends on whether the MSA conditions are met.

According to EPA SW-846 Method 7000, for the MSA results to be valid, the following conditions must be met:

- The slope of the MSA should be nearly the same as the initial calibration slope. If the slope difference exceeds 20 percent, caution must be exercised.
- The effect of the interference should not vary as the ratio of the analyte concentration to sample matrix changes.
- The determination must be free of spectral interference and corrected for nonspecific background interference.

For the data resubmitted in December 2001, the laboratory evaluated the validity of the MSA study for each sample, and if the MSA failed to meet criteria, the hexavalent chromium results were reported from the direct colorimetric analysis. Ceimic evaluated three criteria—the correlation coefficient, the slope, and the y-intercept—to assess the validity of the MSA analysis. The laboratory's criteria for acceptance of the MSA results were:

- The correlation coefficient must be ≥ 0.995
- The percent difference between the slopes of the MSA and the standard calibration curve must be less than 20%
- The y-intercept (the fitted absorbance at zero standard addition) must be positive

These criteria are consistent with EPA Method 7000A. Therefore, TtNUS used professional judgement to accept the above MSA validity criteria for data validation purposes.

For all of the samples for which the MSA was performed, the MSA failed to meet the criteria, and the analyses were rejected. Ceimic reported the hexavalent chromium results for these samples from the direct colorimetric method. The following table summarizes the MSA results.

Sample #	Correlation Coefficient (r)	MSA Slope (m)/% D	y-Intercept (b)	Cr ^{VI} Results* (mg/L) from the MSA Analysis	Action—Accept or Reject the MSA Analysis
D02645	0.999	0.162/ -67.5	- 0.0018	-0.011	Reject
D02649	0.799	0.154/ -69.1	-0.041	-0.266	Reject
D02650	0.983	0.047/ -90.6	-0.0024	-0.051	Reject
D02672	0.850	0.218/ -56.2	-0.058	-0.266	Reject
D02687	0.999	0.148/ -70.3	0.0034	0.023	Reject
D02692	0.942	0.030/ -94.0	-0.0074	-0.25	Reject
D02697	0.961	0.135/ -72.9	-0.018	-0.133	Reject
D02705	0.876	0.0721/ -85.5	-0.0228	-0.316	Reject
D02709	0.994	0.341/ -31.5	-0.0108	-0.032	Reject
D02718	0.991	0.251/ -49.6	-0.012	-0.048	Reject
D02722	0.968	0.339/ -31.9	-0.061	-0.18	Reject
D02727	0.974	0.402/ -19.3	-0.070	-0.174	Reject
D02729	0.976	0.212/ -57.4	-0.031	-0.146	Reject
D02734	0.904	0.095/ -80.9	-0.021	-0.221	Reject
D02743	0.994	0.406/ -18.5	-0.025	-0.062 *	Reject

* - The concentration equals the negative of the x-value resulting from setting y (absorbance) equal to zero in the MSA least-squares equation, $y = mx + b$. Ceimic MDL = 0.01 mg/L.

Most of the MSA plots (absorbance versus spike concentration) with poor correlation coefficients show a relatively flat slope up to the first standard addition, and a sharp increase in slope at the second or third addition. (See enclosed data validation worksheets.) This could reflect the reducing nature of the sample matrix, which may reduce much of the standard added at lower concentrations until the amount of hexavalent chromium standard added is stoichiometrically greater than the amount of reducing agents present in the sample. The lack of linearity resulted in a poor correlation coefficient.

The MSA does not distinguish between the effects of matrix interference and the effect of reduction in these anoxic (reducing) sediment samples. The MSA is designed to compensate for matrix interference that suppresses or enhances the true absorbance reading for an analyte. Under reducing conditions, the MSA may be compensating for matrix interference as well as for the reducing sample characteristics; consequently, the hexavalent chromium results might be false positives. The MSA analysis may not be applicable to calculate hexavalent chromium from samples with reducing matrix characteristics. Most likely, in these sediment samples with observed reducing characteristics, chromium can not exist in the hexavalent form.

The failed MSA and the low post-digestion spike recoveries may be due to the reducing characteristics of the samples, as indicated by the ancillary sediment properties of pH, ORP, and in some cases, by the high sulfide concentrations (Section 8.5.1 of Method 3060A). If soluble reducing compounds such as fulvic acid are present in the sediment samples, they might reduce the hexavalent chromium spiked to the samples producing low post digestion spike recoveries (Section 8.6.2 of Method 3060A). This would be consistent with the non-detected results obtained for most of the samples from the direct colorimetric analysis after subtraction of the background sample color. However, two samples (D02673 and D02679) with reducing characteristics had post digestion spike recoveries within criteria; and four samples with reducing characteristics had low but positive hexavalent chromium results. These inconsistencies raise questions about the validity of the hexavalent chromium results for these sediment samples. It has been reported that high concentration of total organic carbon (TOC) in the samples (high concentration of organic molecules with oxidizable groups like alkanes, alkenes, alcohols, aldehydes, and carboxylic acids) will reduce the hexavalent chromium to the trivalent form (Vitale et al., Contaminated Soil Analysis, Chromium Speciation). The TOC concentration, in addition to ORP, pH, and sulfide, may help determine whether the low post-digestion spike recovery is due to analytical error or is a result of reducing agents in the sediment samples. TOC was not measured for these samples.

For these sediment samples, there is not enough information available to determine whether the low post-digestion spike recoveries and failed MSA are due solely to the reducing characteristics of the sediment samples, or to other matrix interference effects, potential laboratory analytical errors, or a combination of all these factors. The accuracy of the low concentration positive values and non-detected results obtained directly from the colorimetric analysis can not be determined with the analytical information available. Therefore, professional judgement was used to reject (R) the positive and non-detected results for all samples except D02673 and D02679. The non-detected results for D02673 and D02679, whose post-digestion spike recoveries were within criteria, are accepted without qualification for this parameter.

Sample Quantitation

Hexavalent Chromium

The percent solids of many of the samples were below 30 percent. Professional judgement was used not to qualify the sediment sample results based on the low percent solids of the samples because of two main reasons: (a) the sensitivity (MDL) of the alkaline digestion/colorimetric procedure is much lower than the required reporting limit. (b) The water from the sludge sample evaporates during the first minutes of the alkaline digestion and does not interfere with the analysis.

The analysis of the samples for hexavalent chromium was performed by extracting the hexavalent chromium according to Method 3060A and then reacting the extraction solution with a color reagent (diphenylcarbazide) according to Method 7196A. The transmission/absorbance of the resulting red-violet color was then measured photometrically, and the corresponding concentration of hexavalent chromium was calculated directly from the standard calibration curve or by MSA.

For the samples with failed MSAs, Ceimic reported the hexavalent chromium results from the direct colorimetric analysis (December 2001 submittal), which included subtraction of the background sample color. The results for four of the samples were low but positive, and the rest were non-detected. As discussed in above in the Post Digestion Spike Recoveries section, professional judgement was used to reject (R) the positive and non-detected results for all samples except D02673 and D02679. The non-detected results for samples D02673 and D02679, whose post-digestion spike recoveries were within criteria, are accepted without qualification.

Overall Assessment of the Data

There were a number of problems associated with the hexavalent chromium data in this data package that affect usability of the results. The matrix spike recoveries and post-digestion spike recoveries were low, and the MSA failed for all samples for which it was performed. These results may be due to the reducing characteristics of the samples, as indicated by the ancillary sediment properties of pH, redox potential, and high sulfide concentrations. Under these reducing conditions, no native hexavalent chromium could exist and the spiked chromium (VI) would be reduced to the trivalent form. However, some samples with apparent reducing conditions exhibited an ability to sustain hexavalent chromium (as indicated by good post-digestion spike recoveries or positive results). Other factors, such as TOC concentration, may also affect the reducing conditions and explain these inconsistencies, but TOC data were not obtained for these samples.

Not enough bench information was recorded by the laboratory for the hexavalent chromium analysis that would reduce the uncertainty of possible analytical error. The digestion procedure conditions (pH and temperature) performed by the laboratory cannot be verified since no records were kept for these parameters. In addition, a step by step MSA procedure was not documented and only verbal information was obtained from the laboratory. Bench sheets detailing these procedures should be required in future technical specifications.

The reported results for all samples were obtained directly from the colorimetric analysis (including subtraction of the background color absorbance). However, the low post-digestion spike recoveries and other problems discussed above raise questions about the usability of the

results for all samples except D02673 and D02679. The accuracy of the low concentration positive values and non-detected results in these samples cannot be determined with the analytical information available. Therefore, the positive and non-detected hexavalent chromium results in all samples except D02673 and D02679 are rejected (R).

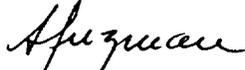
The ion chromatography Method 7699 is suggested as an alternative method, to overcome possible matrix interference in measuring hexavalent chromium in anoxic sediment samples. The TOC concentration may also be a useful ancillary parameter to characterize each sample and assist in the interpretation of the QC data outside the conventionally accepted criteria for total metals.

Please contact L. Guzman at (978) 658-7899 should you have any questions or comments regarding this information.

Sincerely,



Ann L. Franke
Data Validator



Lucy Guzman
RAC Lead Chemist

PMO - @

Tables: Table I: Recommendation Summary Table
 Data Summary Tables

Enclosures: Method 3060A
 "Chromium Speciation Analysis in Soils/Sediments – Zero Percent Matrix Spike Recoveries May Not Equal Unreliable Data"
 "Hexavalent Chromium Extraction from Soils: Evaluation of an Alkaline Digestion Method"
 Eh/pH Diagram (Figure 2 from Method 3060A)
 Data Validation Worksheets
 Communication/Phone Logs

c: J. LeMay (EPA) w/o enc.
 G. Bullard (TINUS) w/o enc.
 File N4123-2.6 w/ enc.

**INDUSTRI-PLEX SITE
DAS Case 0194H, SDG D02645**

Table I - Recommendation Summary for the Sediment Samples

Hexavalent Chromium

R¹

R¹ - Reject (R) positive and non-detected results in all samples except D02673 and D02679 due to low post-digestion spike recoveries and failed MSA.

Sediment Wet Chemistry Analysis*

Site: Industri-Plex

Case: 0194H; SDG: D02645

EPA Sample Number	D02645	D02649	D02650	D02672	D02673	
Station Location	IPSD-ED09-020501	IPSD-ED03-020501	IPSD-DP01-020501	IPSD-WW08-020601	IPSD-TT2702-020601	
Date Sampled	2/5/01	2/5/01	2/5/01	2/6/01	2/6/01	
Date Extracted						
Date Analyzed						
Dilution Factor	1	1	1	1	1	
Percent Solids	56.3	21.0	20.3	8.9	27.0	
QC Identifier	None	Field Dup. IPSD-ED03-020501	Field Dup. IPSD-ED03-020501	None	None	
Chromium VI (mg/kg)		R	R	R	R	1.29 U
Sulfide (mg/kg)	84.4 J	336 J	62.1 J	180 J		50.4 J
pH (S.U.)	6.51	7.17	7.11	6.03		6.15
Redox Potential (Eh) (mV)	191	10.0	8.2	341		231

Sediment Wet Chemistry Analysis*

Site: Industri-Plex

Case: 0194H; SDG: D02645

EPA Sample Number	D02679	D02687	D02692	D02697	D02705
Station Location	IPSD-TT2203-020701	IPSD-CB0209-020801	IPSD-TT3302-020801	IPSD-CB0203-020801	IPSD-CB0310-020801
Date Sampled	2/7/01	2/8/01	2/8/01	2/8/01	2/8/01
Date Extracted					
Date Analyzed					
Dilution Factor	1	1	1	1	1
Percent Solids	23.7	9.4	45.9	14.7	32.1
QC Identifier	None	None	None	None	None
Chromium VI (mg/kg)	1.59 U				
Sulfide (mg/kg)	52.3 J	112 J	37.7 J	231 J	163 J
pH (S.U.)	5.95	5.67	6.70	5.95	6.28
Redox Potential (Eh) (mV)	324	374	119	246	248

U - Not detected; J - Quantitation approximate; R - Rejected;

Sediment Wet Chemistry Analysis*

Site: Industri-Plex

Case: 0194H; SDG: D02645

EPA Sample Number	D02709	D02718	D02722	D02727	D02729
Station Location	IPSD-CB0304-020801	IPSD-CB0109-020901	IPSD-CB0105-020901	IPSD-DP06-020901	IPSD-TT3202-020901
Date Sampled	2/8/01	2/9/01	2/9/01	2/9/01	2/9/01
Date Extracted					
Date Analyzed					
Dilution Factor	1	1	1	1	1
Percent Solids	58.2	17.2	27.2	24.5	16.8
QC Identifier	None	None	Field Dup. IPSD-CB0105-020901	Field Dup. IPSD-CB0105-020901	None
Chromium VI (mg/kg)	R	R	R	R	R
Sulfide (mg/kg)	29.6 J	123 J	93.8 J	88.6 J	297 J
pH (S.U.)	5.44	5.98	5.86	5.71	6.35
Redox Potential (Eh) (mV)	367	324	265	298	146

Sediment Wet Chemistry Analysis*

Site: Industri-Plex

Case: 0194H; SDG: D02645

EPA Sample Number	D02734	D02743	
Station Location	IPSD-TT2901-021201	IPSD-TT3103-021201	
Date Sampled	2/12/01	2/12/01	
Date Extracted			
Date Analyzed			
Dilution Factor	1	1	
Percent Solids	24.0	31.2	
QC Identifier	None	None	
Chromium VI (mg/kg)		R	R
Sulfide (mg/kg)	1100		84.9
pH (S.U.)	6.92		6.32
Redox Potential (Eh) (mV)	78.7		195

METHOD 3060A

ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM

1.0 SCOPE AND APPLICATION

1.1 Any reference in this method to "Method 3060" refers to this version of that method, and does not refer to previously published versions (e.g., in the Second Edition of this manual). When published as a new method to SW-846, a method's number does not include a letter suffix. Each time a method is revised and made a part of SW-846 update, it receives a suffix. However, a method reference found within the text of SW-846 methods always refers to the latest version of that method published in SW-846, even if the method number at that location does not include the appropriate letter suffix.

