

Hexavalent Chromium in Ambient Air.

A Practical Guide to ASTM Method D7614-12 *Determination of Total Suspended Particulate (TSP) Hexavalent Chromium in Ambient Air Analyzed by Ion Chromatography (IC) and Spectrophotometric Measurements.*

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ABSTRACT

In 2005, Eastern Research Group (ERG), under contract with the United States Environmental Protection Agency (EPA), began development of a method to determine hexavalent chromium in ambient air at lower levels than had previously been detectable by other promulgated methods. In 2012, ERG's method was promulgated by the American Society for Testing and Materials as ASTM Method D7614-12 "Determination of Total Suspended Particulate (TSP) Hexavalent Chromium in Ambient Air Analyzed by Ion Chromatography (IC) and Spectrophotometric Measurements."

This paper is a review paper. While some original research and data is contained herein, this paper focuses on Chester LabNet's experience over the past 13 years with the analysis for hexavalent chromium in ambient air samples and the subsequent data interpretation of those results. This paper also compiles information from other sources, creating a narrative of the issues associated with sampling, sample preparation, analysis, chromatographic interpretation and data interpretation when utilizing ASTM Method D7614-12.

Key words: hexavalent chromium, Cr⁶⁺, chromium(VI), ambient air, ASTM D7614-12

DISCLAIMER

The statements and conclusions in this paper are those of the author and do not represent any method-promulgating authority or regulatory body. The mention of commercial products in connection with the material herein implies no endorsement of said products.

INTRODUCTION

Brief History of Cr⁶⁺ Sampling and Analysis in Ambient Air

In October, 1988, Research Triangle Institute (RTI) submitted research findings to California Air Resources Board (CARB) on Cr⁶⁺ in ambient air (Grohse et al. 1988). Seven years later, in 1995, CARB published its first version of Standard Operating Procedure (SOP) MLD039 “Extraction and Analysis of Hexavalent Chromium by Ion Chromatography” (CARB 2002). Three years after that, the Occupational Safety and Health Administration promulgated OSHA ID-215 v1 “Hexavalent Chromium in Workplace Atmospheres” (OSHA 1998). Five more years elapsed before, in 2003, the National Institute of Safety and Health (NIOSH) promulgated its first version of NIOSH Method 7605 “Chromium, Hexavalent by Ion Chromatography” (NIOSH 2016).

In 2004, Eastern Research Group (ERG) contracted with the United States National Environmental Protection Agency (EPA) to study CARB SOP MLD039 for the capture and analytical determination of particulate Cr⁶⁺ from non-workplace ambient air (Swift 2012). ERG’s first method was written in September, 2005 (ERG 2005). ERG continued method development, creating at least three more modified versions of its SOP in 2006 (ERG 2006).

In 2007, the National Air Toxics Trend Station (NATTS) program used ERG’s SOP as a starting point for its own procedure, modified the ERG procedure slightly, and presented their modified procedure back to ERG. Based on NATTS protocols, ERG then modified the sampling aspect of its SOP in 2008. In 2009 ERG modified the filter preparation technique, and in 2011, ERG modified the sample extraction technique (Swift 2012).

In 2012, 24 years after RTI’s in-depth research for CARB, the EPA released ERG from their contract, and requested that the method be submitted to the American Society for Testing and Materials (ASTM) for public promulgation. ASTM reformatted ERG’s method and published it in 2012 as ASTM Method D7614-12, creating the first nationally published method for the determination of Cr⁶⁺ in non-workplace ambient air (Swift 2012).

Brief Summary of ASTM D7614-12

ASTM performed no method validation prior to publishing the method. ERG’s method was reformatted as received by ASTM, including typographical and mathematical errors, then published as an ASTM method. ERG’s method was highly prescriptive rather than performance based, and consequently, many laboratories have deviated from the prescriptions found in the method.

ASTM Method D7614-12 consists of four distinct steps. These are, in order:

1. Preparation of filters for sampling;
2. Collection of samples;
3. Extraction of post-sampling filters; and,
4. Analysis of extracts by Ion Chromatography – Post-column derivatization (IC-PCD).

This paper will examine the four steps of the method above, and, in addition, provide some insight into data interpretation.

Pourbaix Diagram

A Pourbaix diagram indicates the most prevalent speciation state of an element or compound at a given pH and eH (redox potential). The dashed green line indicates 1 atm O₂ (top) or 1 atm H₂ (bottom).

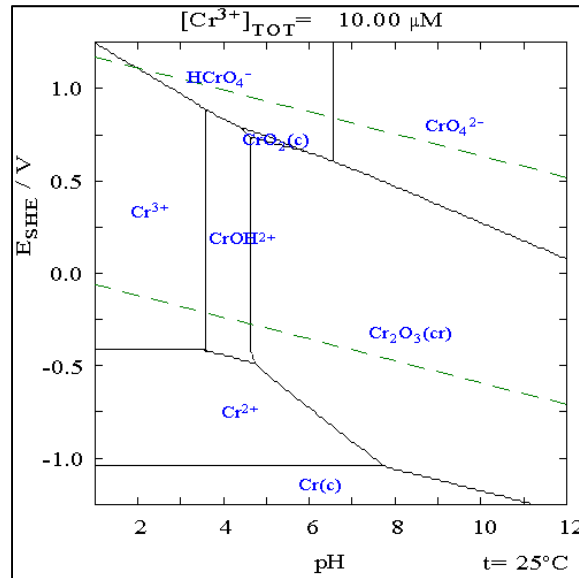


Figure 1. Pourbaix Diagram (in water) of Cr Speciation (Kotaś and Stasicka 2000)

By volume, dry air is 78% Nitrogen and 21% Oxygen, with the balance made up of a variety of other gasses. Thus, assuming the eH of the airshed being sampled is not extremely unnatural, and assuming the partial pressure of oxygen in the gasses being sampled is similar to that of atmospheric air, the biggest contributor to conversion between Cr³⁺ and Cr⁶⁺ is pH.

The pH at which it is unlikely for conversion (in either direction) to occur is the point on the line between Cr₂O₃ and CrO₄²⁻ that corresponds to 0.21 atm O₂. This point occurs at approximately pH 8.5. Above pH 9, the reaction equilibrium will favor Cr⁶⁺. Below pH 8, the reaction equilibrium will favor Cr³⁺. If other components significantly change the eH of the sample airshed or sample extract, the pH necessary to maintain equilibrium between Cr³⁺ and Cr⁶⁺ will also change.

Due to the pH dependency of the Cr³⁺/Cr⁶⁺ equilibrium, all filters upon which the samples are collected are first impregnated with sodium bicarbonate (NaHCO₃), which minimizes the possibility of conversion between chromium species.

FILTER PREPARATION

During method development, ERG tested cellulose, binderless quartz, PVC, and PTFE filters to determine the cleanest available filter type with the best collection efficiency (ERG 2005). ERG found that all filter matrices that were both tested and amenable to impregnation had high and variable concentrations of Cr^{6+} as received from the supplier. ERG did not test acid-hardened cellulose filters.

Acid-hardened cellulose filters are acid washed then solvent rinsed by the manufacturer, in effect performing the acid washing requirements of ASTM D7614-12. Whatman Grade 541 or Ahlstrom Grade 55 acid-hardened cellulose filters are available in 47 mm diameter as a standard product; 37 mm filters are available by custom order. These filters are typically free of detectable Cr^{6+} as received, and thus are less labor intensive to clean. Chester LabNet prescreens each new lot of filters prior to impregnation to determine if the levels of Cr^{6+} observed are significant enough to warrant purchasing a different lot of filters.

