

**Development and Optimization of a Sampling and Analytical Method to Measure
Hexavalent Chromium in Ambient Air**

USEPA grant # XA 97264906

FINAL REPORT

By

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Submitted to

United States Environmental Protection Agency

Marlon Gonzales, Project Officer

October 7, 2009

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1. BACKGROUND

Chromium exists in the ambient air primarily in the trivalent (Cr(III)) and hexavalent (Cr(VI)) states^[1]. Cr(III) is considered to be essential to humans in trace concentrations. In contrast, the Cr(VI) is recognized as a pulmonary carcinogen by the International Agency for Research on Cancer and the US Toxicology Program^[2]. Occupational exposure to airborne Cr(VI) has been associated with an increased risk of lung and nasal cancer^[3]. Toxicological studies have found pathways through which airborne Cr(VI) sabotages normal body functions^[3]. As a result, Cr(VI) compounds have been listed as one of the 188 hazardous air pollutants (HAPs) in the 1990 Clean Air Act, one of the 33 urban air toxics HAPs and one of the 18 core HAPs by the U.S. Environmental Protection Agency (USEPA, 2004). The estimated one in a million cancer risk threshold for Cr(VI) is 0.083 ng/m³. To identify the populations at risk and protect public health, a sensitive and reliable air sampling and analytical technique that can measure Cr(VI) at or below its one in a million cancer risk threshold is essential.

Various methods have been reported for the measurement of Cr(VI) in ambient air in the past decades^[4-9]. For example, two methods that have been documented in the EPA Air Method Database are the National Institute for Occupational Safety and Health (NIOSH) Method 7600 and Method 7604. These methods were designed for occupational exposure monitoring and are not suitable for ambient air monitoring because Cr(VI) concentrations at occupational settings are usually hundreds and thousands of times higher than environmental levels. Recently an EPA method has been established for the measurement of Cr(VI) in ambient air (<http://www.epa.gov/ttn/amtic/airtox.html>) by IC/UV approach. This method is based on the California Air Resource Board (CARB) method 039 and reported an excellent sensitivity, with a method detection limit of 0.029 ng/m³^[7]. However, the recovery of Cr(VI) in ambient air particulate matter (PM) determined by this method was based only upon the recovery of Cr(VI) spiked on blank filters (ERG 2005)^[7], which may not represent the true recovery of Cr(VI) associated with ambient PM due to potential matrix effects. In addition, this method cannot quantify the potential inter-conversion between Cr(III) and Cr(VI) during sampling, sample processing and analysis. Research has shown that Cr(III) and Cr(VI) may interconvert during sampling and sample processing (storage, extraction, analysis)^{[5][10][11][12][13]}. In addition, lower recovery of Cr(VI) spiked on filters prior to sampling than those after sampling and lower recovery of Cr(VI) spiked on freshly collected ambient particles than aged NIST 1648 urban particles was observed during our pilot work in the Urban Community Air Toxics Monitoring Project, Paterson City, NJ (UCAMPP). Those results indicate that the sampling process and particle characteristics could affect the stabilities of Cr(VI) and Cr(III). The inter-conversion and recovery rates previously reported are mostly for soil, water and other matrices^{[14][15][16][17]}, and the results cannot be directly applied for the measurement of Cr(VI) on ambient air particles. This is because the stability and the inter-conversion mechanisms of chromium species in different matrices may differ dramatically^{[18][19]}. As such, it is necessary to characterize the sampling artifacts which would affect the measurement of Cr in the atmosphere, which will then facilitate future ambient Cr(VI) monitoring and exposure studies. In addition, in order to simultaneously quantify the inter-conversion between chromium species and the Cr(VI) recovery during sampling and sample analysis, the combination of the isotope spike technique and Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS) is required.

