Using reference materials to improve the quality of data generated by USEPA analytical methods

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The quality of data generated for the analysis of environmental samples is critical to State and Federal regulatory agencies to ensure that decisions based upon the amounts of contaminants in environmental samples are truly protective of public health. The quality and validation of these measurements using the approved analytical methodology could be significantly enhanced by incorporating certified reference materials as part of the quality control protocols, yet this has not been widely implemented. Data from certified reference materials can provide critical information that can impact assessments regarding data use that is unavailable by other means. Using the analysis of Cr(III) in soil extracts as the test case, some of the issues surrounding the use of certified reference materials for environmental applications are discussed in this paper, including the relative cost, and the availability and applicability regarding element coverage and content.

Environmental impact

Meaningful environmental impact and public health assessments are highly reliant on the quality and validation of environmental measurements using approved analytical methodology that could be significantly enhanced by incorporating certified reference materials into the quality control protocols. To date, this has not been widely implemented. Data from certified reference materials provides a critical information resource that could be used for quality assurance validation and litigation decisions that is unavailable by other means. Using the analysis of Cr(III) in soil reference material extracts as an example test case, some of the issues surrounding the use of certified reference materials for environmental applications are discussed in this paper, including the relative cost and applicability.

1. Introduction

State and Federal environmental regulatory agencies rely upon the documented quality of analytical data to ensure that decisions, based upon the amounts of contaminants in samples of air, water, soil and/or biota, are within legal limits and protective of public health. These analytical data are supplied by laboratories that abide by a series of established administrative and technical requirements and protocols. Administrative mechanisms include state-specific† and multi-state‡ regulations requiring the certification of environmental laboratories. Analytical methods used by certified laboratories are established by the U.S. Environmental Protection Agency (USEPA), ASTM International (formerly the American Society for Testing and Materials), Association of Analytical Chemists (AOAC), National Institute for Occupational Safety and Health (NIOSH) or other sanctioning authorities.

Environmental measurements in the United States most often use methods established by the USEPA. These methods contain a variety of quality assurance criteria that address many aspects of the analytical process (both sample preparation and measurement procedures). Quality assurance tools have defined acceptance limits that vary by analyte and matrix. The types of quality assurance can be divided into two general categories. The first is instrument-centric, covering such areas as instrument stability (controlled by performance checks), accuracy of calibration standards (use of verification materials and the analysis of a laboratory control sample), on-going calibration stability (analysis of a continuing calibration verification sample) and the reliability of low-level detection (method detection limit studies, analysis of blank and reporting limit check samples). The second area is sample-centric, and has two distinct components. The first, sample homogeneity, is addressed via the measurement of replicate sample aliquots known as matrix duplicates. Secondly, method accuracy is addressed by matrix spikes, which is a measure of the recovery of a known amount of analyte to a sample aliquot. The matrix spike protocol is the only quality assurance tool that is present in every USEPA method that directly addresses the central question of greatest importance to environmental regulators “are we accurately measuring how much contaminant is in the
sample using the approved analytical protocol”? However, the percentage recovery of a matrix spike alone may not fully take into account the elemental/mineralogical form associated with the analyte. This may play a dominant role in determining how much of the analyte can be removed from the sample and therefore be measured by the analytical technique. This is especially true for the analysis of metals in media that contain silicates or other matrix components that can hinder sample dissolution. Adding an aqueous matrix spike to a solid material only exacerbates this uncertainty, since the aqueous addition cannot mimic the behavior of an indigenous analyte entrained in a soil or sediment. Using a matrix matched solid material spike would provide a more representative assessment of sample concentrations.