ASTM Method D7614-12 prescribes the use of a nitrogen-purged glove box for all filter handling. The use of a glove box severely limits the number of filters which can be cleaned and impregnated in one batch. It is the experience of Chester LabNet and South Coast Air Quality Management District (SCAQMD) that a glove box is unnecessary as long as the environment in which the filters are handled is clean of particulate Cr^{6+} . Chester LabNet performs all filter impregnation and filter handling in a laminar flow hood of the type typically used in the handling of microbiological media. This hood is located in a small room with a dedicated HVAC unit equipped with a HEPA filter. SCAQMD impregnates filters in capped PTFE bottles and dries their filters on PTFE plates in a nitrogen purged stainless steel oven under no heat. Even with these alterations, the cleaning and impregnation process for a batch of 100 filters may take up to 4 days to complete.

Following ASTM Method D7614-12, the number of filters possible to impregnate in one batch is limited by the size of the glove box, thus impregnation batches may be limited to 20 – 50 filters at a time. Chester LabNet is capable of impregnating over 700 filters per week. SCAQMD is capable of impregnating approximately 600 filters per week. ASTM Method D7614-12 would allow for the impregnation of 150 filters per week, assuming an impregnation batch size of 50 filters. For some projects, the ability to impregnate large quantities of filters in a relatively short period of time is imperative, thus some modification of the method is necessary. Demonstration of the defensibility of the modifications is found in the impregnation lot check analysis. If 10% of filters in the impregnation batch yield results below the detection limit, the modifications are technically defensible.

Given the extremely low detection limit attainable by the method, sporadic contamination is a genuine concern during impregnation. Cleanliness of impregnated filters is not guaranteed simply by using the same impregnation protocol, in the same area of the laboratory, under the same conditions. It is imperative that each batch of impregnated filters be screened for Cr^{6+} prior to their use in sampling. ASTM D7614-12 prescribes that 10% of impregnated filters be screened prior to use. This can pose a burden on laboratories who need to generate large numbers of impregnated filters in a short period of time, as 10% of the impregnated filters are

destroyed during the screening process. Chester LabNet screens 10% of the filters impregnated at their facility, however SCAQMD screens 2% or less, and has found this to be sufficient.

Chester LabNet has determined that the critical components of filter preparation are as follows:

- cleanliness of impregnation location (especially air quality),
- cleanliness of labware,
- cleanliness of drying conditions,
- cleanliness of storage conditions, and
- use of non-metallic labware in all steps of filter handling or reagent preparation.

All new labware, whether glass or plastic, should be metals-cleaned prior to use. Plastic or PTFE forceps significantly minimize the possibility of filter contamination during handling. Plastic spatulas minimize the possibility of contamination during reagent preparation. Any entity attempting this method must heavily scrutinize all aspects of all stages of the method for possible sources of contamination to successfully perform the method.

The most prominent contributor of contamination during impregnation and storage is exposure to air containing metallic particulates. Thus, a typical laboratory airshed is not likely to provide a clean enough environment for the cleaning, impregnation, storage or handling of filters. During impregnation and drying, the filters must be sequestered from typical room air. During cold storage, both at the laboratory and in the field, the filters must be heavily sequestered from the freezer airshed. Depending on the type of freezer used, this sequestration may need to be extreme.

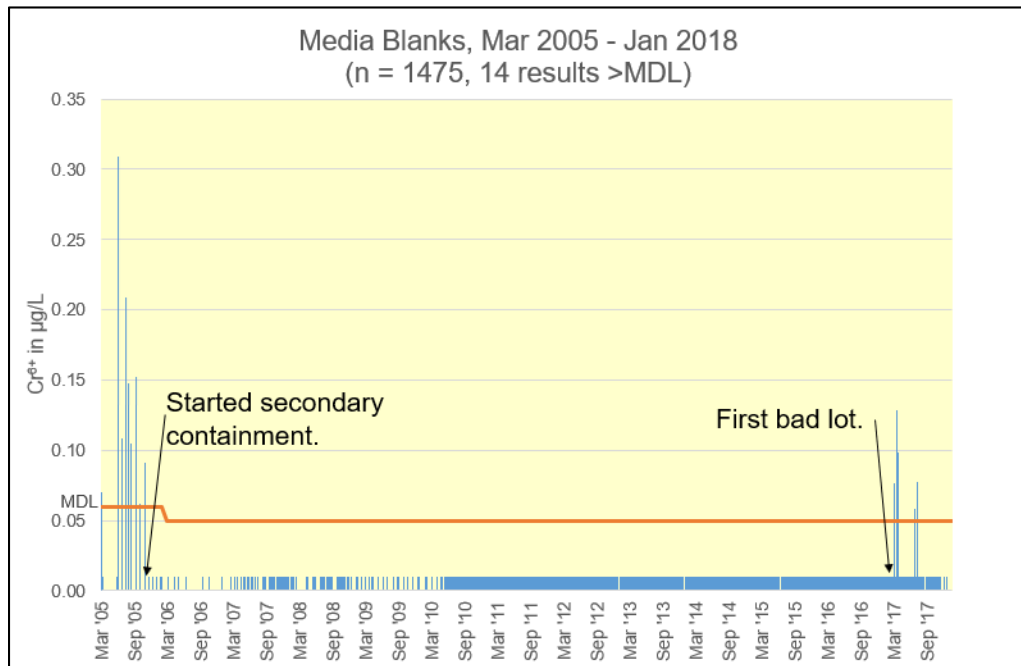




Figure 2. Filter Blank Results After Frozen Storage.

The graph above shows the results of blank filters that were cleaned, impregnated, and stored frozen at Chester LabNet. The short blue lines at a concentration of 0.01 µg/L indicate results below the detection limit and are included for a visual example of the number of filter blanks analyzed by the laboratory between March, 2005 and January, 2018. The red line indicates the detection limit at the time of analysis.

Initially, the laboratory stored filters in a freezer inside plastic petri dishes held closed by rubber bands. Over a period of 3 – 6 months, it became obvious that post-impregnation contamination was occurring. The Petri dishes containing the clean impregnated filters were subsequently placed in a large thick-gauge plastic bag that was rolled up with the petri dishes inside to further sequester the filters from the freezer airshed. The beginning of the use of secondary containment is annotated on the graph. The first bad impregnation lot occurred 12 years after implementation of secondary containment. Chester LabNet now stores filters in plastic Petri dishes, inside glass dishes with snap-on lids fitted with silicone gaskets, contained within sealed plastic bags during frozen storage (primary, secondary and tertiary containment, respectively).

SAMPLING CASSETTES

ASTM Method D7614-12 prescribes the use of Teflon cassettes during sampling. Another option is the use of Federal Reference Method (FRM) cassettes. Each of these cassettes has benefits and drawbacks.

Table 1. Low Volume Sampler Cassettes	
 <p>FRM Cassettes (Mahoney-Watson ©2017)</p>	 <p>Teflon Cassette (Savillex ©2017)</p>

Due to the ease of contamination of the filters, Teflon cassettes are useful in that the filter is entirely contained within the cassette, and the inlet and outlet of the cassettes are capped such that the interior of the cassette remains sequestered from possible contamination. Larger particulate matter (PM) is contained within the cassette during transport, and is much less likely to be lost, especially PM >10 µm. Teflon, however, is very prone to static charge, and the airflow through the cassette creates enough charge that fine particulate will adhere to the walls of the small dilution chamber on the inlet side of the cassette. Thus, particulate matter <2.5 µm (PM_{2.5}) may be lost to the static charge inside the cassette during sampling, as quantitative recovery of this PM is prohibitively difficult without contamination issues. In addition, the cassettes are expensive (~\$100 per cassette) and require the use of a glass funnel as a rain shield during sampling. Transport of the glass funnel must be carefully performed to avoid breakage,

and the funnel must be thoroughly cleaned between uses. Borosilicate glass is similarly prone to static issues, and PM loss in the funnel stems has been observed by Chester LabNet. Loading the filter into the cassette and unloading it after sampling is not easily performed in the field, making rapid re-use of the cassettes difficult.

