Division of Science, Research and Technology

Research Project Summary

March, 2009

Evaluation Of Methods For Quantifying Cr (VI) And Cr (III) In Soils And Wastes

Authors

R. Lee Lippincott Ph.D.[1], Brian Buckley PhD.[2]

Abstract

An interlaboratory study comparing the three quantitation methods EPA 7196A, 7199 and 6800 demonstrated a statistically significant 31.6% difference between method 6800 and the results from the other two quantification methods (7196A and 7199) using the same extraction protocol (3060A). Method 6800 uses a stable isotope spike to adjust for loss of Cr (VI) to reduction during the extraction process. Method 6800 had significantly higher values for soluble Cr (VI) than either of the two methods that do not compensate for reduction or loss of Cr (VI) measured with an external spike. It is however limited by the amount of stable isotope spiked into the matrix. The other methods of quantification (USEPA method 7196A, 7199, or others) can underestimate the amount of soluble Cr (VI) if reduction occurs during the extraction or analysis process. Determination of where in the analytical process the Cr (VI) spike loss occurs cannot be made without the ability to quantitate the Cr (III) species. Therefore, it cannot be assumed that a poor Cr (VI) measurement was caused only by reduction of the Cr (VI). For example, if the Cr (VI) in a sample was either precipitated or absorbed to the soil surface by the addition of the extraction solvent or formed a complex with an organic moiety, it may still be available for oxidation back to Cr (VI) or dissociation to soluble Cr (VI) if conditions in its environment change. While ICP/MS analysis should identify all soluble chromium, species, whether or not they had been complexed with an organic ligand, it cannot compensate for insoluble forms of Cr (VI) that may have been precipitated or absorbed to the soil surface. The process of making all Cr species soluable is key to an accurate determination of the amount of Cr (VI) present.

Introduction

Accurate measurement of Cr species in non-aqueous media such as soils and sediments is complicated by chemical processes that can alter the indigenous amounts of Cr (III), a micronutrient, and Cr (VI), a known carcinogen. The accurate determination of Cr (VI) is therefore critical to remedial actions and the health and safety of the public. For soils or sediments without significant amounts of certain organics, metals or anions, Cr (VI) can be measured with a high degree of accuracy. However, many soils and/or sediments with matrix components including those listed above can oxidize a laboratory spike of Cr(III) species to Cr(VI) species [resulting in the over-reporting the true amount of Cr(VI)], or reduce a laboratory spike of Cr(VI) to Cr(III) [resulting in the under-reporting the true amount of Cr(VI)].

Currently, New Jersey Department of Environmental Protection (NJDEP) requires the use of NJDEPE Modified Method 3060A to extract the sample, with subsequent measurement by the colorimetric Method 7196A. There has been a historical 50% failure rate using these methods utilizing the Department's control level of between 75% - 125% recovery of a known addition of Cr (VI)].

A literature review regarding this topic of method comparability has raised questions as to whether other combinations of methods, such as utilizing 3060A extraction protocols with USEPA method 6800, may generate more reliable and consistent analytical results. These and other issues are currently under review by the Analytical Subgroup of the NJDEPs Cr Workgroup to recommend changes to current NJDEP Cr policies and procedures.

General Methodology: USEPA Method 6800 uses ion chromatography (IC) coupled to inductively coupled plasma mass spectrometry (ICPMS) to separate and quantify each chromium species. In addition stable isotope labeled Cr (VI) and Cr (III) are added after sample collection to monitor for species interconversion in all subsequent processes. Method 7199 uses IC with a post column addition of diphenylcarbizide to detect the Cr (VI) after it elutes from the column. Method 7196A uses the same colorimetric complex of chromium for quantification but the assay is performed in situ on the extract with no separation of the chromium species.

Methods

There are three EPA analysis methods 6800, 7199, 7196A (1) currently being used to quantify the amount of extractable Cr (VI) from a solid sample. All three analytical methods utilize the same extraction protocol, EPA 3060A. This method was created to gently extract and stabilize Cr (VI) . The extraction protocol is limited in the amount of chromium that is solubilized from most soil and waste matrices. The limitations are covered later in this report, but the limitations are critical in trying to assess the true amount of Cr (VI) in the sample. The quantitation methods EPA 6800, 7196A and 7199 cannot compensate for insoluble Cr (III) lost to precipitation during the extraction process because of the chemistry that is utilized for extraction of the chromium species, without making considerable assumptions. Method 6800 can be used to detect changes (up to 80% of the spike) of Cr species conversions that occur during sample digestion and/or measurement.

