

## Response to Peer Review Comments

### Chapter 4: Analytical Chemistry

**Peer Reviewer: Paul Brandt Rauf**

No pertinent comments on Chapter 4.

**Peer Reviewer: Jon Chorover**

No pertinent comments on Chapter 4.

**Peer Reviewer: Herman Gibb**

No pertinent comments on Chapter 4.

**Peer Reviewer: Gary Ginsberg**

No pertinent comments on Chapter 4.

**Peer Reviewer: Gregory Turk**

● *The accurate measurement of Cr VI in environmental samples is one of the most difficult challenges in Analytical Chemistry. The subgroup has clearly demonstrated their understanding of the complexities of the measurement, and I find their recommendations to be logical, reasonable, and based on the present best scientific understanding of the measurement issues.*

**Response:** No response

● *On pg 56, in the 3<sup>rd</sup> paragraph, the report states “... failure of the method to accurately quantify Cr(VI) in certain sample matrices.” I think it would be helpful to list what these “certain sample matrices” are.*

**Response:** The sentence is changed to read – “USEPA Method 3060 was withdrawn from the SW846 methods compendium for solid and hazardous waste in the late 1980s because of data documenting the failure of the method to accurately quantify Cr(VI) in sample matrices that contain reducing conditions.

● *On pg 57, in the first complete paragraph, there is a discussion regarding subtle differences between NJDEP modified 3060 and EPA 3060A. What are the implications of these differences?*

**Response:** The implications are addressed in Paragraph 2, Page 57.

● *Would the NJDEP modified method be more likely to report higher or lower Cr(VI) concentrations than 3060A?*

**Response:** A sentence is added at Paragraph 2 – Page 57 to read “It is unknown what affect the differences between methods 3060 and 3060A may have on the measured amounts of Cr(VI).

● *Is Method 6800 really included in SW846? The EPA website at [http://www.epa.gov/epaoswer/hazwaste/test/6\\_series.htm](http://www.epa.gov/epaoswer/hazwaste/test/6_series.htm) lists 2 methods in the 6000 series of SW846 methods, but not Method 6800.*

**Response:** Method 6800 is listed as a new method in Update IV, SW846. It can be found at <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6800.pdf>.

● *Regarding Method 6800, I agree with the subgroup's opinion that the method should generate reliable data under difficult matrix conditions, but even this rather sophisticated method is not infallible. Any method relying on isotopic spikes requires that the spike be "equilibrated" with the indigenous analyte in the sample. In situations where the indigenous Cr is solid, but the isotopic spike is dissolved in a solution, the spike cannot "equilibrate" until the solid material is dissolved. Thus the method cannot address any species conversions that might take place as the solid material is brought into solution. In the panel's recommendations for needed research, which I support, I suggest the addition of a study in which known amounts of solid water insoluble forms of Cr (perhaps minerals, ores, oxides, pure COPR) are added to various soil types, and the recovery of the known addition is calculated using Method 6800. Such a study would test the weakest aspect of the method.*

**Response:** The Subgroup agrees and the issue will be dealt with in the research proposal on methods evaluation..

● *On pg 63, I agree with the subgroup's recommendation that total Cr measurements be made in addition to Cr(VI) measurements. I only wish to make the obvious point that total Cr(VI) concentration can never be greater than total Cr, and thus total Cr measurements might be used as proof that Cr(VI) concentration are below required levels. In general I would think that total Cr measurements, being simpler to make, would be more reliable than a Cr(VI) measurement.*

**Response:** No response, the Subgroup agrees with the comment.

● *Regarding the need for a reference material-- since I work for NIST my opinions might be considered somewhat biased on this topic, but there is clearly a great need here. As the report notes, NIST has budgeted some funds to collect and prepare a Cr(VI) in soil NIST Standard Reference Material (SRM). The report refers to a proposal that has been "agreed to by the USEPA, NIST, and EOHSI". This is a bit of an exaggeration. I am not aware of any formal agreement at this stage. NJDEP has been advising us on site selection of a COPR contaminated soil to be collected for production of the SRM, and has offered to help us with logistics.*

**Response:** The project to develop reference materials has been accepted by the NJDEP, USEPA, NIST and EOSHI, and is scheduled to begin June 2005.