There are a number of other application areas that use analytical methods similar in scope and intent to those used to measure contaminants in environmental samples. Examples include the cement industry, fossil fuel commodities for pollutant specifications, and testing of materials for consumer product safety. These areas often use methods that incorporate the analysis of reference materials as part of the quality assurance regime to help ensure accuracy of the data being generated. For example, the American Society for Testing and Materials (ASTM) C114 test methods for hydraulic cement, require laboratories to qualify every instrument and every analyst on a regular basis. The use of primary reference materials certified by national metrology laboratories in quality assurance programs, represents the highest level of reliability. In the United States, Standard Reference Materials® (SRM), distributed by the National Institute of Standards and Technology (NIST) are the preferred materials in many applications. Similarly, many committees that write ASTM and International Standards Organization (ISO) test method standards search for suitable reference materials to support their inter-laboratory studies in which the draft method is being validated. The U.S. Consumer Product Safety Commission (CPSC) has published a number of test methods for testing products for regulated elements and compounds. Some SRMs are listed in the published methods for a range of consumer products such as paints, and alloys of tin, lead or other metals. Laboratories also try to use SRMs so they can demonstrate conformity to CPSC.

Certified Reference Materials (CRMs), certified according to ISO guidelines4 are sufficiently homogeneous and stable with respect to one or more specified properties, and are available from a variety of commercial sources and national metrology institutes. CRMs6 are characterized by a metrologically valid procedure for one or more specified properties. They are accompanied by a certificate that provides information on a specific property, its associated uncertainty, and a statement of metrological traceability. NIST offers a number of SRMs, which meet additional NIST-specific certification criteria and are issued with a certificate of analysis (COA) that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. NIST SRMs may contain both (1) NIST certified values,7 for which NIST has the highest confidence in their accuracy and (2) NIST reference values, which are defined as non-certified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods.

Unique to environmental applications is the near-absence of the required use of reference materials for quality assurance. Only USEPA Method 7199 “Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography”8 requires the use of certified reference materials. Many USEPA methods use reference materials for validation, and/or recommend the use of a reference material as a quality assurance tool. However, very few commercial laboratories actually use certified reference materials on a regular basis to quality assure their results. Laboratories often cite the cost of certified reference materials, the availability of suitable materials, and discretionary nature of their use in all other USEPA methods as justification.

This perspectives paper explores the use of reference materials as an essential quality assurance tool for environmental measurements. The development and use of NIST SRM 2700 (hexavalent chromium in contaminated soil, low level), and NIST SRM 2701 (hexavalent chromium in contaminated soil, high level),9 as quality assurance tools for the measurement of hexavalent chromium in soils will be discussed, along with several case studies that used these materials to quality assure results obtained by several USEPA SW-846 determinative methods. Commentary on some of the concerns regarding the use of certified reference materials to quality assure data obtained by USEPA SW-846 methods is also offered.

2. Certification of NIST SRM 2700

The development and certification measurements of NIST SRM 2700 occurred in a manner similar to that used for NIST SRM 2701. A laboratory inter-comparison study was conducted from January 2010 to November 2010, with a total of 33 laboratories, representing a broad spectrum, of commercial, government and academic facilities from the United States, Canada and Australia. Each laboratory was sent samples from the beginning,
middle and end of the approximately 2500 bottle production lot of NIST SRM 2700, and was asked to conduct three individual speciated chromium(vi) analyses. In addition, a small amount of NIST SRM 2701 was also sent to all participants, who were asked to analyze this SRM along with NIST SRM 2700. An individual speciated chromium analysis was defined as an “aliquot of the candidate SRM that has been subjected to USEPA Method 3060A, followed by one or more determinative speciated chromium analytical methods”. These methods are 7196A, 7199 and 6800. Laboratories were afforded the opportunity to analyze the Method 3060A digests by one or more chromium(vi) determinative methods. Laboratories who planned to analyze Cr(vi) by Method 6800 were sent 3 samples of the candidate NIST SRM 2700. Results for the NIST SRM 2700 laboratory inter-comparison study are shown in Table 1.