2. OBJECTIVES

The overall goal of this study was to develop a sensitive and reliable method for the measurement of ambient airborne Cr(VI) by systematically evaluating and optimizing the sampling, sample processing and analytical processes. This method can also simultaneously quantify the inter-conversion rates between Cr(VI) and Cr(III) and the recovery rate of Cr(VI). The specific aims of this study are: 1) to optimize the (IC/ICPMS) method for Cr(VI) analysis, e.g., lower the detection limit to the one in a million risk level i.e., 0.083 ng/m³; 2) to reduce the Cr(VI) background level on the blank filter; 3) to determine the recovery and conversion rate of Cr(VI) and Cr(III) during sampling, storage and extraction; 4) to characterize the factors that have been suggested to potentially affect the stability of Cr(VI), i.e., particle types, relative humidity (RH), temperature (T), ozone (O₃), sulfur dioxide (SO₂) and nitrogen dioxide (NO₂) in the ambient air; and 5) to evaluate the developed method in the field during summer and winter seasons. The results obtained from the study enriches the United States Environmental Protection Agency (USEPA) air monitoring method database, and contributes to the national and local ambient air monitoring, exposure and risk assessment for Cr(VI).

3. METHODS

3.1 Materials and Reagents

47-mm cellulose filters (Filter, MCE, No support Pad, 0.8 μ m, 47 mm, SKC) were used for sample collection and laboratory tests. A desiccator made of Tedlar Air sampling bag (SKC, Eighty Four, PA) was used to dry the cleaned and pre-treated filters. 15 ml centrifuge tubes (VWR, NJ) were used for sample extraction and membrane syringe filters (Acrodisc with 0.2 μ m, PALL Corporation) were used to filter the sample extract before analysis.

The efficiency and stability of extraction of Cr(VI) species were monitored on percolated filters of Urban Particulate Matter (NIST 1648) and two certified soil samples, a common composition of soil (SQC012) from R.T. Corporation (Laramie, WY) and another (SRM 2701) was collected from waste sites in Liberty Park, NJ which was a composition of chromite ore contaminated soil and was provided by Dr. Brian Buckley at EOHSI.

The high purity natural abundance Cr(VI) standard, (1000 ppm Cr(VI) in H₂O solution, High Purity Standards, Charleston, SC) and natural abundance Cr(III) standard (1000 ppm Cr in 2% HCl solution, High Purity Standards, Charleston, SC) were used for all the tests. Stable isotope-enriched ⁵⁰Cr(III) and ⁵³Cr(VI) standard solutions (10 μ g/g) were purchased from AIT (Sunnyvale, CA). To avoid the interconversion between Cr(VI) and Cr(III), standards were prepared fresh daily with de-ionized (DI) water (18.2 M Ω) using the Milli-Q system (Millipore, MA). Fisher optima grade concentrated nitric acid (Fisher, MA) and ACS grade sodium bicarbonate (NaHCO₃, Fisher Scientific, NJ) were used for preparation and pre-treatment of filters.

3.2 Instrumentation

IC: A Dionex ion exchange chromatography system with a GS50 gradient pump was used for Cr speciation. Specifically, Cr(VI) and Cr(III) were separated with an IonPac CG5A (Dionex, IL) IC column, which has both anion-exchange and cation-exchange capabilities to

retain both Cr(VI) and Cr(III) and results in a better separation of Cr(VI) and Cr(III). The sample injection volume was 100 μ L. Each injection was directly introduced into the ICP nebulizer with Teflon tubing (12 μ m I.D.). Optimization of the IC operating conditions was conducted for selecting the mobile phase of the IC system, and optimizing the ion strength and the flow rate of the mobile phase.

ICP-MS: ICP-MS was used for detection because of its high sensitivity and wide linear range. An additional advantage of ICP-MS over traditional detection methods is that it can quantify different chromium isotopes simultaneously, allowing for the use of isotope-enriched standards to monitor the recovery of Cr(VI) and the potential inter-conversion of chromium species during sampling, sample processing and analysis. The quadrupole ICP-MS system that was used for Cr detection in this study was a VG PlasmaQuad PQIII system (VG Instruments, Winsford, Cheshire, UK) with a nickel sampler and skimmer, each with a 1.0-mm orifice. UHP grade helium, argon and air were used for the IC-ICP-MS system (UHP grade, Airgas, NJ). Some of the key operating conditions of the ICP-MS, including dwell time and instrument tuning method, were optimized. The optimization of the torch position and the ion optical lens system were conducted on a daily basis to optimize the chromium signal. Peak areas of Cr(VI) and Cr(III) in each sample were used for quantification.