1.2 Method 3060 is an alkaline digestion procedure for extracting hexavalent chromium [Cr(VI)] from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments, and similar waste materials. To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied: (1) the extracting solution must solubilize all forms of Cr(VI), (2) the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III), and (3) the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI). Method 3060 meets these criteria for a wide spectrum of solid matrices. Under the alkaline conditions of the extraction, minimal reduction of Cr(VI) or oxidation of native Cr(III) occurs. The addition of Mg^{2+} in a phosphate buffer to the alkaline solution has been shown to suppress oxidation, if observed. The accuracy of the extraction procedure is assessed using spike recovery data for soluble and insoluble forms of Cr(VI) (e.g., $K_2Cr_2O_7$ and $PbCrO_4$), coupled with measurement of ancillary soil properties, indicative of the potential for the soil to maintain a Cr(VI) spike during digestion, such as oxidation reduction potential (ORP), pH, organic matter content, ferrous iron, and sulfides. Recovery of an insoluble Cr(VI) spike can be used to assess the first two criteria, and method-induced oxidation is usually not observed except in soils high in Mn and amended with soluble Cr(III) salts or freshly precipitated $Cr(OH)_3$.

1.3 The quantification of Cr(VI) in Method 3060 digests should be performed using a suitable technique with appropriate accuracy and precision, for example Method 7196 (colorimetrically by UV-VIS spectrophotometry) or Method 7199 (colorimetrically by ion chromatography (IC)). Analytical techniques such as IC with inductively coupled plasma - mass spectrometric (ICP-MS) detection, high performance liquid chromatography (HPLC) with ICP-MS detection, capillary electrophoresis (CE) with ICP-MS detection, etc. may be utilized once performance effectiveness has been validated.

2.0 SUMMARY OF METHOD

2.1 This method uses an alkaline digestion to solubilize both water-insoluble (with the exception of partial solubility of barium chromate in some soil matrices, see Reference 10.9) and water soluble Cr(VI) compounds in solid waste samples. The pH of the digestate must be carefully adjusted during the digestion procedure. Failure to meet the pH specifications will necessitate redigestion of the samples.

2.2 The sample is digested using 0.28M Na_2CO_3 /0.5M NaOH solution and heating at 90-95°C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

2.3 The Cr(VI) reaction with diphenylcarbazide is the most common and reliable method for analysis of Cr(VI) solubilized in the alkaline digestate. The use of diphenylcarbazide has been well established in the colorimetric procedure (Method 7196), in rapid-test field kits, and in the ion chromatographic method for Cr(VI) (Method 7199). It is highly selective for Cr(VI) and few interferences are encountered when it is used on alkaline digestates.

2.4 For additional information on health and safety issues relating to chromium, refer to References 10.7 and 10.10.

3.0 INTERFERENCES

3.1 When analyzing a sample digest for total Cr(VI), it is appropriate to determine the reducing/oxidizing tendency of each sample matrix. This can be accomplished by characterization of each sample for additional analytical parameters, such as pH (Method 9045), ferrous iron (ASTM Method D3872-86), sulfides (Method 9030), and Oxidation Reduction Potential (ORP) (ASTM Method D 1498-93 - aqueous samples). Method 9045 (Section 7.2 of Method 9045) is referenced as the preparatory method for soil samples. The ORP and temperature probes are inserted directly into the soil slurry. The displayed ORP value is allowed to equilibrate and the resulting measurement is recorded. Other indirect indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). Analysis of these additional parameters establishes the tendency of Cr(VI) to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria for total metals.

3.2 Certain substances, not typically found in the alkaline digests of soils, may interfere in the analytical methods for Cr(VI) following alkaline extraction if the concentrations of these interfering substances are high and the Cr(VI) concentration is low. Refer to Methods 7196 and 7199 for a discussion of the specific agents that may interfere with Cr(VI) quantification. Analytical techniques that reduce bias caused by co-extracted matrix components may be applicable in correcting these biases after validation of their performance effectiveness.

3.3 For waste materials or soils containing soluble Cr(III) concentrations greater than four times the laboratory Cr(VI) reporting limit, Cr(VI) results obtained using this method may be biased high due to method-induced oxidation. The addition of Mg^{2+} in a phosphate buffer to the alkaline extraction solution has been shown to suppress this oxidation. If an analytical method for Cr(VI) is used that can correct for possible method induced oxidation/reduction, then the Mg^{2+} addition is optional. The presence of soluble Cr(III) can be approximated by extracting the sample with deionized water (ASTM methods D4646-87, D5233-92, or D3987-85) and analyzing the resultant leachate for both Cr(VI) and total Cr. The difference between the two values approximates soluble Cr(III).

4.0 APPARATUS AND MATERIALS

- 4.1 Digestion vessel: borosilicate glass or quartz with a volume of 250 mL.
- 4.2 Graduated Cylinder: 100-mL or equivalent.
- 4.3 Volumetric Flasks: Class A glassware, 1000-mL and 100-mL, with stoppers or equivalent.

- 4.4 Vacuum Filtration Apparatus.
- 4.5 Filter membranes (0.45 μm). Preferably cellulosic or polycarbonate membranes. When vacuum filtration is performed, operation should be performed with recognition of the filter membrane breakthrough pressure.
- 4.6 Heating Device - capable of maintaining the digestion solution at 90-95°C with continuous auto stirring capability or equivalent.
- 4.7 Volumetric pipettes: Class A glassware, assorted sizes, as necessary.
- 4.8 Calibrated pH meter.
- 4.9 Calibrated balance.
- 4.10 Temperature measurement device (with NIST traceable calibration) capable of measuring up to 100°C (e.g. thermometer, thermistor, IR sensor, etc.).
- 4.11 An automated continuous stirring device (e.g. magnetic stirrer, motorized stirring rod, etc.), one for each digestion being performed.

5.0 REAGENTS

5.1 Nitric acid: 5.0 M HNO_3 , analytical reagent grade or spectrograde quality. Store at 20-25°C in the dark. Do not use concentrated HNO_3 to make up 5.0 M solution if it has a yellow tinge; this is indicative of photoreduction of NO_3^- to NO_2^- , a reducing agent for Cr(VI).

5.2 Sodium carbonate: Na_2CO_3 , anhydrous, analytical reagent grade. Store at 20-25°C in a tightly sealed container.

5.3 Sodium hydroxide: NaOH , analytical reagent grade. Store at 20-25°C in a tightly sealed container.

5.4 Magnesium Chloride: MgCl_2 (anhydrous), analytical reagent grade. A mass of 400 mg MgCl_2 is approximately equivalent to 100 mg Mg^{2+} . Store at 20-25°C in a tightly sealed container.

5.5 Phosphate Buffer:

5.5.1 K_2HPO_4 : analytical reagent grade.

5.5.2 KH_2PO_4 : analytical reagent grade.

5.5.3 0.5M K_2HPO_4 /0.5M KH_2PO_4 buffer at pH 7: Dissolve 87.09 K_2HPO_4 and 68.04 g KH_2PO_4 into 700 mL of reagent water. Transfer to a 1L volumetric flask and dilute to volume.

5.6 Lead Chromate: PbCrO_4 , analytical reagent grade. The insoluble matrix spike is prepared by adding 10-20 mg of PbCrO_4 to a separate sample aliquot. Store under dry conditions at 20-25°C in a tightly sealed container.

5.7 Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in reagent water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25°C and prepare fresh monthly. The pH of the digestion solution must be checked before using. The pH must be 11.5 or greater, if not, discard.

5.8 Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, spiking solution (1000 mg/L Cr(VI)): Dissolve 2.829 g of dried (105°C) $\text{K}_2\text{Cr}_2\text{O}_7$ in reagent water in a one-liter volumetric flask and dilute to the mark. Alternatively, a 1000 mg/L Cr(VI) certified primary standard solution can be used (Fisher AAS standard or equivalent). Store at 20-25°C in a tightly sealed container for use up to six months.

5.8.1 Matrix spiking solution (100 mg/L Cr(VI)): Add 10.0 mL of the 1000 mg Cr(VI)/L made from $\text{K}_2\text{Cr}_2\text{O}_7$ spiking solution (Section 5.8) to a 100 mL volumetric flask and dilute to volume with reagent water. Mix well.

5.9 Reagent Water - Reagent water will be free of interferences. Refer to Chapter One for a definition of reagent water.

6.0. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be collected using devices and placed in containers that do not contain stainless steel (e.g., plastic or glass).

6.3 Samples should be stored field-moist at $4 \pm 2^\circ\text{C}$ until analysis.

6.4 Hexavalent chromium has been shown to be quantitatively stable in field-moist soil samples for 30 days from sample collection. In addition, Cr(VI) has also been shown to be stable in the alkaline digestate for up to 168 hours after extraction from soil.

6.5 Hexavalent chromium solutions or waste material that are generated should be disposed of properly. One approach is to treat all Cr(VI) waste materials with ascorbic acid or other reducing agent to reduce the Cr(VI) to Cr(III). For additional information on health and safety issues relating to chromium, the user is referred to References 10.7 and 10.10.

7.0 PROCEDURE

7.1 Adjust the temperature setting of each heating device used in the alkaline digestion by preparing and monitoring a temperature blank [a 250 mL vessel filled with 50 mLs digestion solution (Section 5.7)]. Maintain a digestion solution temperature of 90-95°C as measured with a NIST-traceable thermometer or equivalent.

7.2 Place 2.5 ± 0.10 g of the field-moist sample into a clean and labeled 250 mL digestion vessel. The sample should have been mixed thoroughly before the aliquot is removed.

For the specific sample aliquot that is being spiked (Section 8.5), the spike material should be added directly to the sample aliquot at this point. (Percent solids determination, U.S. EPA CLP SOW for Organic Analysis, OLM03.1, 8/94 Rev.) should be performed on a separate aliquot in order to calculate the final result on a dry-weight basis).

7.3 Add 50 mL \pm 1 mL of digestion solution (Section 5.7) to each sample using a graduated cylinder, and also add approximately 400 mg of MgCl₂ (Section 5.4) and 0.5 mL of 1.0M phosphate buffer (Section 5.5.3). For analytical techniques that can correct for oxidation/reduction of Cr, the addition of Mg²⁺ is optional. Cover all samples with watch glasses.

7.4 Stir the samples continuously (unheated) for at least five minutes using an appropriate stirring device.

7.5 Heat the samples to 90-95°C, then maintain the samples at 90-95°C for at least 60 minutes with continuous stirring.

7.6 Gradually cool, with continued agitation, each solution to room temperature. Transfer the contents quantitatively to the filtration apparatus; rinsing the digestion vessel with 3 successive portions of reagent water. Transfer the rinsates to the filtration apparatus. Filter through a 0.45µm membrane filter. Rinse the inside of the filter flask and filter pad with reagent water and transfer the filtrate and the rinses to a clean 250-mL vessel.

NOTE: The remaining solids and filter paper resulting from filtration of the matrix spike in Section 7.6 should be saved for possible use in assessing low Cr(VI) matrix spike recoveries. See Section 8.5.2. for additional details. Store the filtered solid at 4 \pm 2°C.

7.7 Place an appropriate stirring device into the sample digest beaker, place the vessel on a stirrer, and, with constant stirring, slowly add 5.0 M nitric acid solution to the beaker dropwise. Adjust the pH of the solution to 7.5 \pm 0.5 if the sample is to be analyzed using Method 7196 (adjust the pH accordingly if an alternate analytical method is to be used; i.e. 9.0 \pm 0.5 if Method 7199 is to be used) and monitor the pH with a pH meter. If the pH of the digest should deviate from the desired range, discard the solution and redigest. If overshooting the desired pH range occurs repeatedly, prepare diluted nitric acid solution and repeat digestion procedure. If a flocculent precipitate should form, the sample should be filtered through a 0.45 µm membrane filter. If the filter becomes clogged using the 0.45 µm filter paper, a larger size filter paper (Whatman GFB or GFF) may be used to prefilter the samples.

CAUTION: CO₂ will be evolved. This step should be performed in a fume hood.

7.8 Remove the stirring device and rinse, collecting the rinsate in the beaker. Transfer quantitatively the contents of the vessel to a 100 mL volumetric flask and adjust the sample volume to 100 mL (to the mark for the volumetric flask) with reagent water. Mix well.

7.9 The sample digestates are now ready to be analyzed. Determine the Cr(VI) concentration in mg/kg by a suitable technique with appropriate accuracy and precision, for example Method 7196 (colorimetrically by UV-VIS spectrophotometry) or Method 7199 (colorimetrically by ion chromatography (IC)). Another analytical technique such as IC with inductively coupled plasma - mass spectrometric (ICP-MS) detection, high performance liquid chromatography (HPLC) with ICP-

MS detection, capillary electrophoresis (CE) with ICP-MS detection, etc. may be utilized once performance effectiveness has been validated.

7.10 CALCULATIONS

7.10.1 Sample Concentration

$$\text{Concentration} = \frac{A \times D \times E}{B \times C}$$

where: A = Concentration observed in the digest ($\mu\text{g/mL}$)
B = Initial moist sample weight (g)
C = % Solids/100
D = Dilution Factor
E = Final digest volume (mL)

7.10.2 Relative Percent Difference

$$\text{RPD} = \frac{(S - D)}{[(S + D)/2]}$$

where: S = Initial sample result
D = Duplicate sample result

7.10.3 Spike Recovery

$$\text{Percent Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

8.1 The following Quality Control (QC) analyses must be performed per digestion batch as discussed in Chapter One.

8.2 A preparation blank must be prepared and analyzed with each digestion batch, as discussed in Chapter One and detected Cr(VI) concentrations must be less than the method detection limit or one-tenth the regulatory limit or action level, whichever is greater or the entire batch must be redigested.

8.3 Laboratory Control Sample (LCS): As an additional determination of method performance, utilize the matrix spike solution prepared in Section 5.8.1 or the solid matrix spiking agent PbCrO_4 (Section 5.6) to spike into 50 mL of digestion solution (Section 5.7). Alternatively, the use of a certified solid reference material (if available) is recommended. Recovery must be within the certified acceptance range or a recovery range of 80% to 120% or the sample batch must be reanalyzed.

8.4 A separately prepared duplicate soil sample must be analyzed at a frequency of one per batch as discussed in Chapter One. Duplicate samples must have a Relative Percent Difference (RPD) of $\leq 20\%$, if both the original and the duplicate are \geq four times the laboratory reporting limit. A control limit of \pm the laboratory reporting limit is used when either the original or the duplicate sample is $<$ four times the laboratory reporting limit.