In order to evaluate the efficacy of the methods that quantify the Cr once solubilized, the three instrumental techniques should be compared directly, with the same material containing stable chromium species at known levels. Assuming that the extraction step is reproducible for the material tested, it would then be the quantification process from the instrument that created any differences in the results. By isolating different procedures within the analysis train for chromium, a scientist can determine the uncertainty of each instrument's raw data output by using a representative homogeneous reference material of know chromium species composition. A new standard reference material (SRM 2701) was used in an interlaboratory study, to measure the concentration of Cr (VI) in a soil type. All laboratories used the same extraction protocol but analyzed the SRM with one of the three methods referenced above in the text. Having a representative SRM utilized by all laboratories reduces the uncertainty in the extraction process and allows the assessment of the instrumental method variability for each of the three techniques. This isolates the extraction efficiency from the collaborative study statistics.

Results

The results from this study on extraction protocol improvements, coupled with the interlaboratory study designed to create a certified reference material demonstrate that:

1. The USEPA SW846 extraction protocol 3060A is not effective at removing total chromium and some Cr VI spikes on all matrices
2. EPA method 3060A cannot be used for quantitative extraction of Cr (III) due to the solubility chemistries of the method.
3. Effective measurement of chromium reduction and/or loss of the Cr (VI) spike cannot be estimated without an effective extraction protocol for Cr (III)
4. The use of stable chromium isotope labels will correct for interconversion either in the extraction or analysis processes up to 80% of the conversion of the spike
5. The use of stable isotope labels will account for potential analyte loss due to complexation or precipitation of chromium (VI) spike
6. The use of a standard reference material for interlaboratory comparison may help in establishing a standard method for extraction and analysis for speciated chromium in soil and waste matrices
7. There was a statistically significant difference in chromium analytical results obtained with method 6800 when compared to either method 7199 or 7196A
8. There was no statistically significant difference in results obtained with method 7199 when compared with method 7196A

Conclusions

One of the indirect results of this research was the laboratory community acceptance and utilization of a standard reference material to allow an apples-to-apples comparison of the different extraction condition experiments and instrumental analysis techniques. To assess the performance of these SW-846 methods for the determination of hexavalent chromium and total chromium in SRM 2701 and to provide data which are relevant to users of these SW-846 methods, a multi-laboratory testing program was established jointly by NIST and the New Jersey Department of Environmental Protection (NJDEP), Office of Quality Assurance (OQA). Stratified random samples of SRM 2701 were distributed to a number of cooperating laboratories who were asked to measure the hexavalent chromium concentration in the material and/or the total chromium. The NJDEP Office of Quality Assurance and members of the US Geological Survey were instrumental in obtaining a representative sample for the synthesis of the standard and processing the solid matrix unto a uniform sample SRM-2701 that could be utilized in this research project and allow a controlled interlaboratory collaborative study to occur.

Inefficiencies in the extraction/isolation protocols were demonstrated and detailed in the final report for the project. One of the main conclusions of this research is that the utilization of stable chromium isotopes provides an indication of the chromium species stability of the sample matrix being analyzed when compared to non-determinative methods of analysis.

Prepared By

[1] NJDEP, Division of Science, Research and Technology

[2] Rutgers, The State University of New Jersey
University of Medicine and Dentistry of New Jersey
Environmental and Occupational Health Science Institute

RESEARCH PROJECT SUMMARY

Please send comments or requests to:
Division of Science, Research and Technology
P.O.Box 409, Trenton, NJ 08625
Phone: 609 984-6070

Visit the DSRT web site @ www.state.nj.us/dep/dsr

Division of Science, Research & Technology
Dr. Eileen Murphy, Director

STATE OF NEW JERSEY
Jon S. Corzine, Governor

Department of Environmental Protection
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