FRM cassettes should be familiar to those who routinely perform ambient air sampling, thus, the learning curve for the use of this style of cassette is generally negligible. They are easy to load, unload and transport, although it is recommended that cassette loading and unloading be performed in the same environment as that in which the filters were impregnated. The metal support screens (stainless steel or aluminum) have been observed to cause contamination if the filter is in contact with the screen. The use of a polyester drain disc between the filter and the screen prevents the possibility of Cr⁶⁺ contamination due to the support screen. Because this cassette is open-faced, loss of PM is distinctly possible, especially loss of PM >10 µm. Secondary containment is necessary to capture any PM that falls off of the filter during transport. Tertiary containment is advised to sequester the filter from the surrounding airshed during frozen storage and shipment.

SAMPLING

Sampling plans may need to be adjusted in order to site the samplers away from known sources of particulate Cr⁶⁺. These sources may include, but are not limited to, any source of metal fatigue such as electric motors (particularly those that run at high load), road dust, vehicle exhaust, and/or areas where crushing of metallic materials may be ongoing. In some cases, this may involve elevating the samplers on platforms.

A field blank is useful to ensure cleanliness of the sampler and localized airshed around the sampler. Trip blanks may be used to demonstrate the cleanliness of the shipping container, however, if the cassette and filter remain in their secondary or tertiary containers, contamination is highly unlikely.

Some versions of ERG's method called for chilling the cassettes during sampling. ASTM Method D7614-12 does not require the use of chilled cassettes during sampling for the reasons stated below, however, some still utilize this modification of the method. Chilling the cassettes during sampling helps preserve the chromium in the valence state in which it was collected, but condensation of ambient moisture leads to deliquescence during sampling, which may result in inaccurate data (Torkmahalleh et al. 2013). In addition to deliquescence, problems arise if more moisture is collected during sampling than the filter can absorb. In Teflon cassettes, this extra moisture may be transferable to an extraction vessel with the filter, however, if the cassette is frozen during transport, the moisture turns into ice which is difficult to quantitatively transfer to the filter extraction vessel. FRM cassettes do not capture moisture, rather, the sampler will pull condensed moisture through the filter, compromising the results.

Attempting to quantitate the liquid volume of ice in the Teflon cassettes further complicates matters as the laboratory must either use more total liquid volume during extraction than the method requires (mL extraction solution + mL ambient moisture collected) then determine the total extract volume, or add less extraction solution to compensate for the extra liquid volume of

the ice (mL ambient moisture collected + mL extraction solution less mL ambient moisture). In the first case, mathematical correction must be employed when back-calculating from Cr⁶⁺ per liter of extract to total Cr⁶⁺ per filter. In both cases, the extra liquid will change the pH of the final extract, possibly significantly enough to encourage the conversion of Cr³⁺ to Cr⁶⁺.

SHIPPING AND TRANSPORTATION

Shipment of unused filters to the field should be performed frozen, however, if the cassettes and/or filters are heavily sequestered from ambient air, the likelihood of contamination is minimal. As the filters have been cleaned prior to impregnation, unsampled filters are not likely to experience deleterious effects between the laboratory and the field if the filter/cassette temperature rises above 0 °C.

The reverse, however, is not true. Once particulate has been collected onto the filter, the stability of the chromium valence state becomes temperature dependent. Ensuring that the samples are frozen immediately after sampling requires that the sampler be unloaded immediately after it turns off. If the sampling plan follows the EPA's 3-day or 6-day sampling schedule, removing the sample from the sampler immediately after the sampler has turned off may present a burden to the individuals performing the sampling. This is especially true when sampling is performed from midnight to midnight, as the sample will need to be removed from the sampler in the middle of the night. Unfortunately, it is imperative that the cassettes be frozen immediately post-sampling to retard the conversion of Cr⁶⁺ to Cr³⁺ or vice versa. It has been found that allowing samples to remain in the sampler can lead to a loss of at least 20% of Cr⁶⁺ after 1 day (ERG 2005).

Shipping filters or cassettes in such a manner that they arrive at the laboratory still frozen is an exercise in logistics. Blue ice will typically not keep a shipping container at <0 °C during shipment. Thus, dry ice is the preferred cooling agent; however, dry ice is considered a Hazardous Material and requires HazMat shipping. In addition, priority overnight shipping is necessary, as neither blue ice nor dry ice will be able to maintain the shipping container at <0 °C if the container takes more than ~24 hours to transport between the time of packaging and the time of arrival at the laboratory.

The type of container in which the sample is shipped is also important. Plastic coolers are not ideal for shipping with dry ice, as the interior of the cooler may shatter during shipment. Styrofoam coolers, in the form of cooler boxes, are significantly less likely to shatter in the presence of dry ice, and, due to their uniform shape and lack of handles, are also less expensive to ship than plastic coolers.

SAMPLE RECEIPT AND CASSETTE UNLOADING

Upon receipt at the laboratory, the temperature of the samples or shipping container must be immediately recorded. A "temperature bottle" is not viable when using dry ice, and dry ice has been observed by Chester LabNet to destroy Max/Min thermometer sensors. An infrared (IR) beam thermometer can be successfully used. IR thermometers may encounter difficulties if the sample container lacks a suitable surface for the IR beam (e.g., Petri slides, clear FRM mailers).

In this case, measuring the temperature of the bottom of the shipping container may need to be substituted for measuring the temperature of a sample container. Taking the temperature of the filter itself is not recommended, as the amount of time necessary to remove the filter from its container(s) and cassette is sufficient for the filter to reach ambient temperature.

If the sample has been shipped on dry ice, the temperature may be below the IR thermometer's range. In this case, recording a temperature of "<[low range]" may be necessary, and the laboratory may need to refer to the IR thermometer's user's manual to determine the thermometer's low range. Alternately, if dry ice is still present in the shipping container, a simple notation of "dry ice present" may be satisfactory to the client and/or regulatory authority.

Samples need to remain frozen and must be immediately transferred from the shipping container to a freezer after the arrival temperature has been documented.

To avoid post-sampling contamination, it is recommended that filters be unloaded from the cassettes in the same clean environment in which the filters were cleaned, impregnated, dried, and loaded into the cassettes. Some field engineers prefer to load and unload their own cassettes in the field when working with FRM cassettes, however, this increases the likelihood of Cr⁶⁺ contamination of the filter, as finding a location in the field with a clean working surface and clean airshed may not be feasible. While cassette loading and unloading have been successfully performed by some field engineers without issue, it is not recommended.

ASTM Method D7614-12 prescribes the removal of filters from cassettes using disposable gloves. Both latex and nitrile react with the colorimetric reagent to form a diphenylcarbazone complex that absorbs at 530 nm. Thus, if gloves are used, PVC gloves are preferable.

Once a sample is collected on a filter, the section of filter that was masked by the cassette is very small, making removal of filters using gloved hands problematic as damage to the sample deposit is almost certain, including transfer of the deposit to the glove. The use of plastic or PTFE forceps is preferable, touching the filter only on masked areas where no sample deposit exists. This decreases the likelihood of deposit transference as well as decreasing the likelihood of contamination from the gloves. Plastic or PTFE forceps must be cleaned prior to their first use in handling filters. An effective cleaning technique is to sonicate the entirety of the forceps in extraction solution for one hour. After the first use, forceps may be stored in a clean container, such as a thick gauge antistatic bag, and cleaned between uses with ethanol and a Kimwipe.

When unloading post-sampling filters from their cassettes in the field, the filter should be immediately placed in a Petri slide, the slide should be immediately closed and placed in a secondary container within a tertiary container. If cassette unloading occurs at the laboratory, the filter should be placed directly in an extraction vessel. The extraction vessel must then be tightly capped to prevent exposure to the freezer air, then stored frozen until extraction.