8.5 Both soluble and insoluble pre-digestion matrix spikes must be analyzed at a frequency of one each per batch of ≤ 20 field samples. The soluble matrix spike sample is spiked with 1.0 mL of the spiking solution prepared in Section 5.8.1 (equivalent to 40 mg Cr(VI)/Kg) or at twice the sample concentration, whichever is greater. The insoluble matrix spike is prepared by adding 10-20 mg of PbCrO_4 (Section 5.6) to a separate sample aliquot. It is used to evaluate the dissolution during the digestion process. Both matrix spikes are then carried through the digestion process described in Section 7.0. More frequent matrix spikes must be analyzed if the soil characteristics within the analytical batch appear to have significant variability based on visual observation. An acceptance range for matrix spike recoveries is 75-125%. If the matrix spike recoveries are not within these recovery limits, the entire batch must be rehomogenized/redigested/reanalyzed. If upon reanalysis, the matrix spike is not within the recovery limits, but the LCS is within criteria specified in Section 8.3, information such as that specified on Figures 1 and 2 and in Section 3.1 should be carefully evaluated. The Cr(VI) data may be valid for use despite the perceived "QC failure." The information shown on Figure 1 and discussed below is provided to interpret ancillary parameter data in conjunction with data on spike recoveries.

8.5.1 First measure the pH (Method 9045) and Oxidation Reduction Potential (ORP) (ASTM Method D 1498-93 - aqueous samples, Method 9045 preparatory for soil samples), in the field if possible. If not possible, the measurements are to be made in the laboratory prior to the determination of the spike recovery data. When and where the measurements are taken must be noted by the analyst. Adjust the ORP measurement based on reference electrode correction factor to yield Eh values. The pH and Eh values should be plotted on Figure 2 in order to give an initial indication of the sample's reducing/oxidizing nature. Upon completion of the analysis of the analytical batch, the LCS should be evaluated. If the LCS is not within 80 - 120% recovery or the certified acceptance range, then the entire analytical batch (plus the QC samples) should be redigested and reanalyzed. If the LCS was within acceptance criteria and the pre-digestion matrix spike recoveries for Cr(VI) were less than the acceptance range minimum (75%), this indicates that the soil samples reduced Cr(VI) (e.g., anoxic sediments), and no measurable native Cr(VI) existed in the unspiked sample (assuming the criteria in Section 8.3 are met). Such a result indicates that the combined and interacting influences of ORP, pH and reducing agents (e.g., organic acids, Fe^{2+} and sulfides) caused reduction of Cr(VI) spikes. Characterize each matrix spike sample for additional analytical parameters, such as ferrous iron (ASTM Method D3872-86), and sulfides (Method 9030). Laboratory measurements of pH and ORP should also be performed to confirm the field measurements. Other indirect indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). Analysis of these additional parameters assists in evaluating the tendency of Cr(VI)

to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria for total metals.

A value of Eh-pH below the bold diagonal line on Fig. 2 indicates a reducing soil for Cr(VI). The downward slope to the right indicates that the Eh value, at which Cr(VI) is expected to be reduced, decreases with increasing pH. The solubility and quantity of organic constituents influence reduction of Cr(VI). The presence of H₂S or other strong odors indicates a reducing environment for Cr(VI). In general, acidic conditions accelerate the reduction of Cr(VI) in soils, and alkaline conditions tend to stabilize Cr(VI) against reduction. If pre-digestion matrix spike recovery is not within the recovery limits, the reductive nature of the sample must be documented. This is done by plotting the Eh and pH data on the Eh-pH diagram (Fig. 2) to see if spike recovery is or is not expected in the soil. If the data point falls below the Cr(VI)-Cr(III) line on the diagram, then the data is not qualified or rejected. The sample is reducing for Cr(VI). If the data point falls above the line, then the sample is capable of supporting Cr(VI). In this case, technical error may be responsible for the poor spike recovery, and the extraction should be repeated, along with the Eh and pH measurements. If re-extraction results in a poor spike recovery again, then the data is qualified. At this point, review of other soil characteristics, such as levels of pH, Eh, TSS, CO₂, sulfides, Fe(II), is appropriate to understand why poor spike recovery occurred. This extra review of these soil properties is only necessary if the unspiked sample contains detectable Cr(VI).

8.5.2 If a low or zero percent pre-digestion matrix spike recovery is obtained, an alternate approach can be used to determine the potential contribution of the sample matrix to Cr(VI) reduction. This approach consists of performing a mass balance, whereby total chromium is analyzed (Method 3052) for two samples: (1) a separate unspiked aliquot of the sample previously used for spiking, and (2) the digested solids remaining after the alkaline digestion and filtration of the matrix spike (i.e., the filtered solids from the matrix spike in Section 7.6).

The difference between the total chromium measurements should be approximately equal to the amount of the spike added to the matrix spike. If the LCS (Section 8.3) meets the acceptance criteria and the Cr(VI) spike is accounted for in the filtered solids as total chromium, it is likely that the reduction of the Cr(VI) to insoluble Cr(III) resulted from the reducing matrix of the original sample subjected to Cr(VI) spiking.

8.6 A post-digestion Cr(VI) matrix spike must be analyzed per batch as discussed in Chapter One. The post-digestion matrix spike concentration should be equivalent to 40 mg/kg or twice the sample concentration observed in the unspiked aliquot of the test sample, whichever is greater.

8.6.1 Dilute the sample aliquot to a minimum extent, if necessary, so that the absorbance reading for both the unspiked sample aliquot and spiked aliquot are within the initial calibration curve.

8.6.2 A guideline for the post-digestion matrix spike recovery is 85-115%. If not achieved, consider the corrective actions/guidance on data use specified in Section 8.5 or the Method of Standard Additions (MSA) as specified in Section 8.0 of Method 7000. If the MSA technique is applied post digestion and no spike is observed from the MSA, these results indicate that the matrix is incompatible with Cr(VI) and no further effort on the part of

the laboratory is required. These digestates may contain soluble reducing agents for Cr(VI) such as fulvic acids.

9.0 METHOD PERFORMANCE

9.1 A commercial laboratory analyzed soil/sediment samples containing Cr(VI) with the results found in Table 1.

10.0 REFERENCES

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10.14 ASTM (American Society for Testing and Materials), 1981. Standard Test Method for Shake Extraction of Solid Waste with Water. ASTM Designation:D3987-85.

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TABLE 1
SINGLE LABORATORY METHOD EVALUATION DATA

<u>Sample Type</u>	<u>Eh (mV)_b</u>	<u>pH_d</u>	<u>S²⁻ (ppm)^c</u>	<u>Mean Native, Cr(VI) Conc. (mg/kg)</u>	<u>Mean Cr(VI) Spike Conc. (mg/kg)</u>	<u>Matrix Spike Recovery Range, %</u>
COPR ^a /Soil Blends	550	7.4	<10.0	4.1	42.0	89.8-116
Loam	620	6.4	<10.0	ND	62.5	65.0-70.3
Clay	840	3.0	<10.0	ND	63.1	37.8-71.1
COPR ^a	460	7.4	<10.0	759	813	85.5-94.8
Anoxic Sediment	-189	7.2	25.0	ND	381	0
Quartz Sand	710	5.3	<10.0	ND	9.8	75.5-86.3

Source: Reference 10.3

Notes:

- ND - Not detected
- a - COPR - chromite ore processing residue
- b - Corrected for the reference electrode, laboratory field moist measurement
- c - Field measurement
- d - Laboratory field moist measurement

FIGURE 1
QUALITY CONTROL FLOW CHART

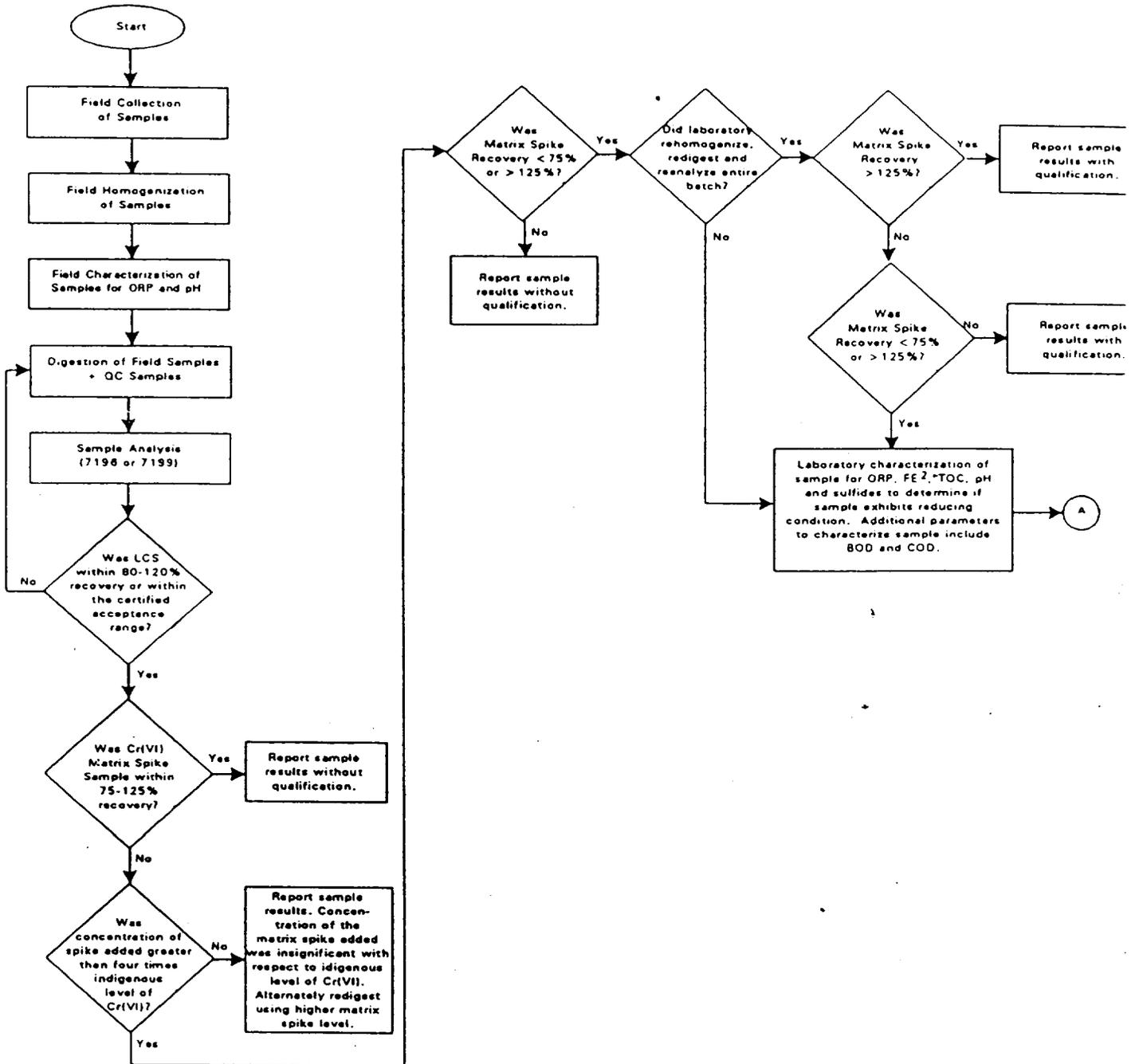


FIGURE 1
QUALITY CONTROL FLOW CHART (Continued)