3. Case study using NIST SRMs 2701 and 2700

The New Jersey Department of Environmental Protection (NJDEP) completed a study to determine the levels of hexavalent chromium in background soils from urban areas in New Jersey. For the purposes of this study, background soils are defined to be those soils that have not been impacted by a known or possible source of hexavalent chromium release or emission. The need for data on background levels of hexavalent chromium in New Jersey results from NJDEP’s adoption of a health-based soil remediation criterion of 1 mg kg\(^{-1}\) for hexavalent chromium, and the stated intention of the agency to propose a formal rule for a hexavalent chromium soil remediation standard based on that health-based criterion.

Soil samples from 197 sites were collected from 10 New Jersey counties. Analyses of all samples were performed by the method pair 3060A/7199. Selected samples that had Cr(vi) above the reporting limit of 1.4 mg kg\(^{-1}\) by Method 7199 were also analyzed by Method 6800. In accordance with the quality control protocols required by Methods 3060A, 7199 and 6800, two quality control procedures involving the use of reference materials were implemented for both Methods 7199 and 6800 measurements:

1. Analysis of a 1/100 stoichiometric dilution of NIST SRM 2701 that had been prepared for this project by the USGS. An aliquot of this material was digested and analyzed with each sample delivery group.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>NJDEP background soil study quality assurance using NIST SRMs percentage recovery</th>
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<tr>
<td></td>
<td>Method 7199(^{a})</td>
</tr>
<tr>
<td>1/100 dilution of NIST SRM 2701 (with quartz sand)</td>
<td>93.1 ± 4.2 ((N = 13))</td>
</tr>
<tr>
<td>Matrix spike</td>
<td>59.0 ± 33.0 ((N = 33))</td>
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\(^{a}\) Mean value and standard deviation.

(2) As required by Section 5.4 of Method 7199, a reference material was analyzed via the addition of 25 mg of NIST SRM 2701 to 2.5 g of a sample aliquot from each sample delivery group. For both types of quality control samples, the amount of Cr(vi) that is present or added is the same (1/100 the amount of Cr(vi) in NIST SRM 2701); the difference is that in the second instance (the matrix spike), the reference material is combined with the soil matrix prior to digestion and analysis, which exposes the added Cr(vi) to potential oxidation/reduction chemistry from the components of the sample matrices.

Table 2 presents a summary of the results for these two reference material-based quality assurance analyses for the New Jersey background soil study.

4. Discussion

4.1 USEPA SW846 analytical methods and quality assurance

The publication SW-846, entitled test methods for evaluating solid waste, physical/chemical methods, is the USEPAs official compendium of analytical and sampling methods. SW-846 (ref. 15) brings together into one reference all sampling and testing methodologies approved by the EPA Office of Solid Waste for use in implementing the RCRA regulatory program. SW-846 methods are most often employed to measure analytes in non-aqueous sample matrices such as soil, sediment, sludge, ash or biota.

Chapter 2 of SW-846 provides guidance on how to use analytical methods and the data they derive. Discussion on specific “method defined parameters” highlights the fact that for certain methods such as Method 1311 “Toxic Characteristic Leaching Procedure”, the analytical result is wholly dependent upon the process used to make the measurement. This implies that the method of analysis has an analytical bias and may not provide information on the actual analyte concentration in the sample. The analytical result is inherently method-specific. To emphasize this important distinction, SW-846 “advises analysts and data users that even for those analytes that are not method-defined, different procedures may produce differences in results”. Examples cited include different measured amounts of phenolic compounds using a separator funnel (Method 3510) or continuous liquid–liquid extraction (Method 3520), and different amounts of metals found when samples are prepared by acid digestion (Method 3050) or by microwave digestion (Method 3051). In fact, in Section 1.0 of SW-846 Method 3052 (ref. 16) “Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices” notes that “this technique is not appropriate for regulatory applications that require the use of leachate preparations (Method 3050, 3051, …)”. This shows that the method used can often determine the measured concentration of an organic or inorganic analyte, and emphasizes the obligations of both the analyst and data user to understand any information the analytical method(s) provide. Another publication\(^{17}\) has addressed this discrepancy directly.