Revisions to the document to address this comment and this project have been made on page 63.

● *I strongly support the subgroup's recommendation and thoughts regarding research on a method to determine Cr(III) and Cr (VI) directly in soils without the need for sample digestion. Such a method would most likely be based on some form of X-Ray spectroscopy. I would point out that such a method would be of great benefit even if it never developed into a practical field testing method. The ability to use such a method to validate more practical extraction-based methods would very much improve our present*

*understanding of this complex measurement. I believe that the X-Ray Photoelectron Spectroscopy is applicable only to the analysis of surfaces, so this could be a weak point.*

**Response:** The Subgroup agrees with the comments. Additionally, the references to X-Ray Photoelectron Spectroscopy in the research proposal will be deleted from the document.

● *I also agree with the research recommendations regarding a systematic comparison of the various methods under different soil conditions. It would be of great benefit to identify correlations between measurable soil parameters (i.e. pH) and the performance of the various methods. If and when such correlations can be identified, the analytical method selection flowchart (Figure 4.1) should be updated so that measured soil properties can be used to guide decisions regarding the choice of method.*

**Response:** The Subgroup agrees with the comment.

**Peer Reviewer: C.P. Huang**

● *Classification of COPR and COPR-soil materials. The Workshop has adequately addressed all charges within sound scientific context. The recommendations are appropriate, reasonable and sound. Regarding recommendations for research needs, it is agreed that non-wet chemistry methods are needed to better characterize COPR and COPR-soil mixture in terms of their Cr(VI) and Cr(III) distribution and transformation. But XPS can not provide quantitative information on the distribution of Cr(III) and Cr(VI), EDAX (X-ray dispersive spectrophotometry) technique does. Additionally, as far as the qualitative analysis of the surface Cr chemistry is concerned, other surface analysis techniques such as XRD (X-ray diffraction), NEXAF (Near edge X-ray absorption Fine Structure) and AFM (atomic force microscopy) can also be extremely useful. XPS will reveal the oxidation state of Cr but not its concentration.*

**Response:** The Subgroup agrees with the comments. Additionally, the references to X-Ray Photoelectron Spectroscopy in the research proposal will be deleted from the document.

● *Soil sampling protocol. While laboratory analysis is important to remediation investigation, other important issue is the soil sampling protocols. EPA Soil Screening Levels for Superfund Sites is a good source of general information. But a specific soil sampling protocol is also useful. Soil sampling schedule should also consider economic constraints, i.e., is it affordable?*

**Response:** The comment is outside the scope of responsibility for the Subgroup.

● *Eh and pH diagram. The reduction potential should be expressed as “E<sub>h</sub>” not “eH” (Please make corrections on pages 61 and 64).*

**Response:** The Subgroup agrees and revisions to the text will be made.

● *Figure 4.6 gives E<sub>H</sub> versus pH plot of the reaction  $\text{HCrO}_4^- + 4\text{H}^+ + 3\text{e} = \text{Cr}(\text{OH})_3(\text{s}) + \text{H}_2\text{O}$ . (Note the symbol E<sub>h</sub> should be E<sub>H</sub>). A more comprehensive Eh-PH diagram as shown in the left may be appropriate.*

**Response:** Although the suggested diagram is more detailed than the one currently in the document, the current diagram provides adequate information.

**Peer Reviewer: Ken Stollenwerk**

● *I agree with the subgroups recommendation to use USEPA Method 3060A for preparation of non-aqueous samples for analysis of Cr(VI). This would provide consistency among sites. However, there should be some room for flexibility given the potential for Cr redox state transformations in some sample matrixes. For example, if there is evidence for oxidation or reduction of Cr in a particular type of sample matrix and if a modification to Method 3060A can prevent the oxidation state conversion, then a modified method should be considered.*

**Response:** The Department has chosen to use USEPA Method 3060A, and expects to continue using this method until the USEPA develops a replacement method or until another method is shown to be more appropriate.