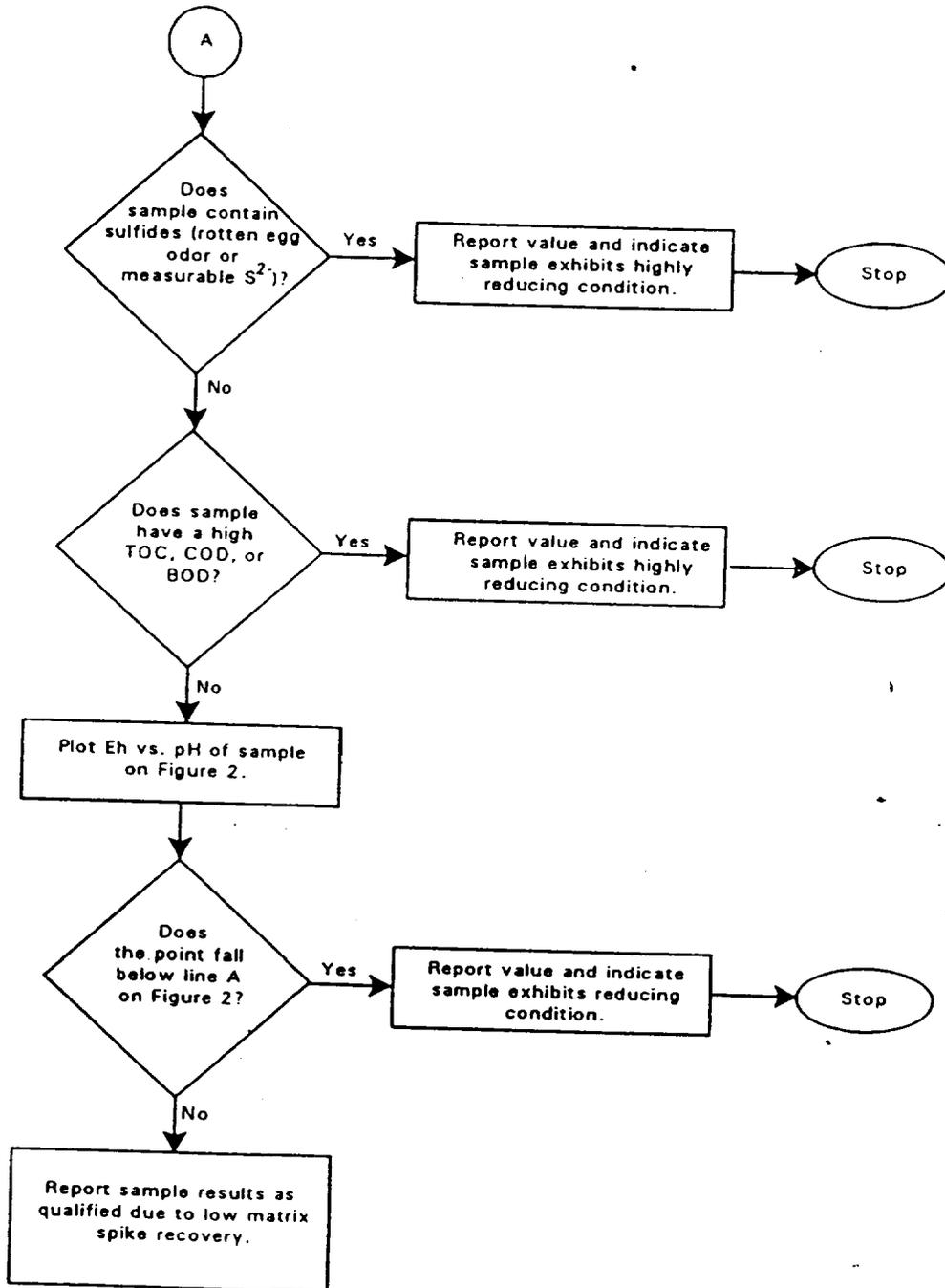
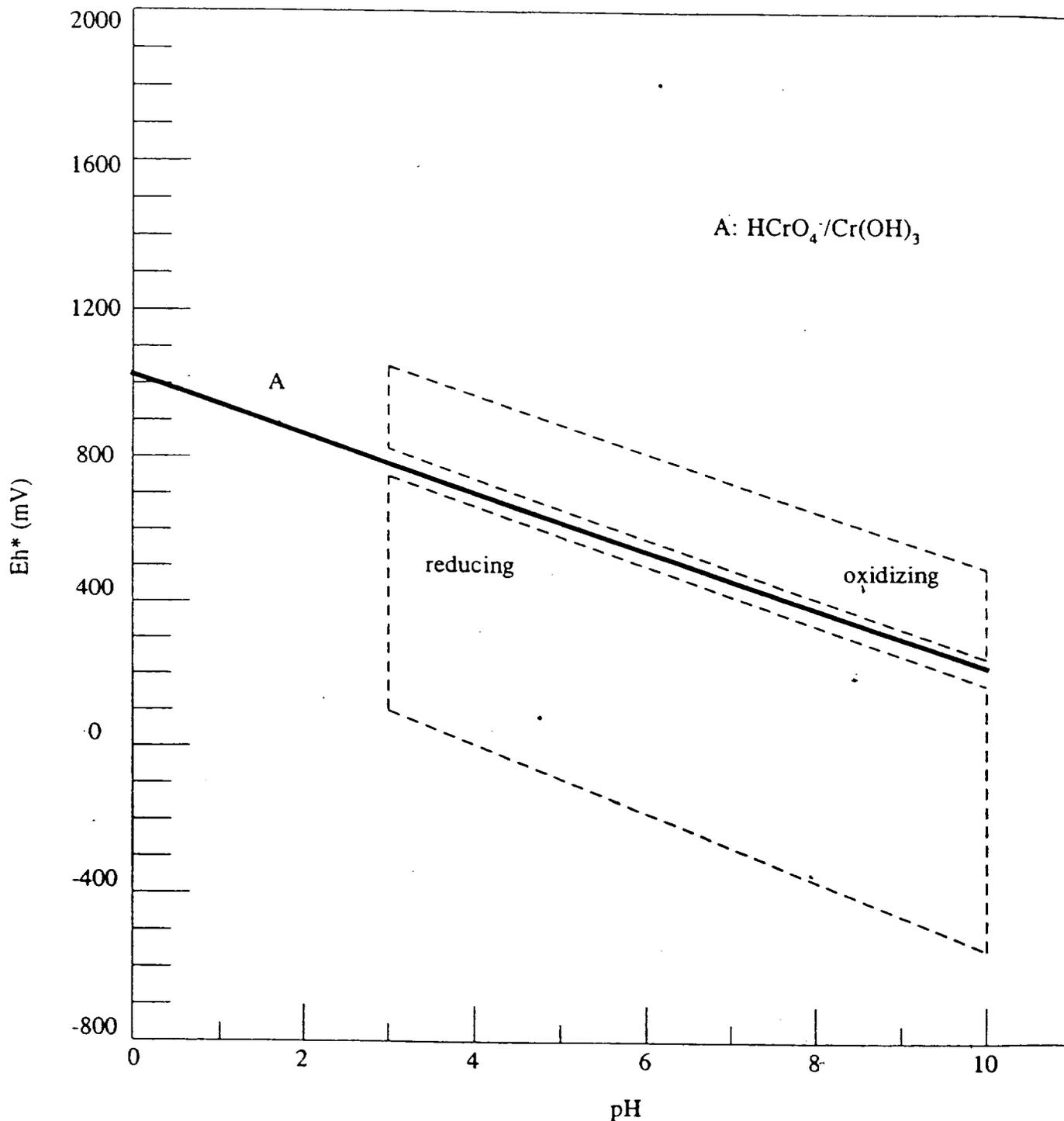


FIGURE 2
Eh/pH PHASE DIAGRAM

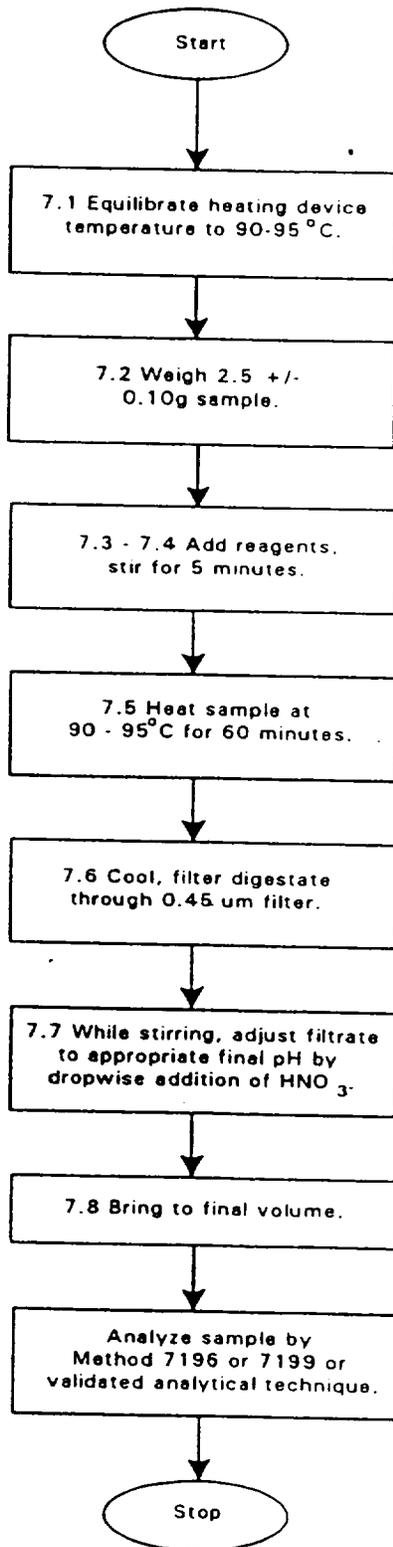
The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

METHOD 3060A

ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM



CHAPTER 15

Chromium Speciation Analysis in Soils/Sediments - Zero Percent Matrix Spike Recoveries May Not Equal Unreliable Data

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BACKGROUND

Under current environmental investigations, total chromium is among the heavy metals on the U.S. Environmental Protection Agency's (USEPA's) target analyte list examined in soil/sediment samples. However, because of the significant difference in toxicity between trivalent (III) and hexavalent (VI) chromium, it is essential to evaluate these individual species during risk assessment and subsequent remediation. Recent advances in soil/sediment sample preparation and analytical techniques have enabled investigators to successfully differentiate between these two chromium species (Vitale et al., 1993). While the preparation and analysis of predigestion matrix spikes has traditionally provided analytical chemists with an indication of data quality for total metal analyses, this quality control (QC) technique has limited utility for chromium speciation analysis, specifically for the analysis of Cr(VI).

The use of SW-846 Method 3060A, an alkaline digestion procedure for the determination of Cr(VI) in soils, recently proposed in the latest update of SW-846, has been documented to be an effective technique for the analysis for soluble and insoluble forms of Cr(VI) (James et al., 1995; Vitale et al., 1995a). In certain soils/sediments that have highly reducing properties, chromium exists exclusively in the Cr(III) species. The matrix spiking of such soils/sediments with Cr(VI) is predicted to yield a zero percent recovery. Traditionally, such recoveries would have been interpreted as an indication that the resultant data are unreliable. Hence, when such recoveries are observed, it is critical that the redox characterization of the sample be determined so that the quality control information can be correctly interpreted.

SW-846 Method 3060A includes algorithms to assist the data user with interpretation of QC analysis results. The topic of this chapter is the discussion and interpretation of actual field sample Cr(VI) quality control data through the use of redox indicators as applied to SW-846 Method 3060A.

INTRODUCTION

SW-846 Proposed Method 3060A (Vitale et al., 1995) is an alkaline digestion method for extracting hexavalent chromium from soils, sediments, and solid wastes. This method is of significance because of the differences in toxicity between Cr(III) and Cr(VI). Cr(VI) is a human carcinogen (via inhalation) and Cr(III) is an essential dietary element for humans (Anderson, 1989; IRIS, 1993; Paustenbach et al, 1991). Method 3060A utilizes a hot alkaline solution containing 0.28 M Na_2CO_3 /0.5 M NaOH 0.28 M Na_2CO_3 to solubilize both sparingly-soluble and water-soluble Cr(VI) compounds in solid samples (James et al, 1995; Vitale et al., 1995a; Vitale et al., 1995b). Once Cr(VI) is solubilized, the digest is analyzed by adding a diphenylcarbazide (DPC) solution in acetone, and adjusting the solution to pH 2 using sulfuric acid. The Cr(VI) reacts with the DPC to produce a red-violet complex, and its absorbance is measured spectrophotometrically at 540 nm. This analytical method is designated as SW-846 Method 7196A (USEPA, 1992). An additional analytical technique (SW-846 Method 7199) using ion chromatography with a post-column reaction provides an alternative to the manual method referenced.

In order to determine the reliability of the extraction procedure, predigestion matrix spike recovery data is one quality control measure that is evaluated. Traditional interpretation of predigestion matrix spike recoveries was such that if the matrix spike recovered well (i.e., within 80-120%), then this was an indication that the analytical method was performing well. Conversely, (in the traditional interpretation of matrix spike recoveries), if the spike recovery was not within 80-120%, then this was an indication of an analytical bias. One of the major points of this chapter is to demonstrate that poor predigestion matrix spike recoveries for the analysis for Cr(VI) in soils/sediments may not necessarily be indicative of a deficiency in the analytical method.

Certain reducing sample types (e.g., anoxic sediments) cannot support chromium in the hexavalent state, regardless of whether the hexavalent chromium was added in the natural field conditions or during the chemical analysis. A major portion of SW-846 Proposed Method 3060A is the assessment of ancillary parameters in order to determine whether or not a sample type exhibits the ability to maintain chromium in the hexavalent valance state. The following ancillary parameters aid in this characterization of a sample: pH, oxidation reduction potential (ORP), total sulfides, total organic carbon (TOC), biological oxygen demand (BOD), and chemical oxygen demand (COD). The analysis of the aforementioned parameters establishes a better understanding of the

tendency of Cr(VI) to exist in the unspiked sample, and assists in the interpretation of quality control data for predigestion matrix spike recoveries.

RESULTS AND DISCUSSION

The analysis of ancillary parameters in Method 3060A is designed to help interpret variable recoveries of Cr(VI) predigestion matrix spikes. Collectively, the following parameters play an important role in determining whether or not the soil is reducing in nature and thus, if the sample can sustain Cr(VI) in the hexavalent oxidation state.

pH

In general, soil samples need to be alkaline in nature ($\text{pH} > 7.0$) in order to sustain chromium in the hexavalent state. It appears that the higher the pH of the soil, the less likely the Cr(VI) will be reduced to Cr(III). Based on the data evaluated, those spike samples with pH values < 7.0 tend to exhibit lower spike recoveries.

ORP

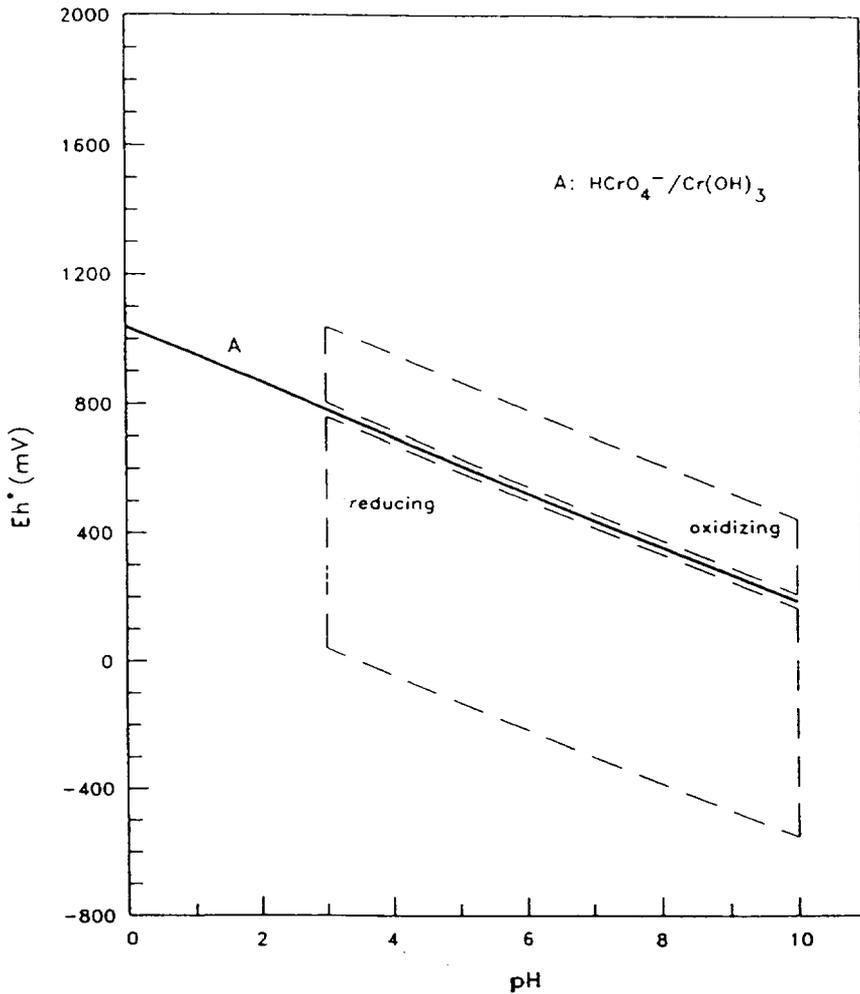
Generally, the larger the negative oxidation reduction potential (ORP) value, the stronger the reducing environment. In addition, the more positive the ORP, the greater the tendency Cr(VI) can be sustained in the soils; thus, the better the possibility of obtaining "acceptable" predigestion matrix spike recoveries. Similarly, negative ORP readings exhibit like degrees of reducing capacity, comparable to their positive value counterparts. As shown in the Eh/pH diagram (Figure 1), a reducing environment may exist at a high pH (10) if the ORP value is between -600 mV and 0 mV. (NOTE: A value of 199 mV was subtracted from the Eh values on Figure 1 in order to convert the measurement to an ORP reading). In addition, a reducing environment can occur at higher ORP values ($-+300$ mV), provided the pH of the soil is acidic (~ 4.0).