FILTER EXTRACTION

The use of extraction vessels made of HDPE, LDPE, or Polypropylene are recommended for extraction by sonication. Polystyrene is not recommended due to its tendency to crack upon sonication, allowing sonicator water containing Cr^{6+} to enter the extract.

ASTM Method D7614-12 prescribes 10 mL of extraction solution per filter during extraction. The same method later calls for 5 mL of sample to be loaded into an autosampler vial. This makes re-analysis (for replicate QC samples, spiked QC samples or re-analysis due to instrumentation errors) problematic, as any re-analysis will require the use of the entirety of the remainder of the extract. The use of 15 mL of extraction solution per filter allows for the analysis of QC samples with enough extract remaining for re-analysis, if necessary.

Initially, ERG's method called for 3 hours of sonication with deionized water based upon CARB's SOP MLD039 (ERG 2005). Prior to the promulgation of the method under ASTM, this was changed to 1 hour of sonication using a 20 mM NaHCO_3 extraction solution. As noted in the Pourbaix diagram above, pH higher than 9 results in the equilibrium of the $\text{Cr}^{3+}/\text{Cr}^{6+}$ speciation to favor Cr^{6+} . ERG found that when impregnated filters spiked with equal amounts of both Cr^{3+} and Cr^{6+} were extracted by sonication, the recovery of Cr^{6+} increased dramatically with increased sonication time (Swift 2012). It is not clear whether the filters were extracted using 20 mM NaHCO_3 or using deionized water. Chester LabNet was unable to replicate these results using either deionized water or 20 mM NaHCO_3 extraction solution.

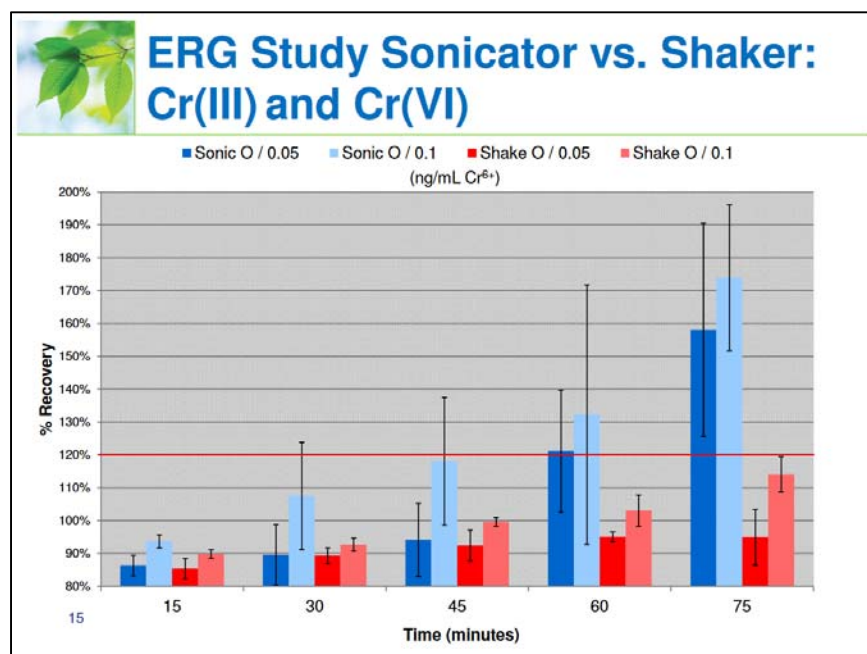


Figure 3. Recovery versus sonication time, unfiltered extracts. (Swift 2012)

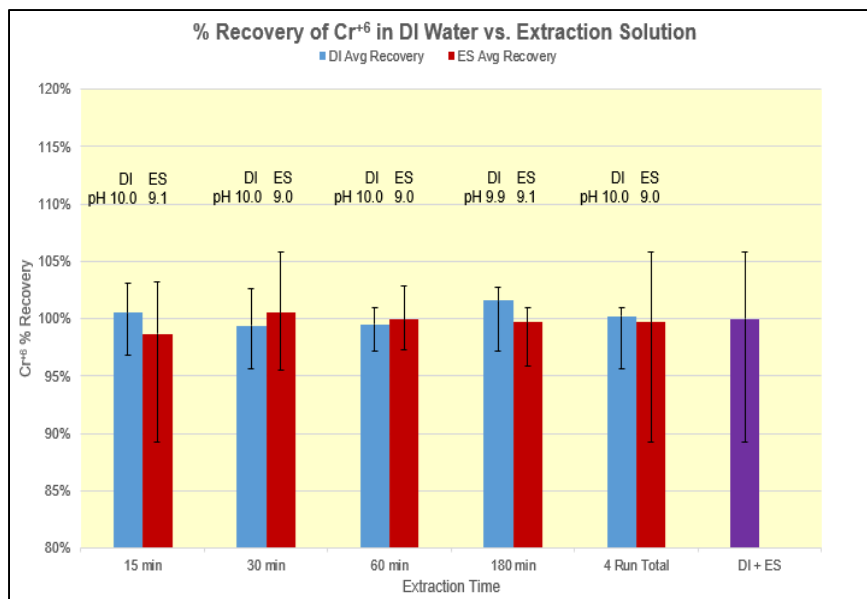


Figure 4. Recovery versus sonication time, filtered extracts. (Chester LabNet 2018)

Chester LabNet found that both the deionized water extracts (DI) and the extraction solution extracts (ES) had a final pH higher than the assumed optimal pH for Cr³⁺/Cr⁶⁺ equilibrium. Several methods state that the optimal pH for equilibrium between Cr³⁺ and Cr⁶⁺ is 8.0 - 8.5 (EPA 1992, 40CFR60 2017 and CARB 1997). The pH difference between the two extraction solutions above is believed to be a result of the buffering effect of the 20 mM NaHCO₃ solution.

During method development, ERG did not filter their extracts. Chester LabNet found post-sonication filtration of the extract to be highly advisable, though it is not mentioned in ASTM Method D7614-12. It is Chester LabNet's and SCAQMD's experience that failure to filter a sample after extraction may lead to the conversion of Cr³⁺ to Cr⁶⁺ within hours after the end of sonication. Filtration of the extract through a 0.2 μm Acrodisc seems to mitigate this problem. The opposite (conversion of Cr⁶⁺ to Cr³⁺) is also possible, however, the laboratory has not encountered this issue to date. Below is a graph showing results of unfiltered real-world sample extracts over time.

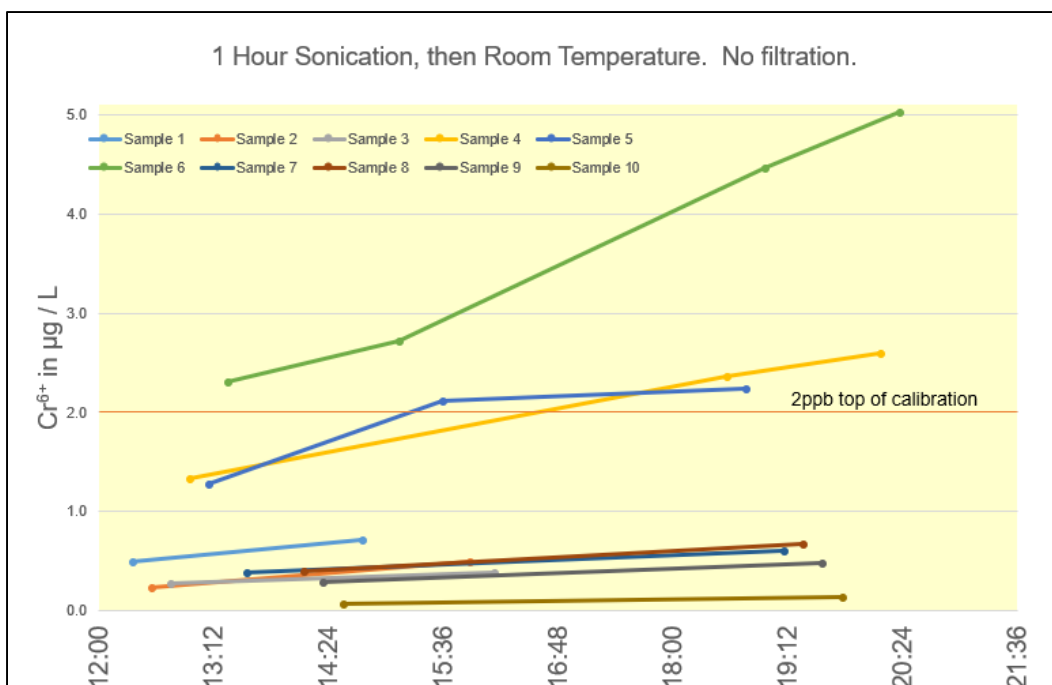


Figure 5. Increase in Cr⁶⁺ Concentration Over Time in Unfiltered Sample Extracts.