3.3 Filter Cleaning and Pretreatment

Cellulose filters were used in this study for sample collection due to their hydrophilic properties. The cellulose filter can be 1) cleaned with HNO₃ for the removal of background of Cr species; and 2) pre-treated with sodium bicarbonate for the stabilization of Cr(VI). Cleaning is a critical step for minimizing the Cr(VI) and Cr(III) background contamination present on the blank filters. During this project, four cleaning protocols were evaluated: A) 10% nitric acid (HNO₃) cleaning solution, which is similar to the ERG method ^[26] but with a longer (~16 hours) soaking time. In the ERG method, the filters are soaked in 10% HNO₃ for 2 to 16 hours. B) Sonication in 10% HNO₃ cleaning solution. Filters were sonicated in 60°C HNO₃ (10%) bath for an hour. C) Ethylenediaminetetra acetic acid (EDTA) cleaning solution. Filters were soaked in 0.1M EDTA in 5%-10% ammonia hydroxide overnight. D) Cleaned by both EDTA and HNO₃ solutions. Filters were first soaked in 0.1M EDTA in 5%-10% ammonia hydroxide overnight. Then the filters were washed with DI-water until pH value equaled the pH of the DI-water. The EDTA cleaned filters were then soaked in 10% HNO₃ overnight. All cleaned filters were finally washed with deionized water until the pH value of the filter equaled the pH of the DI-water. After being dried in a nitrogen environment in the dessicator, the filters were soaked in 10 g/L NaHCO₃ for 5 minutes and dried in the nitrogen environment. All pretreated filters were stored at -15°C in a bag filled with nitrogen until use. It is necessary to note that in ERG method, the pre-cleaned filters are soaked in 10 g/L NaHCO₃ overnight, but in our method, the filters are soaked for 10 minutes. Our protocol can provide a weak basic (pH = 8-9) microenvironment. If the clean filters are soaked in 10 g/L NaHCO₃ overnight, the pH value of the extracts will reach ~10. The stronger basic environment may promote oxidation of soluble Cr-III during heated ultrasonic extraction. In addition, a higher concentration of NaHCO₃ can interfere with ICPMS analysis via formation of ArC.

3.4 Extraction Stability and Efficiency

Experiments were conducted to examine the extraction efficiency of Cr(VI) and the conversion rates between Cr(III) and Cr(VI) using the pH = 4 HNO₃ solution. To achieve high extraction efficiency, sonication was used for extraction because 1) it is easy to operate; and 2) no significant differences in extraction efficiency were observed between sonication and other extraction methods^[6]. The sonication temperature was set at 60°C. A higher temperature was not used because it could promote conversion between Cr(VI) and Cr(III)^[18], even although higher temperatures can produce a higher extraction efficiency. In this study, Cr(VI) standards (both natural abundant ⁵²Cr species or isotope-enriched chromium standards) were spiked on the filter coated with different types of particles to test the extraction stability and efficiency. These test results are more representative of an ambient particle matrix than those obtained from previous evaluation results which were obtained from blank filters only^{[7][26]}. Particle types used for test included 1) NIST 1648 PM; 2) certified soil SQC012 and 3) Certified soil SRM 2701.

3.4.1 Extraction Efficiency as the function of Extraction Time

Four types of samples were prepared using ⁵²Cr(VI) and ⁵²Cr(III) natural abundant solution to examine the extraction efficiency and recovery as a function of extraction time. Sample types were: 1) 0.8 µg (40 µL of 20 µg/mL standard solution) natural abundance Cr(VI) spiked on a pre-cleaned, pre-treated filter (Test 1); 2) 0.8 µg natural abundance Cr(VI) spiked on 10 mg NIST 1648 PM pre-cleaned, pre-treated filter (Test 2), 3) 0.8 µg natural abundance Cr(III) spiked on 10 mg NIST 1648 PM pre-cleaned, pre-treated filter (Test 3), and 4) 10 mg NIST 1648 particles only (Test 4) to test the effect solely from the particles. The amount of NIST 1648 PM was based on the consideration of matrix homogeneity. The amount of the spiked Cr species was based on the Cr(VI) concentrations (1 ng/m³) that may be present in ambient air^{[1][25]}. After NIST 1648 particles were grinded on the pre-cleaned, pre-treated filters, all filter samples were stored in the freezer for 4 days to allow Cr species to diffuse into particles before extraction. Please note that this is a common practice for preparing spiking samples. However, whether the spiked Cr species can diffuse thoroughly to the filter under freezing temperature is not known. The prepared samples were extracted with 40 mL of pH = 4 HNO₃ solution at 60 °C with sonication. Different extraction times, i.e. 5, 10, 20, 40, and 60 min, were tested in order to find the optimal extraction time to achieve high extraction efficiency and low conversion rates. At each of the designated extraction times, 2 mL samples were withdrawn from each sample tube and analyzed for Cr(VI) or Cr(III).