TOC

Chromium may exist in a number of oxidation states; however, they are not all of the same stability. As shown in the reduction potential diagram for chromium (Figure 2), the reduced form is favored when positive values are observed for the standard electrode potential (E°), whereas the oxidized form is relatively stable when negative values are obtained for the standard electrode potential. Since considerable energy would be required to convert Cr(III) to lower or higher oxidation states, Cr(III) is the most stable form of chromium in solution at acidic pHs. Although CrO_4^{2-} (a hexavalent form of chromium) is relatively stable, its high positive reduction potential denotes that it is strongly oxidizing and is unstable in an acid solution, as well as in the presence of organic molecules with oxidizable groups (alkanes, alkenes, alcohols, aldehydes, ketones, carboxylic acids, etc.). Therefore, the greater the levels of total organic carbon (TOC) in the soil, the more

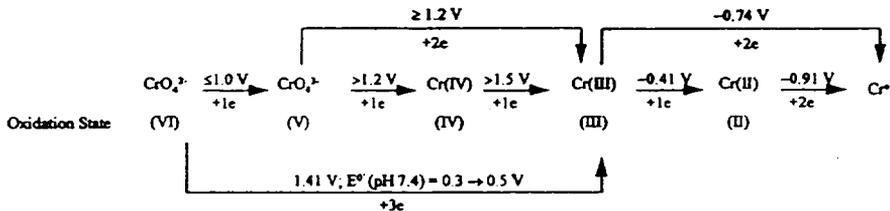
Figure 1. Eh/pH Phase Diagram

The dashed lines define Eh - pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

Figure 2. Reduction potential diagram for Chromium.



likely the hexavalent chromium will be reduced to trivalent chromium (*Chromium in the Natural and Human Environments*, 1988a).

Sulfides

The presence of sulfides in soils is a strong indicator that the soil is reducing in nature. A water-soluble reagent such as sodium sulfide can reduce hexavalent chromium and precipitate it to chromium hydroxide. This reduction seems to occur in nature when a secondary metal is present, such as iron. One method that is used by wastewater treatment plants for removing heavy metals (i.e., chromium) from water samples, is through sulfide precipitation (*Chromium in the Natural and Human Environments*, 1988b).

BOD

Biochemical oxygen demand (BOD) is an empirical analytical procedure which measures the dissolved oxygen consumed by microbial life while absorbing and oxidizing the organic matter present in a sample. It is expressed as the quantity of dissolved oxygen required during stabilization of the decomposable organic matter by aerobic biochemical action (Lewis, 1993). Therefore, the greater the levels of BOD, the greater the levels of organic matter, and the more likely Cr(VI) can be reduced.

COD

Chemical oxygen demand (COD) is designed to determine the amount of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time. Because the test utilizes a specific chemical oxidation, the result has no definite relationship to the BOD or TOC of the sample. The greater the levels of COD, the higher the levels of organic matter, and the less likely Cr(VI) will remain in the +6 oxidation state.

If numerous indicators are observed for a reducing environment for a given sample, poor Cr(VI) predigestion matrix spike recoveries are predicted to be the result of soil reduction, and not representative of a method-induced reduction or technical error. The characterization of the above parameters is essential in establishing the sample's oxidation/reduction environment.

Discussion of Eh/pH

The following discussion will refer to the data presented in Table 1. Plotting Eh/pH ancillary parameter data for samples S-01-1, S-01-2, and S-01-3 demonstrated how additional field data aid in interpreting Cr(VI) pre-digestion matrix spike recoveries. When the Eh value for sample S-01-1 is plotted against the pH value for this sample, the result falls in the reducing area on Figure 1. Low recoveries were observed for both the low-level predigestion matrix spike (0%) and high-level pre-digestion matrix spike (15%) samples analyzed for Cr(VI) for sample S-01-1. When the Eh value for sample S-01-2 is plotted against

the pH value for this sample, the result again falls in the reducing area on Figure 1. This result (alone) would indicate the presence of a reducing soil. However, the recoveries for both the low-level predigestion matrix spike (97%) and high-level predigestion matrix spike (98%) that were observed for hexavalent chromium in sample S-01-2 would indicate that Cr(VI) was not reduced to Cr(III) (these recoveries were within the traditional acceptance range of 80 - 120 %). When the Eh value for sample S-01-3 is plotted against the pH value for this sample, the result falls in the oxidizing area on Figure 1. This would indicate that reducing characteristics do not appear to be present in this sample. Again, the low-level and high-level predigestion matrix spike recoveries (97%, 97%) observed for the Cr(VI) analysis of sample S-01-3 were within the traditional acceptance range of 80%-120% and confirmed the nonreducing soil type.

The Eh/pH diagram (Figure 1) indicates that sample S-01-2 would be a reducing sample matrix; however, "traditionally acceptable" predigestion matrix spike recoveries were observed for this sample. The plot of Eh/pH is a good first indicator of the oxidation/reduction potential of a sample; however, the additional ancillary parameters must be evaluated to further clarify the sample's potential for oxidation/reduction of Cr(VI). The use of any one of the ancillary parameters alone may not be sufficient to characterize the oxidation/reduction potential of a sample type.

Discussion of Additional Data

Based on the data evaluated, recoveries within the traditional acceptance ranges were observed for the low-level predigestion, high-level predigestion and postdigestion matrix spikes for samples S-01-2 and S-01-3 analyzed for hexavalent chromium. The ancillary data collected were successful in the prediction that "acceptable" recoveries should have been obtained, even though sample S-01-2 indicated a reducing sample matrix and sample S-01-3 indicated an oxidizing sample in their respective Eh/pH plots on Figure 1. Low levels of TOC and COD indicate that these samples are low in organic matter. In addition, BOD was not detected in the samples. These data indicate that Cr(VI) can be stable under these conditions, and that one could expect to observe "acceptable" recoveries of Cr(VI) added to a sample matrix. The plot of sample S-01-2 on Figure 1 was close to the cross-over threshold for an oxidizing/reducing environment. Because of this proximity to the cross-over threshold, the additional ancillary parameter data was instrumental in further characterization of sample S-01-2 as an oxidizing sample matrix.

In the traditional interpretation of matrix spike data, poor recoveries were observed for the low-level and high-level matrix spikes for sample S-01-1 analyzed for hexavalent chromium. As seen in Table 1, high levels of TOC, COD, and BOD were observed in the sample, indicating high levels of organic matter present in the sample. In addition, the ORP and pH values measured for sample S-01-1 indicate that the sample is reducing in nature. These data are indicative

of reducing tendencies of the soil type, and therefore Cr(VI) may not be sustainable. These additional parameters were utilized to predict that native Cr(VI) cannot be present in sample S-01-1. Unlike samples S-01-2 and S-01-3, sample S-01-1 had high levels of organic matter and an ORP that would indicate that the sample would reduce Cr(VI) to Cr(III) regardless of whether the source of the Cr(VI) was from an environmental source, or if the Cr(VI) was added to the sample matrix in the laboratory. Figure 3 graphically interprets the differences observed in the oxidation/reduction capacities, as well as the organic content of samples S-01-1, S-01-2, and S-01-3.

Example of How Ancillary Data Is Interpreted

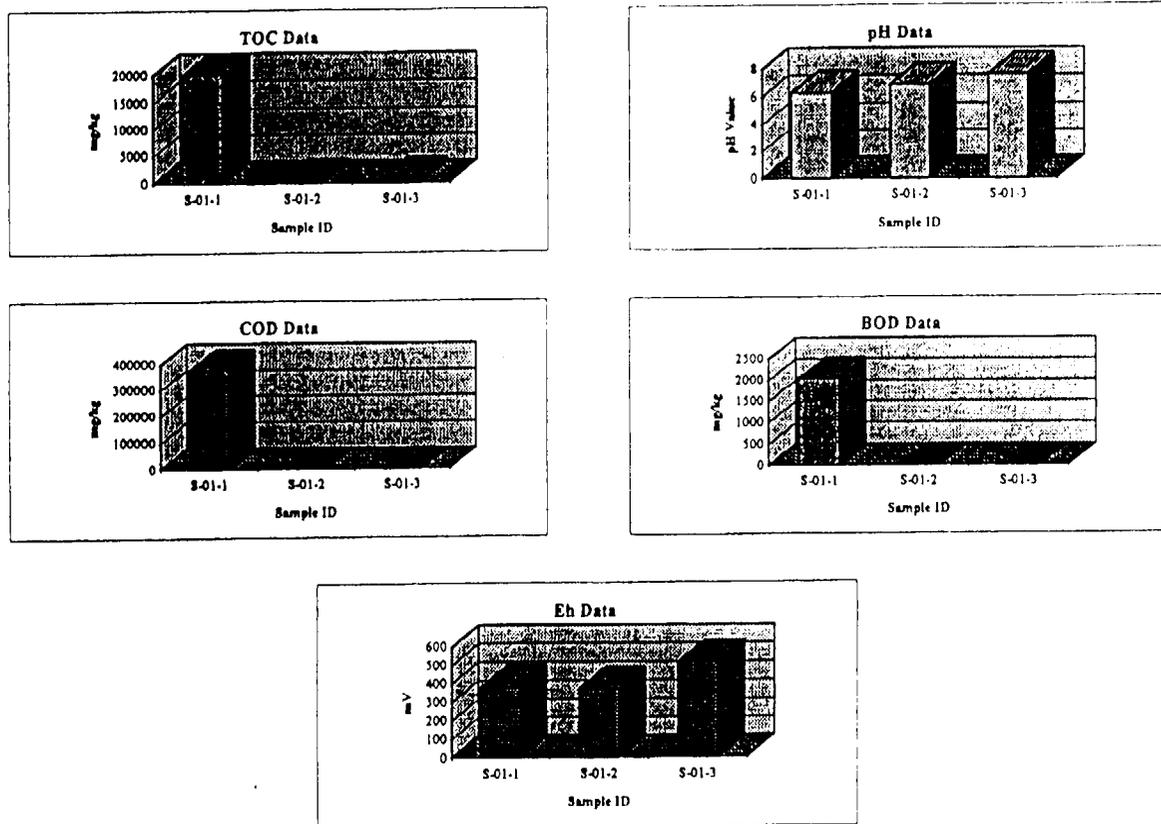
Since Cr(VI) does not readily exist in reducing samples in the field or during chemical analysis, it is clear that the ancillary parameter data noted herein will aid in the interpretation of the predigestion matrix spike recovery data. For example, if the predigestion matrix spike recovery is less than the traditional acceptable limits of 80%-120%, then the ancillary data need to be assessed. The predigestion matrix spike recovery data for Cr(VI), in conjunction with the ancillary data of the soil, will aid data users in the understanding of the soil chemistry, and aid in the development of an explanation for any reduction of Cr(VI) under field conditions and during chemical analysis.

In assessing the characteristics of samples, it is necessary to determine whether the soil type has reducing propensities: the pH and ORP values should be within the reducing dashed lines as seen in Figure 1, high levels of TOC, COD, and BOD may be observed, and the soil may contain some level of sulfides. It should be noted that each of these parameters by themselves cannot definitively determine whether or not the sample is reducing (as demonstrated by sample S-01-2). The ancillary parameters must be evaluated collectively to give a better understanding of the chemical properties of the soil.

Table 1. Soil Sample Characterization

SDG	Sample ID	Percent Moisture	TOC (mg/kg)	COD (mg/kg)	BOD (mg/kg)	pH	Eh (mV)	Cr(VI) (mg/kg)	Cr(VI) QC Results
SDG 1	S-01-1	79.7	20000	377000	2040	6.28	380	N.D.	-
	S-01-1DUJ	76.7	30000	381000	2320	6.13	370	N.D.	-
	S-01-1UMS	76.7	-	-	-	-	-	N.D.	0.0%
	S-01-1HMS	76.7	-	-	-	-	-	250	15.0%
	S-01-1PDS	76.7	-	-	-	-	-	1570	91.0%
SDG 2	S-01-2	19.2	200	1600	N.D.	6.85	370	N.D.	-
	S-01-2DUJ	19.2	160	1600	N.D.	7.05	390	N.D.	-
	S-01-2LMS	19.2	-	-	-	-	-	48	97.0%
	S-01-2HMS	19.2	-	-	-	-	-	486	98.0%
	S-01-2PDS	19.2	-	-	-	-	-	198	100.0%
SDG 3	S-01-3	21.3	550	1800	N.D.	7.61	510	N.D.	-
	S-01-3DUJ	21.3	420	2300	N.D.	7.58	530	N.D.	-
	S-01-3LMS	21.3	-	-	-	-	-	49	97.0%
	S-01-3HMS	21.3	-	-	-	-	-	492	97.0%
	S-01-3PDS	21.3	-	-	-	-	-	200	98.0%

Figure 3. Ancillary Parameter Data.



CONCLUSION

It is to be concluded that zero or low predigestion matrix spike recoveries do not necessarily mean the data obtained are unreliable. Ancillary parameter data need to be evaluated to determine if the sample type is reducing in nature and cannot support Cr(VI), either in the natural environment or after being spiked into a sample by a laboratory. If reducing conditions are observed (high levels of TOC, BOD, COD and/or sulfides, acidic pH, negative ORP values), and other quality control samples such as a laboratory control samples (*viz.*, blank spikes) are acceptable, then the data should be viewed as acceptable for use.