4.2 NIST SRMs: certified values vs. ancillary reference values

Data on the COAs for many NIST non-aqueous SRMs quantify the relationship between the total amount of specified analytes
in a given sample and the amounts measured via application of USEPA SW-846 methodologies. For example, consider NIST SRMs 2709a (San Joaquin Soil) and 2781 (Domestic Sludge). Both of these SRMs contain method independent certified element concentrations, which represent the total element concentrations in the samples. The certificates also report ancillary values, which are derived through applications of combinations of SW-846 sample preparation (acid leach) and determinative (atomic absorption or emission spectroscopic) methods. The ancillary values for NIST SRM 2709a range from 4% to 200% of the certified values for 23 metals. Eighteen of the 22 metals show recoveries (which are defined as ancillary value/certified value × 100) of less than 81%. For NIST SRM 2781, recoveries for 11 metals range from 50% to 96%. Clearly, for these types of samples, use of SW-846 methods may not generate data that reflects the total amount of metal in the sample, but rather method specific results.

While quality assurance protocols are contained in every analytical method to document the accuracy and precision of analyte measurement, most SW-846 methods do not require the use of SRMs as part of the method quality assurance. As noted above, Method 7199, at Section 5.4 does. Therefore, the use of reference materials as quality assurance tools for the analyses of Cr(VI) in soils provides a unique case study to examine their effectiveness.

4.3 Certification data: NIST SRM 2701

The COA for NIST SRM 2701 (ref. 21) lists the certified value for Cr(VI) as 551 mg kg⁻¹. The appendix shows that following extraction of Cr(VI) by USEPA Method 3060A, the mean for the reference value, obtained by Method 7199, is only 70.6% of the certified value, which was obtained using Method 6800. A similar comparison for data generated by Method 7196A to that generated by Method 6800 yields a nearly identical value of 69.7%. These differences are attributed to the ability of Method 6800 to correct for species interconversion (in this case, predominately reduction of Cr(VI) to Cr(III) during extraction or measurement). Methods 7196A or 7199 cannot correct for species interconversion; thus, using Methods 7196A or 7199 to measure Cr(VI) in digests of reducing soils may not accurately measure all of the Cr(VI) actually present in the sample digest. Concurrent analyses of reference materials with sample delivery groups can provide quantitative evidence for the effect of the chemistry of the measurement process on Cr(VI) quantitation.

4.4 Certification data: NIST SRM 2700

Since the mass fraction of Cr(VI) in NIST SRM 2701 is quite high (the certified value is 551 mg Cr(VI) per kg), NIST SRM 2700 (ref. 22) was created to contain a Cr(VI) mass fraction closer to that found in background or mildly contaminated soils. NIST SRM 2700 is a stoichiometric 1:40 dilution of NIST SRM 2701 with quartz sand used as the diluent. Comparing the ratios of [Cr(VI)] in SRM 2701 to that in SRM 2700 by Methods 7196A (38.4), 7199 (35.6) and 6800 (35.5), we note that the inter-laboratory means of the measured amounts of [Cr(VI)] are within 10% of the value expected from the dilution.

The summary results from the NIST SRM 2700 laboratory inter-comparison study show remarkable consistency with the results from similar studies conducted to certify NIST SRM 2701. The ratio of data by Method 7199 to that obtained by Method 6800 for NIST SRM 2700 is 0.703, while the ratio of data by Method 7196A to that obtained by Method 6800 is 0.652. The conclusion that can be drawn from these data is that even with lower concentrations of both Cr(VI) and sample matrix in NIST SRM 2700, some Cr(VI) is being reduced to Cr(III) during either digestion or analysis. The availability of both certified and reference values for each determinative method, provides critical interpretative information to both the analyst and data user.

4.5 Case study for Cr(VI) in soils using NIST SRMs for quality assurance

These two reference materials afford the analyst several options for their use, particularly as required by Section 5.4 of Method 7199:

(a) Analyze either as a quality control sample to accompany a sample delivery group, depending upon the anticipated [Cr(VI)] in the samples to be analyzed, or

(b) Use NIST SRM 2701 as a matrix spike (as was done in the NJDEP background soil study).