● *Development of standard reference samples for COPR would be useful. Until such standards can be developed for routine use, spike recovery data will be an important measure of analytical accuracy. Both Cr(III) and Cr(VI) should be considered to evaluate Cr(III) oxidation as well as Cr(VI) reduction during sample preparation.*

**Response:** The Subgroup agrees the comment.

● *Ch. 4, p. 61: The meaning of this sentence is unclear. It seems to imply that Fe(III) should oxidize Cr(VI) but is oxidizing DPC instead. How can Fe(III) oxidize Cr(VI) which is already oxidized?*

**Response:** The following sentence “Fe(III) has been shown to oxidize DPC (diphenylcarbide), thus not allowing the DPC to react with the actual Cr(VI) present in the sample” will replace the sentence on page 61 that reads “ Fe(III) has been shown to oxidize DPC(diphenylcarbide) and not the actual Cr(VI) present.”

● *Ch. 4, p. 67: Direct measurement of Cr in solids by techniques such as XPS would not necessarily determine worst case scenarios. If high concentrations of Cr occurred in discrete mineral phases that comprised a small percentage of the total sample, XPS types of analyses might miss these Cr-rich particles. Another example would be extensive coatings of Cr(VI) on iron oxide minerals that are below detection but soluble, potentially resulting in ground water contamination.*

**Response:** The Subgroup agrees with the comments. Additionally, the references to X-Ray Photoelectron Spectroscopy in the research proposal will be deleted from the document.

**Peer Reviewer: Chunming Su**

● *Chapter 4, page 54, line 30. Delete the extra word “that”.*

**Response:** The Subgroup agrees with the comment. The revision will be included.

- *Chapter 4, page 54, line 36. Insert the acronym “(SRWMP)” after the word “Program”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 55, line 6 from bottom. Change “eH” to “Eh”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 61, line 12 from bottom. Change “eH” to “Eh”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 61, line 3 from bottom. Should read “shown to oxidize”.*  
**Response:** The sentence was previously changed in response to a separate comment.
- *Chapter 4, page 62, line 7 from bottom. Misspelled word for “species”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 62, line 1 from bottom. Should read “used to assess”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 63, line 6. Should read “has already had”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 64, line 3 from bottom. Change “copra” to “COPR”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 64, last paragraph. Another X-ray method, X-ray absorption spectroscopy, may also be useful for detecting Cr(III) and Cr(VI) in COPR waste. It has been used successfully in many cases to study chromium speciation in geological materials.*  
**Response:** The Subgroup agrees with this comment, but no change in the text of the document is necessary.
- *Chapter 4, page 65, line 8. Change “COPRA” to “COPR”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 65, line 15. Change “specie” to “species”.*

- Response:** The Subgroup agrees with the comment. The revision will be included.
- *Chapter 4, page 65, line 25. Should read “distributed for”.*  
**Response:** The Subgroup agrees with the comment. The revision will be included.
  - *Chapter 4, page 67, line 4 and line 14. Change “copra” and “COPRA” to “COPR”, respectively.*  
**Response:** The Subgroup agrees with the comment. The revision will be included. (Could not find language noted for line 4)
  - *Chapter 4, page 68, References.*  
*Kingston, H.M., Huo, Lu ... should be read “Kingston, H.M., Huo, D., Lu...”.*  
*USEPA, (1996a) and (1996b), titles are mixed up.*  
**Response:** The Subgroup agrees with the comment. The revisions will be included.
  - *James et al., 1997. This paper is not cited in the text.*  
**Response:** The reference in the text of the document was inadvertently omitted. It has been inserted in the middle of page 61.
  - *Griffing et al., 1997. Check the paper title, it does not seem right.*  
*Grove and Stollenwerk, 1985. Journal title and page numbers missing.*  
*Korte et al., 1976. Paper title missing.*  
*Ramos et al., 1994. Two journal names?*  
*Schroeder et al., 1975. Check the names of authors.*  
*Tzou et al., 2002. Change “want” to “Wang”.*  
**Response:** This group of references do not apply to Chapter 4.