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Hexavalent Chromium Extraction from Soils: Evaluation of an Alkaline Digestion Method

R. J. Vitale, G. R. Mussoline, J. C. Petura,* and B. R. James

ABSTRACT

The accurate quantification of total Cr(VI) in soils is relevant to human health concerns because Cr(VI) is significantly more toxic than Cr(III). Hot alkaline solution has been shown to extract soluble and insoluble forms of Cr(VI) from soils, but incomplete recovery of Cr(VI) spikes and the oxidation of soluble Cr(III) spikes in certain soils have been suggested as method deficiencies. A laboratory method study was performed to (i) test the method's accuracy, (ii) understand the soil chemical processes responsible for poor Cr(VI) spike recoveries, and (iii) develop definitive interpretations for Cr(VI) spike recovery data. Test results for >1500 field soil samples and the method study of eight diverse soil materials demonstrated dissolution of soluble and insoluble Cr(VI) spikes and the method's reliability for Cr(VI) characterization. Complete dissolution of K_2CrO_4 , $BaCrO_4$, and $PbCrO_4$ spikes confirmed the extraction of soluble and insoluble Cr(VI) forms. Ancillary soil chemical parameters, including oxidation-reduction potential (ORP) (reported herein as E_h), pH, S^{2-} , and total organic C were quantified and interpreted to explain poor Cr(VI) spike recoveries. Highly reducing samples yielded 0% Cr(VI) spike recoveries, as predicted from E_h -pH relationships, and unspiked soil samples contained no detectable Cr(VI). In soils containing Cr(VI) and in most aerobic soils without native Cr(VI), acceptable Cr(VI) spike recoveries were obtained. Ancillary parameter characterization demonstrated that strongly reducing samples cannot maintain Cr(VI) laboratory matrix spikes. Correct interpretation of poor Cr(VI) spike recovery data should avoid labeling these data as unacceptable method results without ancillary parameter characterization of such samples.

AN ACCURATE AND PRECISE METHOD for extracting and analyzing Cr(VI) from soils, sediments, and waste materials is needed because of human and ecological concerns related to Cr(VI) in the environment (Eisler, 1986; Nieboer and Jusys, 1988; Sheehan et al., 1991; WHO, 1988). A lack of regulatory agency-approved methods for Cr(VI) has prevailed since 1986, when a U.S. Environmental Protection Agency (USEPA) research study did not achieve consistent results with Method 3060, an alkaline digestion procedure for solid samples (USEPA, 1984a; USEPA, 1986). Subsequently, the method was removed from the USEPA manual *Test Methods for Evaluating Solid Wastes*, SW-846, 3rd ed. (USEPA, 1990a). The research report concluded that "the stability of the chromium oxidation state once solubilized in either acid or base media is matrix dependent and cannot be predicted in environmental samples" (USEPA, 1986).

The removal of Method 3060 as an acceptable method is important because of the significant difference in toxicity between Cr(VI) and Cr(III): Cr(VI) is a human carcinogen (via inhalation), and Cr(III) is an essential dietary

element for humans and other mammals (Eisler, 1986; Anderson, 1989; USEPA, 1993). Thus, a reliable method is needed to distinguish these valence states of Cr, and to quantify total Cr(VI) in soil matrices. There are several USEPA-approved methods to differentiate between the Cr(III) and Cr(VI) in solution (e.g., the diphenylcarbazide colorimetric method [Method 7196A] and ion chromatography [Method 7199]), and to analyze aqueous samples and soil digests for total Cr using atomic absorption or inductively coupled plasma (ICP) atomic emission spectroscopy (USEPA, 1983, 1990a). For the determination of total Cr(VI) in solid media, however, there are only recently developed techniques available that are not applicable to soils, such as ASTM Method D5281-92 (ASTM, 1992) for collecting airborne particulate matter in an alkaline impinger solution with analysis by ion chromatography/visible absorption spectroscopy.

Method 3060 is a procedure for digesting solid samples in a hot, alkaline (pH 12) solution containing 0.28 M Na_2CO_3 and 0.5 M NaOH that solubilizes both soluble and insoluble Cr(VI) compounds (James, 1994). Once Cr(VI) is in solution, the digest is analyzed by adding a diphenylcarbazide (DPC) solution in acetone, and adjusting the solution to pH 2 using H_2SO_4 . The Cr(VI) reacts with DPC, which is highly selective for Cr(VI), to produce a red-violet complex, and its absorbance is measured spectrophotometrically at 540 nm. This analytical method is designated Method 7196A, an approved method in SW-846, 3rd ed. (USEPA, 1990a). The use of DPC for measuring Cr(VI) has been known and in use for almost a century (Cazeneuve, 1900). Ion chromatography coupled with postcolumn DPC chemical reaction provides an acceptable alternate methodology for measuring Cr(VI) in the alkaline digest (SW-846, Method 7199) (USEPA, 1990a).

Over the past several years, modifications of Method 3060 have been made to enhance the efficiency of the digestion process, both in terms of the time required and consistency needed for accurate and precise analytical data for quality control purposes. These modifications have included reducing the soil sample weight, and decreasing the sample weight/digest volume ratio, as well as several other changes (Table 1). The achievement of acceptable spike recoveries as specified in Table 1 in most nonreducing soils has established the reliability of the method. Minor modifications, which do not alter the basic chemistry of Methods 3060 and 7196A, evolved from analyzing >1500 diverse, field soil samples for total Cr(VI), ranging from anoxic sediments to chromite ore processing residue (COPR), representing a wide

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Abbreviations: USEPA, U.S. Environmental Protection Agency; ORP, oxidation-reduction potential; ICP, inductively coupled plasma; DPC, diphenylcarbazide; COPR, chromite ore processing residue; TOC, total organic carbon; RSD, relative standard deviation.

Table 1. Differences between Modified Methods 3060/7196A and Methods 3060/7196A.

Item	Method 3060†	Modified Method 3060
Sample weight (wet)	100 g	2.5 g
Alkaline digest solution volume	400 mL	50 mL
Final digest volume	1000 mL	100 mL
Digestion temperature	Near boiling	90-95°C
Digestion time	30-45 min	60 min
Nitric acid acidification	pH 7-8	pH 7-8, but if <7, discard digestate and start over
Item	Method 7196A‡	Modified Method 7196A
Volume used for analysis	95 mL	45 mL
Amount of diphenylcarbazide (DPC) added	2.0 mL	1.0 mL
Acidification with H ₂ SO ₄	pH to 1.5-2.5	pH 1.6-2.2
Turbidity	Subtract absorbance observed before DPC addition from absorbance after DPC addition	Same as 7196A, plus filter through 0.45 µ or 0.1 µ membrane
Initial calibration	0.5-5.0 mg L ⁻¹	0.05-2.0 mg L ⁻¹
Continuing calibration	After every 15 samples	After every 10 samples
Blanks	One per batch, maximum 20 field samples	One preparation blank per batch. Reagent blank after every continuing calibration
Spike duplicate	Every 10 samples (postdigestion) with 85-115% acceptance criterion	A duplicate every 20 samples. A predigestion spike (75-125%) and a postdigestion spike (85-115%)
Laboratory control sample (LCS)	None mentioned	One LCS per 20 samples with acceptance criterion 80-120%

† As appeared in the 2nd ed. of SW-846.

‡ As appears in SW-846 3rd ed.

range of Cr(VI) (<3-16 000 mg kg⁻¹) and total Cr (7-31 000 mg kg⁻¹) concentrations.

New ideas, however, have been adopted by the authors to interpret matrix spike results, and to evaluate the potential for method-induced oxidation of Cr(III) or reduction of Cr(VI) in a particular soil sample during analysis. For the >1500 field sample analyses, acceptable Cr(VI) spike recoveries (75-125%) were obtained in many soils containing Cr(VI) (i.e., nonreducing soils), but low or 0% recoveries were obtained in anoxic sediment samples and those with high organic matter and/or low pH. As a result, questions arose as to the interpretation of spike recovery data when Cr valence speciation was the goal. These questions included: (i) Was Cr(III) oxidized in the procedure, as suggested in the USEPA study (1986)?, (ii) Was Cr(VI) reduced in the alkaline extracting solution during the digestion process?, and (iii) Did poor spike recovery mean *method failure* or simply reduction of the Cr(VI) spike by the soil sample? Based on the results obtained from the aforementioned testing of field samples, a laboratory method study was performed to address the above questions and to establish the applicability of Method 3060 to multiple soil types

representing a range of total Cr and Cr(VI) levels, organic matter contents, and pH.

Because Cr(VI) may not persist in reducing samples in the field or during chemical analysis, we hypothesized that these redox-indicating ancillary parameters would aid in interpreting spike recovery data: pH, ORP, S²⁻, and total organic C (TOC). If recovery of a Cr(VI) spike is less than a specified level, then these ancillary redox data (most obtained in the field) would be assessed. We hypothesized that spike recovery data for Cr(VI), in conjunction with ancillary data on redox status of the soil, would aid in understanding the properties of a soil that explain solubility and reduction of Cr(VI) under field conditions and during chemical analysis.

MATERIALS AND METHODS

Soil Sample Collection and Preparation

The study was divided into three segments following the field sampling of soils: (i) sample homogenization; (ii) alkaline digestion with spiking studies using Cr(VI) and Cr(III), and (iii) a mass balance study to determine the fate of Cr(VI) and Cr(III) spikes with respect to potential Cr oxidation and reduction. The selected sample types ranged from quartz sand, with low levels of total Cr, to COPR, waste from a high-temperature roasting process used to produce Na₂CrO₄ and other related materials from FeCr₂O₄ (Austin, 1984). The individual source samples selected were: (i) quartz sand, (ii) loam soil, (iii) Woodbury clay, (iv) low-Cr COPR, (v) high-Cr COPR, and (vi) an anoxic sediment. The low- and high-Cr COPR were tested both in their field-moist conditions and after drying and sieving to determine if drying caused Cr(VI) reduction (Puls et al., 1992). The drying of field-moist soils has been shown to have significant effects on the redox behavior of the soils (Bartlett and James, 1980). Because this facet was added to the method study design after the initial COPR samples had been collected, the field-moist samples were collected at a different time (same location) than were the air-dried COPR samples. A ninth sample matrix, soluble Cr(III)-spiked quartz sand, was used to address the potential oxidation of Cr(III) to Cr(VI) during alkaline digestion. The 10th sample matrix, quartz sand spiked individually with sparingly soluble BaCrO₄ and PbCrO₄, was included to ascertain the efficacy of the modified extraction method to solubilize insoluble forms of Cr(VI).

The quartz sand was purchased at a garden center in Jersey City, Hudson County, New Jersey, and had the characteristics of fine to medium, reddish-brown sand (2.5 YR 5/4). The loam soil was collected at a residential excavation site (0.3-0.6 m depth composite) in Lopatcong Township, Warren County, New Jersey, designated as Washington series (deep, well-drained soil consisting of reddish-brown [2.5 YR 3/4] fine-loamy, mixed, mesic Ultic Hapludalfs [USDA, 1979]). The Woodbury clay sample originated from the excavated face (0.3-1.8 m depth composite) of a geologic formation of sediments deposited under shoaler inner shelf conditions during the Late Cretaceous period. It was light to dark gray (10 YR 6/1), micaceous, chloritic, silty clay with minor amounts of glauconite, siderite, and lignite (Manspeizer, 1980).

The low- and high-Cr COPR samples were obtained from a former chromite ore processing facility, and contained varying amounts of silt, clay, and sand, varying in color from grayish brown (10 YR 6/2) to reddish-brown (5 YR 5/3). The anoxic sediment sample originated from tidal New Jersey marshlands, and contained black silt (2.5 YR N2.5/0) with minor amounts

of fine sand, noticeable decaying organic matter, and the odor of H₂S.

Bulk samples were collected in the field from preselected locations and placed in precleaned sample tubs. The samples were labeled and packed in ice for shipment to the analytical laboratory, where they were stored at $4 \pm 2^\circ\text{C}$. The ORP and pH were measured in the field using precalibrated instruments with platinum and glass electrodes, respectively (Stumm and Morgan, 1981). Sulfide measurements were obtained in the field via headspace analysis using Sensidyne hydrogen sulfide-specific detector tubes (Sensidyne, 1991).

Homogeneity Procedures

The homogenization process involved drying (except the field-moist samples) and sieving each sample type through a 4-mm sieve, followed by splitting each sample type into four batches, and thoroughly mixing the sample by cone and quartering (ASTM, 1987). Homogenization was performed to reduce potential confounding spike recovery results due to sample inhomogeneity. An acceptance criterion of 20% relative standard deviation (RSD) was used as a quality control guideline for establishing and documenting homogeneity, based on previous experience in testing a wide variety of well-mixed, homogeneous soils and other environmental solid samples for metals content, and based on its use for determining precision on a single digest for graphite furnace atomic absorption analysis in the USEPA contract laboratory program (USEPA, 1990a).

Alkaline Digestion

The soil samples were prepared, extracted, and analyzed for Cr(VI) using a modification of the alkaline digestion method, which solubilizes both insoluble and soluble Cr(VI) (USEPA, 1984b). Fifty milliliters of digestion solution (0.28 M Na₂CO₃-0.5 M NaOH) were added to 2.5-g samples of soil in 250-mL Pyrex beakers. The soil suspensions were stirred at room temperature ($25 \pm 2^\circ\text{C}$) for at least 5 min, and then heated to maintain 90 to 95°C with constant stirring for 60 min. After gradually cooling to room temperature, the digestates were filtered through 0.45- μ cellulosic or polycarbonate membrane filters, adjusted to pH 7.5 ± 0.5 using concentrated fresh HNO₃, and diluted with water to a final volume of 100 mL.

Color development and measurement were performed using Modified Method 7196A (USEPA, 1990a), with a calibration range of 0 to 2.0 mg Cr(VI) L⁻¹ and a detection limit of 0.01 mg L⁻¹. To 45 mL of the digestate, 1.0 mL of DPC solution was added, followed by 1.8 M H₂SO₄ addition to a pH of 2.0. After effervescence ceased, the digestate was quantitatively diluted to 50 mL with water, allowed to stand 5 to 10 min, and the absorbance was measured at 540 nm. If the sample was turbid after adding the DPC, it was filtered using a 0.45- μ membrane, and if visually turbid thereafter, it was refiltered using a 0.1- μ membrane filter. Analytical reagent grade materials and Type I water were employed for the method study.

Total S²⁻ analyses were performed using Method 9030 (USEPA, 1990a). Analysis for TOC employed the USEPA Region II method in which organic compounds are decomposed by pyrolysis in the presence of O₂ or air (USEPA Region II, 1993, personal communication). The pH and ORP were measured using USEPA Method 160.3M and ASTM D1498-76, respectively (ASTM, 1976; USEPA, 1983). The ASTM method for ORP was slightly modified through the use of 0.05 M CaCl₂ to create a soil slurry with constant ionic strength for the soil samples. Total Cr was analyzed using ICP in

accordance with the USEPA contract laboratory program protocols (USEPA, 1990b).