ANALYSIS

Reagents and Reagent Preparation

It is recommended that all laboratory glassware used in the performance of ASTM Method D7614-12 be cleaned with 10% HNO₃ and rinsed thoroughly prior to use. After cleaning, the glassware should be dedicated to one purpose only (e.g., the volumetric flask used to make the eluent should be used only for making the eluent and for no other purpose). Plastic labware generally does not have problems with contamination. The use of metallic labware (e.g., metal spatulas for weighing reagents, metal forceps) should be avoided to prevent contamination.

The reagent preparation in ASTM Method D7614-12 is fairly straight-forward, however, due to historical artifacts during method development and subsequent reformatting and publication by ASTM, some of the reagent preparation requirements are mathematically or factually incorrect.

Table 2. Reagent Preparation Errors Found in ASTM Method D7614-12		
ASTM Method D7614-12	Correction	Assumed Cause of Error
Ammonium hydroxide ... 28.0 – 30.0% NH ₄ basis, specific gravity 0.99 [sic] (g/cm ³)”	Ammonium hydroxide has a specific gravity of 0.899 g/mL (Budavari 1996)	Typographical error.

ASTM Method D7614-12	Correction	Assumed Cause of Error
Eluent Stock, 250 mM ammonium sulfate...and 100 mM ammonium hydroxide ... dissolve 66 g of ammonium ... Add 7 mL of ammonium hydroxide and dilute to [2 L] with DI water.”	100 mM NH ₄ OH ≈ 13 mL of ~30% NH ₄ OH diluted to 2 L. [ASTM Method D7614-12 has incorrect formulation of this reagent]	One of the changes to ERG’s method during method development doubled the amount of eluent prepared, however, documentation doubling all of the component reagents was not performed.
Sodium Bicarbonate Impregnating Solution (1.2M) ... [5g NaHCO ₃ diluted to 500 mL DI]”	5g/0.5L x mol/84g = 0.12M [ASTM Method D7614-12 has correct formulation for this reagent, but incorrect nominal concentration]	Originally, ERG’s method referred to this as 120 mM. Typographical or mathematical error in changing units from “mM” to “M”.

In addition to these published errors, crucial elements were also omitted. Two omissions pertain to the reagents utilized in the method.

After making the filter impregnation solution, it is crucial that a 1 mL aliquot of solution be diluted to 5 mL with 20 mM NaHCO₃ extraction solution and analyzed prior to use. If Cr⁶⁺ is detected (peak present), the glassware must be cleaned with 10% HNO₃ again and the solution remade to avoid filter contamination during impregnation.

The other crucial element omitted is that the stability of the diphenylcarbazide (DPC) colorimetric reagent (H₂SO₄/DPC) is temperature dependent. Heat will cause the reagent to degrade faster. When making the reagent, it is important to combine the H₂SO₄ with approximately ½ the final volume of deionized water and allow it to cool first. Then add the DPC to methanol (MeOH), sonicating the solution until all DPC is dissolved, and take to volume. After the H₂SO₄ has cooled to near room temperature, the DPC/MeOH solution may be added to the dilute H₂SO₄ solution and brought to volume. Immediately after combining the two solutions, this reagent should be clear. It should also be either colorless or very slightly colored, depending on the manufacturer of the DPC. Over time, the solution will darken. Given enough time, the solution will turn black. The darkest color at which the solution is still reliable is honey. If the solution is darker than honey (approximately 8 to 9 days after preparation), it should be remade.

Instrumentation

ASTM Method D7614-12 is highly prescriptive regarding some aspects of instrumentation but is vague about some critical components. Almost any Ion Chromatography system will work with this method, as long as it has post column derivatization capabilities, a UV/Vis detector, the ability to ensure that a 3:1 ratio of eluent to colorimetric flow, columns capable of separating out metals cations, and reasonable software control.

In 1989, researchers at CARB found that concentrations of extraction solution >50 mM NaHCO_3 caused degradation of their column (Papa and Castillo 1989). Chester LabNet has found modern columns to be slightly more robust, but at concentrations >0.1 M, column degradation has been observed.

The 3:1 flow rate ratio of eluent to colorimetric solution is critical. The eluent is a hydroxide eluent (ammonium-based), and the colorimetric solution is acidic. The diphenylcarbazone complex formed by the reaction of diphenylcarbazide and Cr^{6+} is pH dependent. Variability in the flow rate of either the eluent or the colorimetric reagents will lead to lower precision and accuracy as the colored complex formation becomes weaker or stronger with the changing pH of the combined solutions.

The key components of the instrument are as follows:

- Eluent Pump;
- Colorimetric Pump (older pneumatic delivery systems may suffice; however, control of flow rate will be diminished resulting in higher detection limits);
- 1 milliliter (mL) sample loop;
- Guard and separatory columns capable of separating Cr^{6+} from other analytes (e.g., Thermo NG1 guard and CS7 separatory columns);
- Mixing Tee;
- Reaction coil;
- Flow-through, small-bore UV/Vis cell capable of reading at 530 or 540 nm; and,
- Software capable of governing the instrument and manipulating the chromatograms.

Draining all waste lines into a carboy containing concentrated H_2SO_4 is recommended. If this is not performed, the high pH of the waste will result in volatilization of NH_3 in quantities large enough to create a health hazard, burning mucous membranes. Any analyses for NH_3 or NH_4 occurring nearby will be contaminated by the volatilized NH_3 . If using a waste carboy, 40 mL concentrated H_2SO_4 to 1 L of waste is sufficient to prevent volatilization of NH_3 .

Quality Control Samples

Due to the different terminology used by different entities, the following table is a summary of the Quality Control elements recommended to be included with each preparation and analytical batch of samples. Control limits are given only for those QC samples required by ASTM Method D7614-12.