4.5.1 New Jersey background soils study. The flexibility in applying the use of reference materials was highlighted in the summary of the quality assurance data for the New Jersey urban background soils study shown in Table 2. The analysis of the USGS-prepared 1/100 dilution of NIST SRM 2701 as a quality control sample showed good agreement with the certified value of Cr(VI) [an addition of 5.5 mg kg⁻¹ of Cr(VI)] for both Methods 7199 and 6800, implying that for this sample no matrix-induced reduction of Cr(VI) to Cr(III) was observed. However, when the same amount of Cr(VI) [5.5 mg kg⁻¹ of Cr(VI)] is added to an actual soil sample as a matrix spike using NIST SRM 2701, the average recovery of the Cr(VI) spike was only 59% of the true value when measured by Method 7199, while near quantitative recoveries were observed when measurements were performed by Method 6800. The matrices of the soil samples to which the reference material was added caused some Cr(VI) to be unavailable for detection using Method 7199; any species conversion was compensated for when Method 6800 was used for measurement of Cr(VI). Even though data for ancillary parameters such as total organic carbon (TOC) may indicate conditions where species conversion is supported, the quantitative information provided by concurrent analyses of CRMs, which contain a known amount of analyte in an actual sample matrix, is far more useful to users of the Cr(VI) data.

These quality assurance data are supported in the portion of the NJDEP report that states that the mean concentration difference for samples for this study analyzed by two determinative methods (Method 6800–Method 7199) was 1.40 mg kg⁻¹ (±1.42 mg kg⁻¹), and that the positive value of the mean difference indicates that, on average, the Method 6800 values were larger than the Method 7199 values. The report’s conclusion acknowledges the potential for conversion of some Cr(VI) to
Cr(III) during the analytical procedure involving Method 7199, which the results of the reference material analyses support.

Even when Cr(VI) matrix spike recoveries are negligible, the use of CRMs as quality assurance tools can be extremely useful. A report\(^1\) issued by the Missouri Department of Natural Resources (DNR), discusses the sampling and analysis of soils from northwest Missouri that were contaminated with tannery waste containing Cr(VI). Analyses were performed by the Method pair 3060/7199, and used NIST SRM 2701 as a matrix spike for all sample delivery groups in addition to aqueous Cr(VI) spikes. Poor recoveries for both the aqueous and reference material spikes were noted, and the report attributes this quality assurance data from the analysis of reference materials to supporting evidence for the reducing nature of these soils that profoundly impacts measured values of Cr(VI) in the contaminated soils. The failure to recover any Cr(VI) when the reference material was spiked directly into the soil confirms that these sample types are incapable of supporting the existence of Cr(VI). Without the use of reference materials, this important conclusion could not have been reached.

These important observations from both the New Jersey and Missouri studies about the behavior of Cr(VI) and the resultant sample concentration would have been impossible without the data provided by analysis of reference materials.

Concerns regarding the efficacy of removal of analytes from non-aqueous matrices must be addressed on a matrix- and species-specific basis and should involve determinative methods that are independent of measurement bias. The efficacy of USEPA Method 3060A has been challenged using NIST SRM 2701 (ref. 24). Studies evaluating the ability of Method 3060A to remove indigenous Cr(VI) from a variety of sample types are currently being performed.\(^2\)

5. Perspectives on using reference materials for method quality assurance

Several areas of concern are raised by commercial environmental testing laboratories to avoid using CRMs to support measurements performed by other USEPA SW-846 analytical methods. These areas of concern are: (1) CRMs are too expensive, (2) CRMs do not exist to address all sample types and analytes, (3) the levels of analytes in CRMs are not at levels that coincide with the concentrations of analytes in most analytical samples, and (4) most methods don’t require the use of CRMs. Some perspectives on each of these issues are offered below:

5.1 Cost

NIST SRMs cost several hundreds of dollars typically for less than 100 g of sample. For example, NIST SRM 2701 costs $877 USD for 75 g of material, or approximately $12 per gram. When this SRM is used to quality assure Method 7199, the cost for its use as a laboratory control sample involves using 2.5 g of the SRM as part of a sample delivery group of 20 samples. This would add a cost per sample (assuming a sample delivery group of 20 samples) as 2.5 g × $12 per g/20 samples, which is an additional cost of $1.50 per sample. If the per sample price of analysis of Cr(VI) in soils by the method pair 3060A/7199 is approximately $100 per sample, the use of the SRM in this manner would add about 1% to the per sample cost (assuming a sample delivery group that consists of 20 samples). If the SRM were used as a matrix spike (as was done for the NJDEP background soils study), only 25 mg of the SRM would be needed per sample delivery group, making the additional cost approximately $0.01 per sample!

5.2 Availability of CRMs

As an example, the Chemical Sciences Division of NIST maintains an inventory of approximately 1200 SRMs of which about 12% are currently intended to support USEPA-driven environmental measurements. These include approximately 29 inorganic wastes, soils, sludges, paints, 37 organic compounds related to water analysis, 40 fossil fuels for supporting air quality measurements and 44 non-aqueous materials containing organic contaminants in non-aqueous materials. Other CRM providers have additional materials available. While this inventory does not cover every analyte or sample matrix, the majority are commonly-requested analyses and have a CRM available for quality assurance. Those gaps that exist can be addressed by creating additional, new CRMs as part of a strategic development program in collaboration with CRM producers.

It should be noted that SRMs need not always be used to ensure a defined level of data quality for a given project. A NIST publication describes the terms associated with various types of reference materials.\(^7\)

5.3 Levels of analytes in CRMs

It is true that values of analytes in most CRMs are often much higher than the values found in most environmental samples. Several remedies exist for this concern: (1) if choices of CRMs exist, select one which has analyte values closest to the expected concentrations of those analytes in your samples, (2) use a small amount of the CRM with high analyte levels as a matrix spike, adjusting the amount of the CRM to create an analyte addition that is closer to the concentration(s) of the indigenous analyte concentrations (within the confines of the established sample portion homogeneity) or (3) a reference material customized to the laboratory’s needs could be prepared.

5.4 Discretionary nature of CRM use in USEPA methods

Some options exist for the use of CRMs for these applications. The USEPA could modify SW-846, making CRM use mandatory for all methods as it has for Method 7199. Alternatively, project managers can require the use of CRMs for method QC as part of the quality assurance project plan.

Where no suitable CRMs are available, the use of other secondary QC materials (sometimes derived from proficiency testing programs) and/or the use of in-house prepared QC materials (as per ISO Guide 80) might be useful alternatives. It should be noted that such materials lack the rigor and traceability afforded by higher-order CRMs.
6. Summary

Referring back to the original question “are we accurately measuring how much contaminant is in the sample using the approved analytical protocol?” this can be greatly helped by using CRMs regularly as part of the quality control protocols of USEPA SW846 methods. In many cases, data from CRMs provide critical information on data quality that is simply unavailable by other means.

This paper shows that without the concurrent analysis of matrix matched reference materials, this question cannot be fully evaluated. Simple analysis of a sample by a certified lab, using an EPA-approved method does NOT address this critical issue. The use of a liquid recovery spike, which is often cited in analytical procedures does not fully assist in this evaluation process. The concurrent analyses of reference materials could provide this critical information at relatively low cost to the data user.

Disclaimer

Certain commercial equipment, instruments or materials are identified in this work to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.

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References

8 USEPA, EPA Method 7199, Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography, Revised, 1996.
10 USEPA, EPA Method 3060A, Alkaline Digestion for Hexavalent Chromium, 1996.
16 USEPA, EPA Method 3052, Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices, 1996.
23 M. Stroh, Tannery Sludge Farm Fields Site Andrew, Buchanan, Clinton and DeKalb Counties, Missouri, Missouri Department of Natural Resources, September 2010.