3.4.2 Recovery and Inter-conversion of Chromium Species on NIST 1648 PM and two Cr(VI) Certified Soil Material During Extraction Process

According to the experimental results in 3.4.1, the optimal extraction condition is sonication in pH = 4 HNO₃ solution at 60°C for 40 minutes. The extraction efficiency and recovery rate using this method were further evaluated using isotope spikes on NIST 1648, and two types of Cr(VI) certified soil material SQC012 and SRM2701. Lower mass of Cr species (4 ng of ⁵³Cr(VI) and 4 ng of ⁵⁰Cr(III)) and particle mass (~5 mg NIST 1648 PM) were used for the test to mimic ambient air sampling. More soil material (~25 mg of certified soil material) and isotope spikes (200 ng of ⁵⁰Cr(III) and ⁵³Cr(VI)) were used for this test given the relatively lower homogeneity of soil particles than ambient PM (NIST 1648). The concentrations of the isotopes

determined in each sample (3 samples for each type of particles) were used to examine the interconversion rate and the recovery of Cr species on the three different types of particles during the analytical process. All samples were stored at -15°C for 4 days before analysis. Isotope enriched standards were also spiked on the blank filters (n=3) to check the effects from the filter material. After being stored in the freezer for 4 days, the prepared samples were extracted with 5 mL pH = 4 HNO₃ solution at 60 °C with sonication for 40 minutes, i.e. the conditions determined in Section 3.4.1, and the extracts were analyzed by the IC-ICP-MS.

3.4.3 Method Accuracy

Since there is no certified value of ⁵²Cr(VI) content for the NIST SRM 1648, two types of certified soil samples (SQC012 and SRM2701) were used to examine the method accuracy for Cr(VI) detection. A total of 12 samples of each type of soil sample, including the 3 samples described in the above section 3.4.2, were analyzed for ⁵²Cr(VI) concentrations. The Cr(VI) concentration determined in the study was compared to the certified values to evaluate the method accuracy.

3.5 CEF Tests

Tests were conducted in a controlled environment facility (CEF) to characterize the effects of temperature (T), relative humidity (RH) and various air pollutants on the stability of Cr(VI) on fresh diesel particles (DPM) and secondary organic aerosols (SOA). The chamber is made of stainless steel, in which the temperature, humidity, and air exchange rate (AER) are controlled. It is 2.2 m high by 4.1 m wide by 2.7 m deep with a volume of 25 m³ and a surface/volume ratio of 2.1 m⁻¹. The air supply is treated with a series of conditioning processes, which include air cooling/heating, humidification/dehumidification, and filtration through carbon and HEPA filters. The air supply enters the CEF through two diffusers in the ceiling and exits through the perforated stainless steel floor. Constant concentrations of chemical compounds can be maintained in the CEF by the continuous injection of the chemicals into the air supply, which flows through the CEF without recirculation. Eight small brushless fans (to prevent unwanted particle generation from brush degradation) are used in the CEF to ensure that the air is well mixed.

Both ⁵⁰Cr(III) and ⁵³Cr(VI) were spiked on pre-collected particles (either DPM or SOA) to monitor the interconversion of chromium species aged under different conditions, including clean air, air containing SO₂, O₃, and NO₂ at 20°C and 40% relative humidity (RH), high temperature (31 °C) and humidity (68%, the highest RH that could be achieved in the CEF). All test conditions as well as number of test samples are summarized in Table 1. To prepare filter samples containing fresh DPM and SOA, PM_{2.5} at a concentration of 300 µg/m³ for DPM or SOA were generated in the CEF. About 0.4 mg particle mass, which is similar to the particle mass collected during ambient monitoring, were collected on 47 mm pre-cleaned and pre-treated cellulose filters. One hundred ng of each isotope (i.e. ⁵³Cr(VI) and ⁵⁰Cr(III)) was spiked on the filters and then stored in the freezer for 4 days to allow Cr species diffusion into the particles. The control samples (CA-L), which were prepared in the same manner as the samples above, did not go through any air sampling process, and were stored in the freezer till analysis. For the test, the filters were loaded into Partisol Speciation Sampler-Model 2300 (Thermal Fisher Scientific). The sampled air contained O₃, NO₂, or SO₂ from the CEF and sampling occurred at a flow rate of