QC Element	ASTM	TNI 2016	Chester LabNet
Calibration	6 points plus blank. [R ² >0.995 and RSD <10%]	5 points plus blank. [%RE or %RSE in control]	7 points plus blank. [%RE in control for all calibration points]
Init. Cal. Verification	Secondary Source [±15% Rec.]	Secondary Source [none given]	Secondary Source [±10% Rec.]
Init. Cal. Blank	[<DL]	[<DL]	[<DL]
Method Blank ¹	Not Mentioned	1 every ≤20 samples	1 every ≤20 samples
Media Blank ²	1 every ≤10 samples [<DL]	Not Mentioned	1 every ≤20 samples [<DL]
Low Level LCS ³	Not Mentioned	Not Required	1 every ≤20 samples
Laboratory Control Standard (LCS) ⁴	1 every ≤10 samples [80% - 120% Recovery]	1 every ≤20 samples [none given]	1 every ≤20 samples [80% - 120% Recovery]
LCS Duplicate ⁵	Not Mentioned	1 every ≤20 samples	1 every ≤20 samples
Replicate	Not Mentioned	Not Mentioned	1 every ≤20 samples
Post Extract Spike	Not Mentioned	Not Mentioned	1 every ≤20 samples
Continuing Cal. Verification	Every 10 injections and end of run. [±15% Rec.]	Every 10 injections and end of run. [none given]	Every 10 injections and end of run. [±10% Rec.]
Continuing Cal. Blank	Every 10 injections and end of run. [<DL]	Every 10 injections and end of run. [<DL]	Every 10 injections and end of run. [<DL]

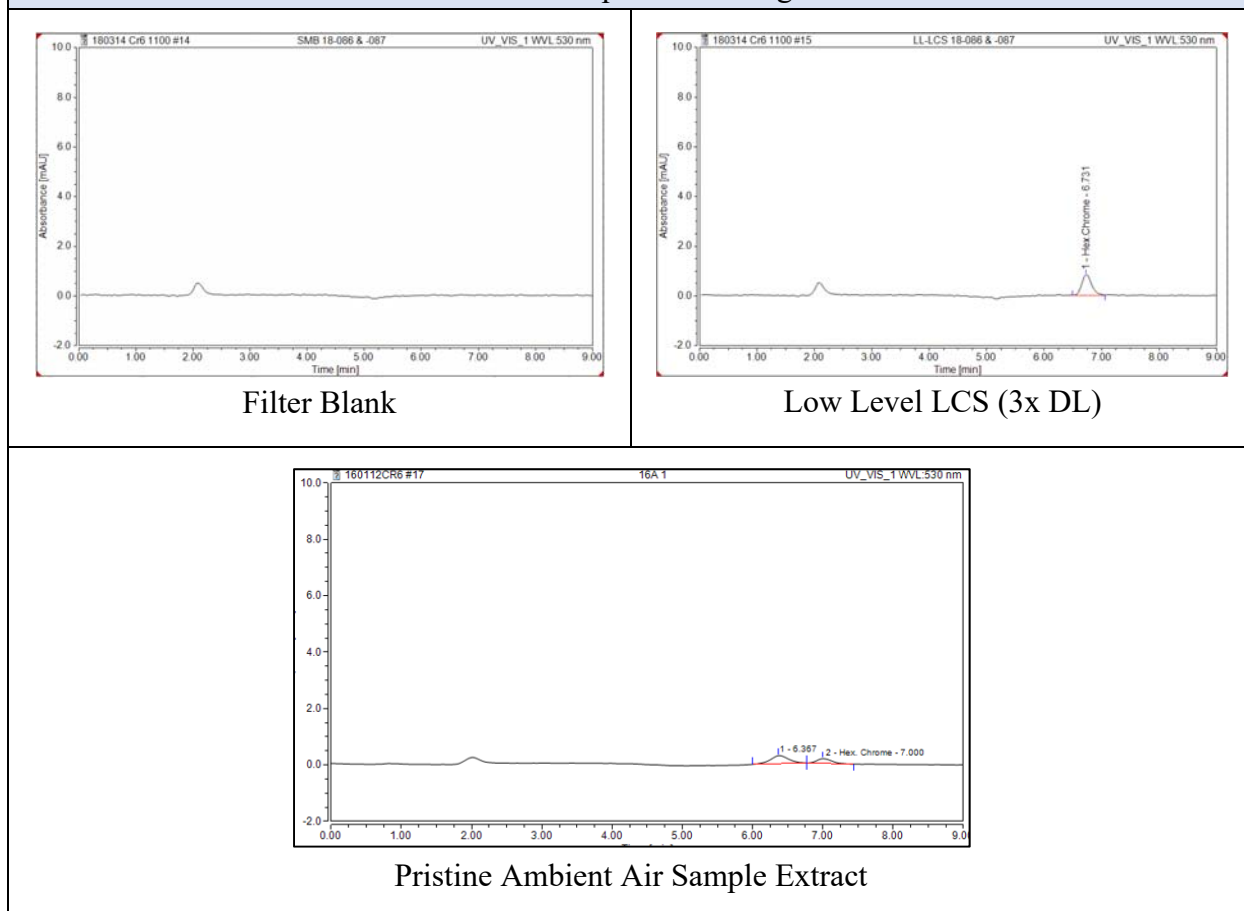
Notes:

1. Method Blank consists of all reagents taken through the extraction and analyzed. No filter is contained in this blank (TNI 2017).
2. Media Blank consists of a blank impregnated filter and all reagents taken through the extraction and analyzed (ASTM 2012).
3. Low Level LCS is a blank impregnated filter spiked at approximately three-times the Detection Limit. It verifies the low end of the calibration curve and may be used in determination of detection limits (TNI 2017).
4. Called a “Method Spike” in ASTM Method D7614-12 (ASTM 2012).
5. Required by the 2016 TNI Standard for any method for which a true duplicate analysis cannot be performed (TNI 2017).

Chromatographic Interpretation

A clean chromatogram will yield a flat baseline at the beginning, followed by a slight elevation of the baseline as the liquid in the sample loop (at ambient pressure) pressurizes in the columns to the normal operating pressure of the instrument. If Cr⁶⁺ is present, it will appear as a triangular peak.