Spiking Studies

The spiking studies used a Na₂CrO₄ solution and BaCrO₄ and PbCrO₄ powders for Cr(VI), and a CrCl₃ solution and Cr₂O₃ solid were used as sources of Cr(III). The same reagents were used for the mass balance studies, for which total Cr was analyzed by ICP after digestion in either an acid or alkaline medium.

The CrCl₃ solution was used to spike the quartz sand at 5000 mg Cr(III) kg⁻¹ shortly before spiking the other sample types with Cr(VI). Accordingly, the *Cr(III)-spiked quartz sand* was a separate matrix within the study design, and was spiked with about 24 mg Cr(VI) kg⁻¹ solution at the time that the other native samples, either field-moist or dried/sieved, received varying levels of the Cr(VI) spiking solution.

To assess the effects of Mg²⁺ on oxidation of Cr(III) in the alkaline digestion, different volumes of CrCl₃ solution (38.5 mM) were added to 2.5-g samples of sand to attain concentrations of 0, 10, 50, 100, 500, and 5000 mg Cr(III) kg⁻¹. Each of these treatment levels was prepared in triplicate with and without the addition of 10 mL of 0.42 M MgCl₂, equivalent to adding 100 mg Mg²⁺ per beaker. In addition, the loam soil was amended with 1000 mg Cr(III) kg⁻¹ (as Cr[NO₃]₃ solution) with and without 100 mg Mg²⁺ plus 0.5 mL 1.0 M P buffer (0.5 M KH₂PO₄/0.5 M K₂HPO₄, pH 7). We hypothesized that oxidation of added Cr(III) would be suppressed by adding Mg²⁺ and P by coprecipitation with Cr(III). Also, the Mg may sorb onto Mn(III, IV) oxides, rendering them less prone to oxidize Cr(III) in this Mn-bearing (1820 mg kg⁻¹) soil.

Mass Balance Study

Mass balance studies were conducted to determine whether the filtered solids that were separated from the alkaline digest solution contained Cr after spiking with Cr(III) or Cr(VI), recognizing the significant solubility differences between Cr(III) and Cr(VI) in the alkaline medium. The filtered solids were dissolved in acid and tested for Cr by ICP. The alkaline digested filtrate was also analyzed for total Cr by ICP to determine the final form of the spiked Cr. The mass balance study consisted of preparing three aliquots of each soil type as follows: (i) native sample digested by alkaline digestion performed by Modified Method 3060, (ii) Cr(VI)-spiked sample digested by alkaline digestion performed by Modified Method 3060, and (iii) Cr(III)-spiked sample digested by alkaline digestion performed by Modified Method 3060.

RESULTS AND DISCUSSION

Homogenization Study

A number of sample types did not initially meet the 20% relative standard deviation criterion and these samples were rehomogenized, after which all the samples met the 20% RSD criterion for both Cr(VI) and total Cr, except for the loam soil. The loam results exhibited a 45% RSD for Cr(VI), ranging in concentration from <1.3 to 4.8 mg kg⁻¹, which was likely attributable to inherently greater variability obtained close to the method

Table 2. Source sample characteristics.

Sample type	pH† units	H ₂ S† μL L ⁻¹	TOC g kg ⁻¹	E _h † mV	Cr(VI) — mg kg ⁻¹ —	Cr
Quartz sand	5.4	<10	<1	294	<1.3	2.6
Loam soil	6.5	<10	17	467	2.6	23.9
Woodbury clay	3.4	<10	41	673	<7	34.1
Low COPR DS‡	6.5	<10	45	412	39.8	612
High COPR DS‡	8.5	<10	45	354	825	7250
Anoxic sediment	6.8	25	210	-154	<30	712
Low COPR FM¶	6.2	<10	44	349	47.8	673
High COPR FM¶	8.0	<10	49	329	453	6530

† Field measurement.

‡ DS = dried and sieved.

¶ FM = field moist.

COPR = chromite ore processing residue.

detection limit. Nonetheless, because the Cr(VI) spiking levels anticipated for the spiking study were greater than 10 times the calculated *native* Cr(VI) concentration in the loam, additional homogenization was considered unnecessary.

Sample Characterization

The characteristics of the soil samples are summarized in Table 2. The quartz sand served as a relatively inert solid matrix as it contained 2.6 mg kg⁻¹ total Cr, no detectable Cr(VI), and trace levels of TOC. In contrast, dried and sieved high-Cr COPR contained 825 and 7250 mg kg⁻¹ of Cr(VI) and total Cr, respectively. The field-moist COPR characteristics compared favorably with the dried and sieved COPR data; however, the field-moist and dried/sieved COPR samples were not identical samples, because they were collected a few days apart from the same area.

The anoxic sediment exhibited several unique characteristics when compared with the other samples, including the largest organic C content and the most negative E_h (-154 mV) measurement. The presence of S²⁻, the negative E_h, and large TOC content indicated a reducing sample. In contrast, the loam soil sample exhibited an oxic condition (+467 mV E_h and pH 6.5), suggesting the capacity to sustain Cr(VI). However, it also had 17 g kg⁻¹ TOC, and was slightly acidic (pH 6.5), both indicative of a potential to reduce some Cr(VI). The Woodbury clay exhibited a lower pH (3.4) compared with the other samples. The acidic pH, TOC content of the clay, and Fe²⁺-containing minerals glauconite and siderite, suggested the potential for reduction of Cr(VI), even though the E_h was significantly positive (+673 mV) (Stumm and Sulzberger, 1992).

In a number of instances, the digestates were so intensely colored and turbid (e.g., the anoxic sediment and loam soil), due to small-particle dispersion at high pH in the presence of Na⁺, that the interfering absorbance readings exceeded the upper limit of the Cr(VI) calibration range. Consequently, these digestates were filtered and diluted to allow the subsequent absorbance values of the DPC-Cr complex solutions to fall within the requisite calibration range, which resulted in higher detection limits for these samples than for the undiluted ones. When such intensely colored or turbid conditions

were encountered, background absorbance measurements were obtained for the samples, prior to DPC addition, and the results for each sample were corrected for the measured background.

Spiking Studies

Prior studies showed that Cr(VI) is stable in aerated alkaline solutions as CrO₄²⁻, and a small fraction of Cr(III) exists as Cr(OH)₄⁻ in equilibrium with insoluble Cr(OH)₃ (Cox and Linton, 1985; Deltcombe et al., 1966; USEPA, 1986). However, with aging and heating, an insoluble Cr(III) precipitate, Cr(OH)₃, is formed while the soluble Cr(VI) is found to be quite stable (Zatka, 1985). Aging of Cr(OH)₃ decreases the tendency of Cr(OH)₃ to oxidize in soils (James and Bartlett, 1983a), and Cr₂O₃ is inert with respect to oxidation (Amacher and Baker, 1982).

Figure 1 presents a summary of the Cr(VI) spiking results by sample type. The average matrix spike recoveries ranged from 0% for the anoxic sediment to 80 to 120% for the low- and high-Cr COPR samples. Plotting E_h-pH ancillary parameter data for the clay, loam, and anoxic sediment (Fig. 2), demonstrated how these field data aided in interpreting Cr(VI) spike recovery data. The anoxic sediment contained H₂S and was an anaerobic soil material, and is plotted on Fig. 2 close to the intersection of the FeOOH/Fe²⁺ and SO₄²⁻/H₂S half-reaction lines, indicating that H₂S and Fe²⁺ were likely present and probably reduced the Cr(VI) spikes.

The clay had lower electron activity than the anoxic sediment, but its low pH positioned it below the HCrO₄⁻/Cr(OH)₃ line. Thus, the presence of Fe²⁺ would be expected to reduce a Cr(VI) spike under these conditions, especially Fe²⁺ sorbed as hydrolyzed forms (Stumm and Sulzberger, 1992). The loam is plotted below the HCrO₄⁻/Cr(OH)₃ line, but well above the FeOOH and SO₄²⁻ reduction potentials. Therefore, Fe²⁺ and H₂S would not be expected in this soil. Although Cr(VI) spike recoveries of 60 to 70% were observed in the loam, further investigations have observed up to 100% recoveries, perhaps due to decreased reducing agent activity in the soil since it was sampled.

The results show how ancillary parameter data for redox status of a soil can be used to understand and help interpret variable recoveries of Cr(VI) spikes. If reducing conditions are shown for Cr(VI), poor spike recovery is probably due to soil reduction, and not attributable to method-induced reduction or technical error. If oxic conditions are indicated by the ancillary parameters, poor spike recovery is probably the result of technical error, because method-induced reduction is improbable under the alkaline and aerated conditions of the extraction. Similarly, the alkaline (pH 12), aerated extraction conditions (large positive E_h values) would inhibit Cr(VI) reduction.

To test the effectiveness of the hot, alkaline solution in solubilizing and maintaining Cr(VI), three different Cr(VI) reagents were added to alkaline digestion solutions, cooled, and analyzed following phase separation and DPC addition. Two of the reagents, solid BaCrO₄

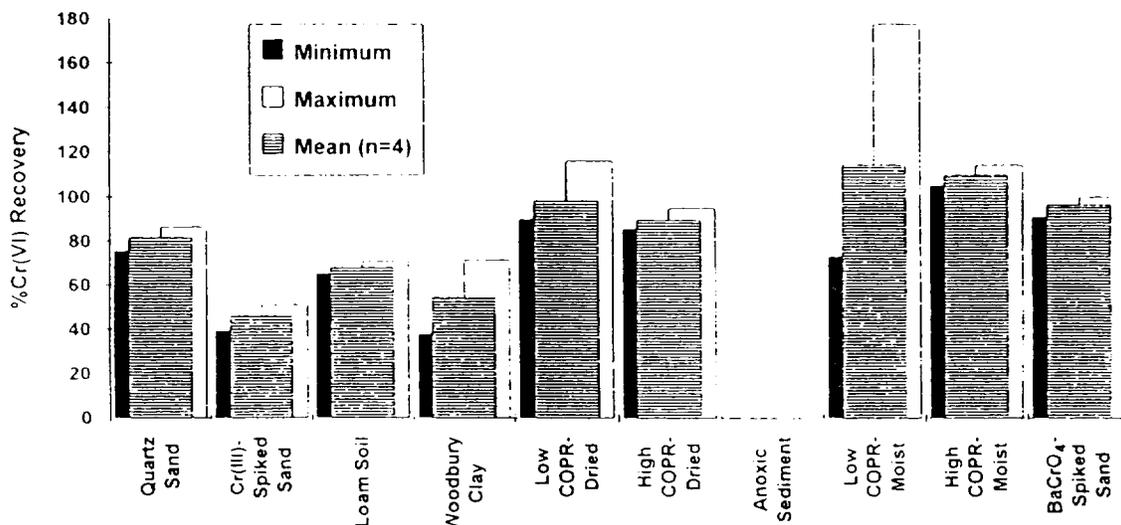


Fig. 1. Chromium(VI) spike recovery by sample type. Three vertical bars for each of 10 sample types represent the minimum, average, and maximum %Cr(VI) spike recovery using Modified Method 3060. The anoxic sediment had 0% recovery.

and PbCrO₄, were salts that are among the most insoluble Cr compounds. The third reagent was a solution of soluble K₂CrO₄. The results, shown in Table 3, demonstrated that Cr(VI) spikes were effectively recovered (93–103%) in the alkaline digestate. Furthermore, to verify that Cr(VI) was not reduced by sample constituents once the sample digests were generated, postdigestion spikes (spikes added to digestates after heating and phase separation) were performed on a number of selected samples. In all instances, recoveries of 80 to 120% were observed.

Difficulty was encountered, however, when using solu-

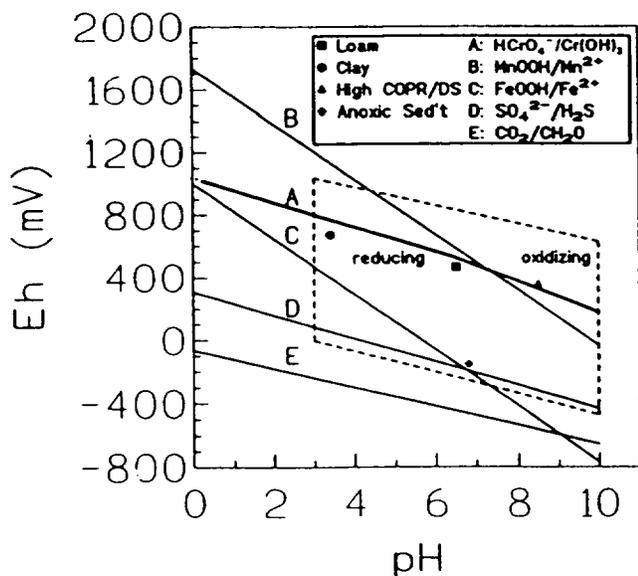


Fig. 2. E_h-pH phase diagram for HCrO₄⁻/Cr(OH)₃ and reducing agents for Cr(VI) (Fe²⁺, H₂S, CH₄O, and Mn²⁺). The dashed box circumscribes an area of redox conditions typical of most soils, and the diagonal, dashed line below the HCrO₄⁻/Cr(OH)₃ line separates soil conditions expected to maintain Cr(VI) (above line) from those expected to reduce it.

ble Cr(III) spikes to assess the potential oxidation of Cr(III) to Cr(VI) during sample digestion. Although the Cr(OH)₃ precipitate from such a soluble Cr(III) spike can partially oxidize to Cr(VI), this fresh precipitate is not representative of most soil-borne Cr in the field, which the Cr(III) spike studies were designed to simulate. Soluble Cr(III) spikes were initially used to reproduce the previous work reported by USEPA (1986). Figure 3 shows the effects of soluble Cr(III) spikes during the alkaline digestion and subsequent analysis for Cr(VI) for quartz sand that did not contain any native Cr(VI). As the concentration of Cr(III) spikes into quartz sand increased to levels greater than about 500 mg kg⁻¹, the amount of Cr(VI) measured reached a plateau between 20 and 25 mg Cr(VI) kg⁻¹.