16.7 LPM for 24 hours. The filters were then extracted and analyzed to determine the interconversion of Cr(VI) and Cr(III). High concentrations of O₃ (100 ppb), SO₂ (160 ppb) and NO₂ (150 ppb) which are found in ambient air were used for the tests. A low concentration of SO₂ (50 ppb, the national health standard for airborne SO₂), was an additional test that was not scoped out in the original proposal since low recovery of Cr(VI) was observed at high SO₂ concentration.

3.6 Field Evaluation

The field evaluation was conducted for 7 days in both summer (late August 2008 to September 2008) and winter (February 2009 to early March 2009). The sampling site was located in Rahway, NJ. Rahway is served by U.S. Routes 1/9, and Route 27. The city is between the Garden State Parkway and the New Jersey Turnpike, with each road located about two miles from the city. Newark Liberty International Airport is located 10.2 miles northeast of Rahway. The largest known source of chromium and chromium compounds in Rahway is API Foils. The company emitted 440 lbs in 2007. An additional source of chromium and chromium compounds in Rahway is Covanta Union. Covanta Union emitted 10 lbs in 2007. Therefore, measurable Cr(VI) was expected in Rahway.

The Partisol Speciation Sampler-Model 2300 (Thermal Fisher Scientific) was used to collect PM₁₀ samples. The PM₁₀ sampler has 4 channels, the one with a PTFE-coated inlet was used to collect samples for the quantification of Cr(VI). The sampling flow rate was 16.7 L/min, and the sampling period was from midnight to midnight, for a sampling duration of 24 hours, leading to sample volumes around 24 m³. Prior to each sampling event, the flow rate was checked by the Streamline flow meter (Thermal Fisher Scientific) to make sure the variation of the flow rate was less than 5%.

Isotopes were spiked on filters at different stages of the field tests. As shown in Table 2, isotope-enriched standards were spiked on filters (duplicate samples) prior to sampling (BS) to monitor the recovery and inter-conversion of Cr species during the entire measurement process and after sampling (AS) to monitor those parameters during sample storage and processing. The difference between BS and AS would indicate the impact of sampling process on the stability of Cr species. During each field test, lab and field controls were also prepared. Lab control (CA-L) were filter samples spiked with isotopes and stored in freezer until analysis, and field control (CA-F) were filter samples spiked with isotopes, taken to the field, loaded in the cartridge without the sampling pump turned on, and brought back to lab for analysis after sampling. The difference between CA-L and CA-F would indicate the influence of transportation between lab and field and the ambient conditions (i.e. ambient temperature, humidity etc and storage time in the field). During each test, one lab blank (LB) and one field blank (FB) were also analyzed. LB was used to check the filter background of Cr(VI) and Cr(III) and FB was used to check the background concentration by field trip. During the winter sampling season, one additional duplicate sample was collected for the measurement of ⁵²Cr(VI) in ambient air so that we have more power for checking the method precision. These samples were collected on a co-located filter without isotope spikes.

Meteorological measurements were collected with the Davis Weather Monitor II system (Hayward, CA).

4. RESULTS

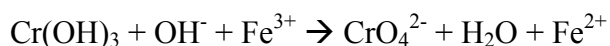
4.1 Instrument Condition Optimization

4.1.1 Optimization of IC Separation

For ion-chromatography separation of Cr species, the mobile phase, the ion strength of the mobile phase, and the flow rate of the mobile phase were optimized.

The selection of the IC column should be based on the properties of the target compounds that are to be separated. The major difference between Cr(VI) and Cr(III) is that Cr(VI) is in the form of $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- , and Cr(III) is the form of Cr(OH)_n ($n = 0-2$) in an acidic environment. Therefore, either a cation exchange column or an anion exchange column could separate Cr(VI) and Cr(III) by retaining either Cr(VI) or Cr(III). However, instead of using a cation or anion exchange column singularly, a better solution for the separation of Cr(VI) and Cr(III) is to use a column with both cation and anion exchange capacities. This dual capacity column can achieve a better separation of Cr(VI) and Cr(III) [16]. IonPac CG5A (Dionex, IL) is an IC column with both anion-exchange (Ion-Exchange Group: Quaternary ammonium) and cation-exchange (Ion-Exchange Group: Sulfonic acid) capabilities, resulting in the retention of both Cr(VI) and Cr(III), and therefore a better separation of Cr(VI) and Cr(III). As a result, the CG5A column was selected for separation in the study.