Table 4. Example Chromatograms

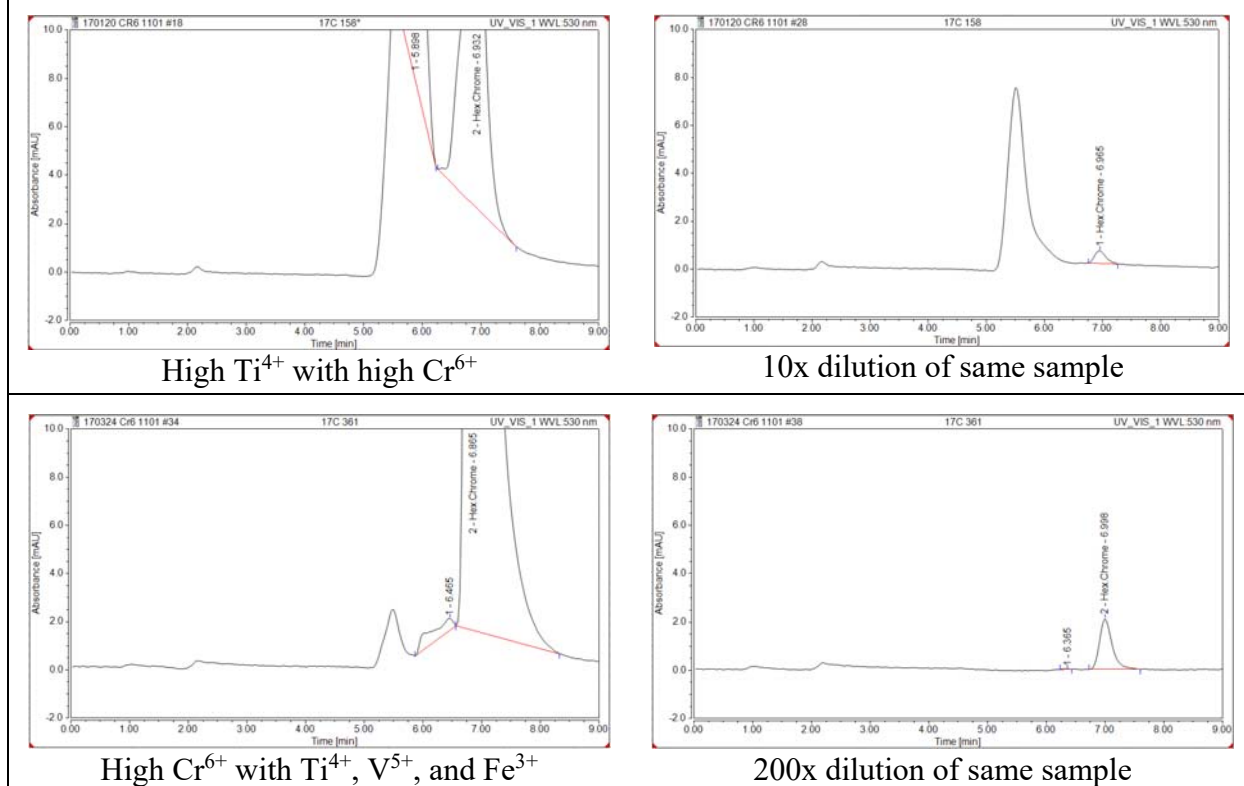


Due to the crustal availability of Fe, a small Fe^{3+} peak appears immediately prior to the Cr^{6+} peak in nearly all samples, including pristine ambient air samples. In airsheds with larger amounts of Fe present than can be attributed to crustal availability, this peak can sometimes overwhelm the Cr^{6+} peak or cause the Cr^{6+} peak to ride on the tail of the Fe^{3+} peak. Dilution of the sample or chromatographic manipulation of baselines (e.g., shape shoulder, split peak) may be required to accurately quantitate Cr^{6+} .

The four most common analytes, aside from Cr^{6+} , which have an affinity for the column matrix and form diphenylcarbazone complexes that absorb at 530 nm resulting in peaks, are Fe^{3+} , Ti^{4+} , V^{5+} , and Mo^{6+} (Chester LabNet historical experience, BAAQMD 1991, CARB 1997, EPA 1992, NIOSH 2016, SCAQMD 2017). As noted above, Fe^{3+} will elute off just prior to the Cr^{6+} peak. Of the four elements listed above, Fe^{3+} is the most common one observed by Chester LabNet.

Less common elements seen in chromatograms tend to occur in urban or industrial airsheds. In airsheds adjacent to some aerospace industries, a Ti^{4+} peak may elute off several minutes before Cr^{6+} . V^{5+} elutes off between Ti^{4+} and Fe^{3+} and is most commonly found in industrial airsheds with ore refining or high purity metal production. Mo^{6+} elutes off slightly after Ti^{4+} and is commonly found in airsheds containing industries specializing in coatings, inks, or some types of lubricants.

Table 5. Example Chromatograms Containing Interferents.



A large body of methods exist for the determination of Cr⁶⁺ that can provide some guidance on interferences. Some of these methods and their listed interferences are as follows:

- ASTM Method D7614-12 and CARB SOP MLD039 list NaCO₃ as an interferent, presumably due to baseline changes that occur in the presence of a CO₃⁻ peak (ASTM 2012 and CARB 2002).
- SCAQMD SOP 0046 and NIOSH Method 7605 list Fe, Cu, Ni and V as interferences that will form diphenylcarbazone complexes which resolve as peaks that interfere with the absorbance of Cr⁶⁺ during spectrophotometric readings (SCAQMD 2017 and NIOSH 2016).
- CARB Method 425 lists Mo⁶⁺ and V⁵⁺ as interferences that will form diphenylcarbazone complexes which resolve as peaks that interfere with the absorbance of Cr⁶⁺ during spectrophotometric readings (CARB 1997).
- BAAQMD Method 34 lists Hg, Mo and V as possible interferences that will form diphenylcarbazone complexes which resolve as peaks that interfere with the absorbance of Cr⁶⁺ during spectrophotometric readings (BAAQMD 1991).

- EPA SW-846 Method 7196A lists Hg and Mo as possible interferents that will form diphenylcarbazone complexes which resolve as peaks that interfere with the absorbance of Cr^{6+} during spectrophotometric readings (EPA 1992).

To date, this author has been unable to find a means of removing these interfering peaks without also eliminating Cr^{6+} . At this time, the best available means for obtaining accurate Cr^{6+} data is to dilute out any interfering peaks.

DATA INTERPRETATION

Interpretation of the results starts with ascertaining the definition of hexavalent chromium for the project. Based on ASTM Method D7614-12, the definition, by necessity, must be a functional one. Hexavalent chromium is any form of chromium that, when captured on a Sodium Bicarbonate impregnated cellulose filter, will remain in the form of Cr^{6+} throughout sampling and storage, then solubilize when extracted with 20 mM Sodium Bicarbonate. The Cr^{6+} in the extract will remain stable between extraction and instrumental analysis. It will have an affinity for the column matrix such that it elutes off at the same time as a Cr^{6+} standard and will form a diphenylcarbazone complex that will absorb light at 530 nm. This is a large number of variables to consider between the airshed being sampled and the final aqueous extract being analyzed.

For pristine ambient sites, these variables are not typically an issue as there are very few other oxidizing or reducing substances available to convert the available Cr^{6+} to a different valence state, and the airshed should already be in equilibrium. In urban areas or for fence-line monitoring, where the composition of both the gaseous and particulate content of the airshed may be quite different from pristine ambient airsheds, this becomes a much more complicated issue.

Sample Collection and Analysis

Many opportunities exist during sample collection and analysis for changing the valence state of the chromium being captured. The most significant conditional states to which the particulate is exposed are summarized as follows:

Airshed → particle-to-gas → particle-to-particle → solute-to-solute

Initially, in the air shed, any given particle is in contact only with the gasses in its nearby vicinity. For instance, a single particle in 24 m^3 of otherwise particulate-free gas would be highly unlikely to contact every molecule of gas in the 24 m^3 over a 24-hour period. It would contact some of the gas due to Brownian motion, but to contact all of it would be statistically unlikely. Upon collection, the first particle collected will, however, have nearly 24 m^3 of gas pulled across its surface, increasing the amount of particle-to-gas interaction. In addition, a particle is not likely to remain in contact with another particle for any significant period of time, but during sampling, the particles are concentrated into a small area, increasing the possibility of particle-to-particle interaction. Finally, any interferents on the interior of a particle will not come into contact with the exterior of another particle, but this becomes a possibility after extraction.

Particle-to-gas reactions: It has been shown that a filter spiked with Cr^{6+} in the presence of 6.7 ppbV HNO_3 will convert to Cr^{3+} in approximately 4 hours but will stabilize at roughly 11% conversion prior to the end of a 4-hour period. (Grohse et al. 1988). However, if the amount of HNO_3 is increased to 46 ppbV, roughly 90% conversion occurs by the 24-hour mark (Grohse et al. 1988). Other gasses may also cause chromium conversion, be it oxidation or reduction. The increased amount of gas to which the particle is exposed during the sampling process itself may affect the observed results of Cr^{6+} .

Particle-to-particle reactions: By being collected on the filters, the particles, which are assumed to be suspended in the airshed and not agglomerating, now physically contact each other for a significantly longer period of time than they would in the airshed. Grohse et al. found that Cr^{6+} in the presence of Li^+ had a demonstrated Cr^{6+} loss of 95% over 26 hours (Grohse et al. 1988). In addition, any oxidizing agents present in particulate form may convert Cr^{3+} to Cr^{6+} simply by particle-to-particle contact. As mentioned above, ionic exchange may also happen with some particulates such as bone ash (Cassell 2018).

Solute-to-solute reactions: Upon sonication, oxidizing and reducing agents which were encased in a particle prior to extraction may become dissolved in the extract and affect the valence state of the chromium species in solution, as shown in Figure 5, above.

Chemical Interferents

OSHA Method ID-215 lists Fe^{2+} as a negative interferent, decreasing the observed Cr^{6+} concentration (OSHA 1998). EPA Drinking Water Method 218.6 lists “oxidized Mn” as a possible cause of conversion of Cr^{3+} to Cr^{6+} (EPA 1991).