Separately, two Cr(III) reagents were used for spiking into alkaline extraction solution; one soluble compound (Cr(NO₃)₃) and one insoluble compound (Cr₂O₃). Added at 21 mg Cr(III) L⁻¹ of digestate (as 2000 mg Cr(NO₃)₃ L⁻¹ solution), 0.6% (average of four values ranging from 0.5 to 0.8%) of the spiked amount was detected as Cr(VI) following alkaline digestion, and Cr(VI) was not detected when Cr₂O₃ was added at 180 mg Cr(III) L⁻¹ of digestate. Thus, freshly precipitated Cr(OH)₃ in the alkaline digestion solution resulted in a method-induced oxidation of <1% of the Cr(III) added. Subsequent testing in which aged Cr(OH)₃ was added to the

Table 3. Dissolution of Cr(VI)-containing compounds in alkaline digestion solution.

Cr(VI) reagent	Mean concentration added	Mean recovery	Recovery range
	mg L ⁻¹	%	%
BaCrO ₄ (solid)	70	93	84 to 102
PbCrO ₄ (solid)	70	102	98 to 104
K ₂ CrO ₄ (solution)	5	103	94 to 107

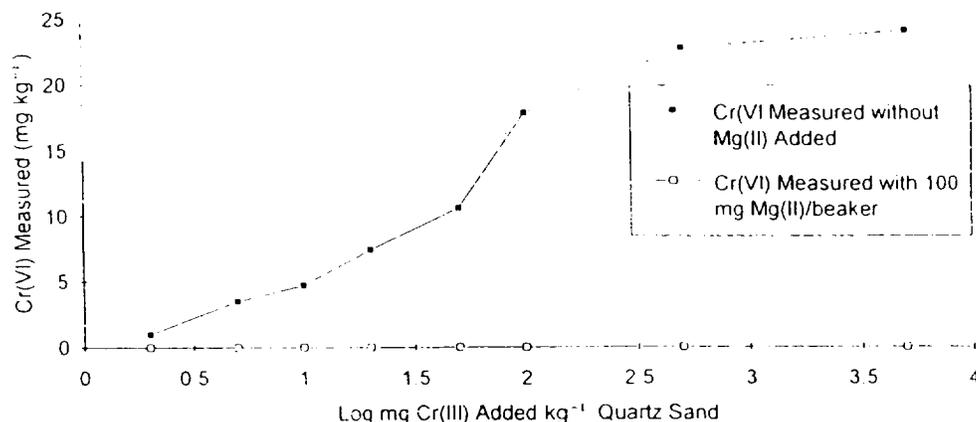


Fig. 3. Amount of Cr(VI) measured in Cr(III)-spiked quartz sand with and without Mg(II) added to suppress Cr(III) oxidation. The upper line exhibits a sharp increase in Cr(VI) measured at low Cr(III)-spiking levels that reaches a plateau near 25 mg Cr(VI) kg⁻¹. The lower line shows complete suppression, no Cr(VI) measured, at all Cr(III) spiking levels.

alkaline digestion solution indicated method-induced oxidation of about 3% of the spiked level after 14 d, and less 0.5% method-induced oxidation after 30 d (data not shown). Additional testing showed no oxidation when Cr₂O₃, an insoluble form of Cr(III), was used as a spiking agent. These and the above findings are significant in that aged Cr(OH)₃ and Cr₂O₃ are believed to be the two most common forms of Cr(III) found in COPR-amended soils in the field.

Based on prior findings pertaining to this phenomenon (Bartlett and James, 1988) and the results of these spiking studies, it is apparent that the aged Cr(OH)₃, as well as solid Cr₂O₃, do not oxidize when subjected to Modified Method 3060. Furthermore, it was concluded that soluble Cr(III) spikes are not appropriate to assess the potential for Cr(III) oxidation by the alkaline digestion method for most soils, unless they are recently amended with soluble Cr(III) salts.

When freshly precipitated Cr(OH)₃ is suspected to be present in samples, the addition of Mg²⁺ was previously shown to reduce or eliminate the occurrence of oxidation, although a definitive mechanism was not reported (Zatka, 1985). As shown in Fig. 3, the addition of Mg²⁺ to the Cr(III)-spiked quartz sand completely suppressed the oxidation of freshly precipitated Cr(OH)₃ formed during analysis of the quartz sand. Although this confirmed earlier findings, additional study will be needed to determine the degree of suppression over time, and other potential factors that may be operative in various soil types.

The USEPA study (1986) suggested that the oxidation of Cr(III) to Cr(VI) was occurring during the Method 3060 digestion procedure. In the present study, when loam was amended with 1000 mg Cr(III) kg⁻¹ as Cr(NO₃)₃ and subjected to the alkaline extraction, the measured Cr(VI) was reduced from 19 to 9% of the added Cr(III) by adding Mg²⁺ and phosphate buffer. As this particular soil contained Mn (1820 mg kg⁻¹), it was not possible to separate oxidation of Cr(III) by the soil from that induced by the method. However, the oxidation by O₂ of hydroxochromate anion, Cr(OH)₄⁻, formed by hydrolysis of CrCl₃, and in equilibrium with freshly

precipitated Cr(OH)₃, is well documented and is not likely to occur with aged Cr(OH)₃ (James and Bartlett, 1983a; Zatka, 1985). Furthermore, insoluble forms of Cr(III) found in environmental samples, such as Cr₂O₃, which is the predominant form of Cr found in soils, have not been observed to oxidize under the Modified Method 3060 procedure (data not shown) (USEPA, 1984b). Furthermore, soil organic matter is expected to convert soluble chromate to insoluble Cr(III) as Cr₂O₃ (Calder, 1988). Thus, the appropriateness of using a soluble Cr(III) salt, such as CrCl₃ or Cr(NO₃)₃, as spiking material for soils to monitor for the potential oxidation of Cr(III) to Cr(VI) (viz., simulating native Cr(III) oxidation) may be of questionable utility (Bartlett and James, 1979). Future research efforts may be appropriately focused on examining the potential for oxidation of other Cr(III) complexes that may be present in polluted and unpolluted soils. Nonetheless, it has been reported that such oxidation of soluble Cr(III) spikes in the laboratory has been prevented or minimized by the addition of MgCl₂ to the alkaline digestion solution (Zatka, 1985).

The USEPA study (1986) also suggested that reduction of Cr(VI) to Cr(III) could occur during the Method 3060 digestion procedure. Although this may have been a plausible explanation at the time, certain sample types that are strongly reducing in nature (e.g., anoxic sediments containing organic matter and sulfides) do not have the capacity to sustain Cr in the +6 valence state, either in the natural environment or after spiking with Cr(VI) during the alkaline digestion. The strong reducing potential of such samples would be expected to almost instantaneously reduce the Cr(VI) to an insoluble form of Cr(III) (James and Bartlett, 1983b; Masscheleyn et al., 1992). As a result, low or 0% recoveries of Cr(VI) matrix spikes were observed for Cr(VI) spiked into such samples. On the other hand, if a sample contains native Cr(VI), it should be capable of maintaining a Cr(VI) matrix spike (i.e., acceptable spike recoveries will be measured).

Consequently, conventional interpretations of total elemental spike recovery information (e.g., for total Zn or Cd) cannot be utilized when multiple valence states of

an element are encountered. The effects of redox reactions on the speciation of Cr in environmental samples need to be understood or predicted through the use ancillary soil parameters such as pH, ORP, S^{2-} concentration, and TOC content. Another measure of redox status that was not included in the method study is Fe^{2+} , which should also be considered as an ancillary parameter. Data associated with low or 0% matrix spike recoveries should not be automatically considered unreliable, but should be evaluated in accordance with established redox chemistry of Cr in soils and sediments (Adriano, 1986; Bartlett and James, 1988; Rai et al., 1989; Richard and Bourg, 1991).

The collective method study data showed that method induced oxidation only occurred with freshly precipitated $Cr(OH)_3$, which is not expected to be present in soil-borne Cr found in environmental samples. Additionally, the data showed that method induced reduction, which is cited as a possible reason for method failure in the literature, did not contribute to low or 0% matrix spike recoveries. The soils that exhibited highly reducing properties could not maintain Cr(VI) spikes. Thus, the nature of the sample must be assessed via other parameters before interpreting the meaning of low or 0% Cr(VI) matrix spike recoveries. Until recently, such spike recovery results would have been considered as method failure and the results may have been mistakenly rejected as suspect data.

Mass Balance Studies

The results of the mass balance studies and associated supplemental testing demonstrated that Cr conservation was observed for each sample type. The solids collected on the filter paper (not part of the extract used for Cr(VI) measurement) during filtration of the digestate were tested for total Cr. For samples that exhibited low or 0% matrix spike recoveries, the total Cr in the filtered solids accounted for the remainder of the Cr(VI) spikes added. This mass balance confirmed that these samples reduced Cr(VI) to Cr(III) as a solid precipitate. The fact that this reduction only took place in highly reducing samples demonstrated that such reduction was not attributable to the method.

SUMMARY AND CONCLUSIONS

The results indicated that Modified Methods 3060/7196A for determining total Cr(VI), as applied to a variety of different soil samples, provided satisfactory performance in quantifying the amount of total Cr(VI) in the solid samples, and the combined methods were considered to be a suitable means of measuring total Cr(VI) in commonly encountered soil samples. Matrices which exhibit highly reducing characteristics (e.g., anoxic sediment) do not support the existence of Cr(VI), either in native environmental settings or after being spiked in the laboratory with Cr(VI). When low or 0% matrix spike recovery data are encountered, that previously would have been perceived as unreliable, it is necessary to characterize ancillary parameters, such

as ORP, pH, TOC, Fe^{2+} , and S^{2-} to make an affirmative determination regarding the capacity of the sample to contain Cr(VI). Reducing conditions, as defined by the Cr E_h -pH phase diagram, the presence of TOC, S^{2-} , or Fe^{2+} , or acidic soil conditions, singularly or in combination, indicate the potential for a sample to (i) reduce a laboratory Cr(VI) spike or (ii) not sustain the existence of Cr(VI) in the sample's native environment. When such ancillary data affirm the reducing capacity of a sample, and other quality control indicators, such as laboratory control samples, indicate correct method application, the Cr(VI) results obtained using Modified Methods 3060/7196A should be considered acceptable for use.

The results also showed that both soluble and insoluble forms of Cr(VI) can be used to obtain satisfactory matrix spike recovery results, including both liquids and insoluble chromate salts. It was also shown that (i) method-induced oxidation only occurs with freshly precipitated $Cr(OH)_3$, which is not likely to be present in environmental samples, and (ii) method induced reduction is not the cause of low or 0% matrix spike recoveries.

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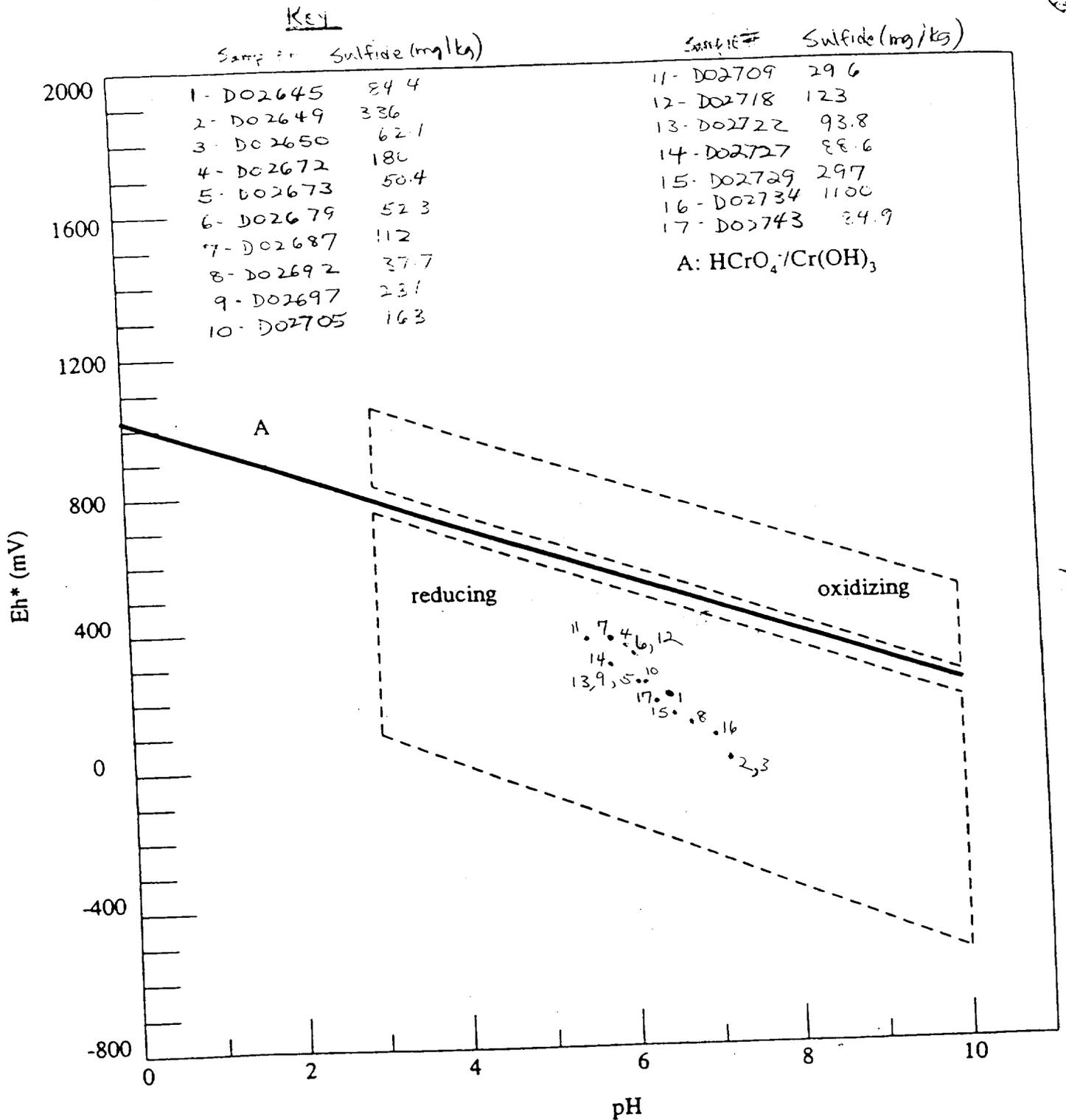
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FIGURE 2
Eh/pH PHASE DIAGRAM

The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.