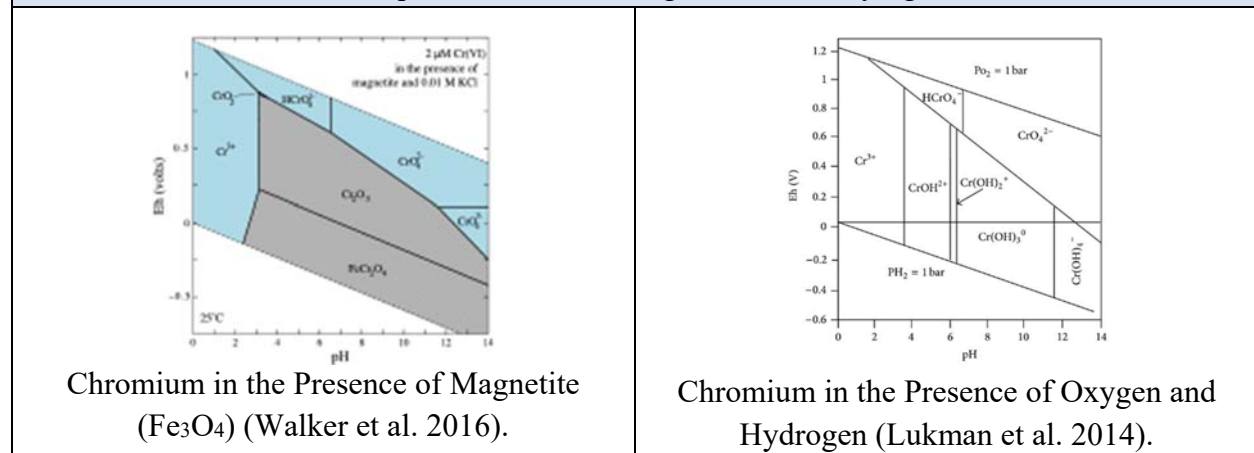
A plethora of research is available showing that Cr^{6+} in the presence of SO_x or NO_x fumes converts to Cr^{3+} (Grohse et al. 1988, Huang et al. 2013). Similarly, easily obtainable research demonstrates that Cr^{3+} converts to Cr^{6+} in the presence of ozone (O_3) (Grohse et al. 1988, Huang et al. 2013). Likewise, sulfides and certain microorganisms can convert Cr^{6+} to Cr^{3+} (Grohse et al. 1988, Joutey et al. 2015).

In addition to the above redox reactions, the interpreter of this data must also consider the possible presence of any other substances, such as bone ash, which may permanently bind Cr^{6+} into a non-soluble structure or compound (Dahbi et al. 1999). Bone ash is used industrially in the manufacture of fertilizers, and is derived from hydroxyapatite, known for its ability to perform ionic substitution in solid form (Cassell 2018). Thus, in an airshed, the presence of a rendering plant, crematorium, or fertilizer plant needs to be considered during data interpretation.

The potential for reduction of Cr^{6+} to Cr^{3+} or for permanent chemical sequestration to occur during sampling or sample extraction should not be an issue, as the human health risk is low for chromium in those forms. The larger concern is the oxidation of Cr^{3+} inflating the observed concentration of Cr^{6+} in a given airshed. This raises the question: If a facility is sited in an airshed where oxidizers are abundant, should the public health hazard assessment include oxidized Cr^{3+} as the human health hazard that Cr^{6+} presents, even if the local airshed composition is responsible for the formation of Cr^{6+} ?

There are many sources of information outside of air quality literature that may be applicable to the data interpretation of Cr^{6+} results. Both soil and geologic literature can help shed light on the interconversion of chromium species. In the two Pourbaix diagrams below, note that in the presence of Magnetite, chromium is less likely to exist in the +6 valence state than in the presence of only oxygen and hydrogen.

Table 4. Examples of Pourbaix Diagrams with Varying Conditions



Non-process Sources of Cr^{6+}

Finding the source of Cr^{6+} in an airshed can also be difficult. As engineers, data interpretation typically focusses on a process under scrutiny, however, many things outside of a given facility's processes may be contributors.

One facility that performed fabrication of titanium parts was experiencing high Cr^{6+} concentrations at the fenceline - with higher concentrations near points of ingress/egress to the buildings - yet the fabrication process used no Cr^{6+} in any capacity. Eventually the source of the Cr^{6+} was traced to metal fatigue in the motors, engines and various attachments of the tools used during fabrication. All tools were then fitted with exhausts which vented into a baghouse and the Cr^{6+} fenceline concentrations dropped to near ambient levels.

A different facility had resolved their initial Cr^{6+} emissions, then abruptly had higher emissions than had been encountered in any previous sampling event. The process ran under high heat load, which had been degrading the facility's ductwork, resulting in replacement of the aluminum ducting approximately once per quarter. To avoid the downtime involved in replacing ducting, the facility decided to replace the ducts with stainless steel ducting, which, under the same heat load, also degraded, producing particulate Cr^{6+} as part of the degradation. The facility replaced the ducting again, using higher gauge aluminum. This resolved the sudden increase in Cr^{6+} concentrations.

A sheet glass production facility was under scrutiny for high fenceline Cr^{6+} concentrations. Eventually, a "non-running-process" test was performed, which showed the same concentration

of Cr⁶⁺ as when the process was running at full load. The source of the Cr⁶⁺ was eventually traced back to the fire brick used in the kiln. The firebrick was 40% chromium.

Another facility being investigated for Cr⁶⁺ emissions found that when a neighboring facility's process was shut down over the weekend, the first facility's fence line Cr⁶⁺ concentrations were near ambient. When the neighboring facility started its process up on Mondays, the Cr⁶⁺ fence line concentrations rose and by Wednesdays were stable. The first facility was eventually able to demonstrate to their regulatory body that their processes were not involved in the Cr⁶⁺ concentrations of concern.

CONCLUSION

Ambient air samples provide unique and difficult sampling and data interpretation challenges. As the sample exists in the form of particulates suspended in gas, yet the sample is analyzed in a liquid extract form, there are many possibilities for reactions to occur that have the potential to either increase or decrease the observed Cr⁶⁺ concentration from its concentration *in situ*.

An issue is the fact that there is no financially or physically feasible mechanism by which a "slice" of air may be taken and every single molecule present quantitated to accurately determine the amount of Cr⁶⁺ present in the airshed being sampled. Even if it were possible, for industrial airshed monitoring, where would this hypothetical "slice" be taken? At the property line? At points of ingress and egress of the buildings? At the nearest point of human habitation?

The laboratories are challenged with detection limits so low that creating clean impregnated filters is difficult. They are further challenged with the need to keep samples frozen without contamination, then extract them with as little conversion as possible occurring between the valence states.

The field engineers are challenged with attempting to determine what may be contained within the airshed that could bias the observed concentration of Cr⁶⁺ high. Those responsible for interpreting the data in urban airsheds must take into account the limitations of the method, the possible gas-to-particle and particle-to-particle interactions, the non-process contributors, and the possible contribution of other industries within the airshed.

Until such time as it is possible to take a slice of air and analyze it without any further manipulation of the sample, the engineers and the laboratory must be diligent in all aspects of method performance and data interpretation.

NOTES

The information contained in the section "Non-process Sources of Cr⁶⁺" is anecdotal. The facilities involved and the outcome of testing are anonymized due to client confidentiality requirements.

Chester LabNet is NELAP/ORELAP accredited for ASTM Method D7614-12 and CARB SOP MLD039. In addition, Chester LabNet has passed multiple onsite audits by representatives from

the National Air Toxics Trend Station (NATTS) program and Oregon Department of Environmental Quality (ODEQ). Chester LabNet's data and procedures have been heavily scrutinized with favorable findings by the Bay Area Air Quality Management District (BAAQMD) and South Coast Air Quality Management District (SCAQMD).

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