The choice of the mobile phase solution must be consistent with the aqueous chemistry of Cr, so that Cr(VI) and Cr(III) can be effectively separated. Other concerns regarding the choice of the IC mobile phase are 1) the stability of Cr(VI) and Cr(III) during analysis, and 2) the avoidance of polyatomic interferences for ICP-MS detection. Although some basic eluent solutions (e.g. NaOH) and chelating agent (e.g. EDTA) can provide sufficient separation of Cr(VI) and Cr(III), these agents are typically used when Cr(VI) is detected by colorimetry method. For ICP-MS, these agents can significantly elevate the chromatographic baseline at m/z of 52 and 53 by forming $^{40}\text{Ar}^{12}\text{C}^+$, $^{16}\text{O}^1\text{H}^{35}\text{Cl}^+$, etc. In addition, Cr(III) might convert to Cr(VI) under basic conditions and the existence of oxidant, such as Fe^{3+} and trace level of O_2 [13], which limits the use of basic solution as eluent in IC-ICPMS:



Weak acid eluent (i.e. $[\text{H}^+] < 0.35$ mol/L) is an alternative option, in which both Cr(VI) and Cr(III) are stable [16]. Also HNO_3 doesn't form any major polyatomic ions interfering in the detection of Cr with ICP-MS. Another benefit of HNO_3 as the mobile phase is that when it flows through the CG5A column, NO_3^- and H_3O^+ ions replace the Cr(VI) and Cr(III) ions retained on the column, respectively. In addition, the use of nitric acid, instead of a chelating agent like EDTA, reduces the disturbance of the agent to be analyzed and preserves the nature of the original species as much as possible. Thus HNO_3 was selected as the eluent. The optimized IC conditions, including mobile phase acidity and flow rate, are reported in the following sections.

The Cr(VI) and Cr(III) response and the chromatographic resolution were optimized by adjusting the ionic strength (acidity) of the mobile phase (Figure 1). Figure 1a shows the retention time of both Cr(VI) and Cr(III) as a function of the acidity of the eluent. While the retention time of

Cr(III) was reduced dramatically with the increase of the eluent acidity, there was no significant change in the retention time of Cr(VI). Figure 1b illustrates the peak height (intensity) change of both Cr species with the increase in eluent acidity. The peak height of Cr(VI) reached its maximum when eluted with 0.4M HNO₃ solution. For Cr(III), the maximum peak height was achieved with the 1M HNO₃ as the eluent. Figure 1 suggests a two-step elution of Cr species: Cr(VI) was eluted first at low acidity (0.4M HNO₃) and then Cr(III) at strong acidity (1M HNO₃). However, the strong acid solution (1M HNO₃) was found to gradually leach the instrument and led to higher background concentrations of Cr(VI) over time. Therefore, the isocratic program of the mobile phase (60% 1M HNO₃ and 40% DI water) was used. Compared to the 2-step elution program, no obvious changes in Cr(VI) signal were observed but the Cr(III) signal intensity was compromised.

Mobile phase flow rate is another parameter affecting chromatography separation. Flow rate impacts the analysis time, IC system pressure, and chromatographic quality. A flow rate of 1.0 – 1.5 ml/min would be appropriate for the column and the IC system^[20]. Three different flow rates (1, 1.25 and 1.5 mL/min) were tested for separation. Under each flow rate, baseline separation of Cr(VI) and Cr(III) was achieved within 5 minutes, and no significant differences of Cr(III) and Cr(VI) peak heights were observed. Therefore, the flow rate of 1.25 mL/min was chosen for the subsequent tests.

4.1.2 Optimization of ICP-MS Operating Conditions

The optimization of ICP-MS analytical conditions included choosing proper dwell time to obtain the optimal signal-to-noise ratio for the measurement of Cr(VI) and a suitable instrument tuning method in order to maximize the signal of the target ion and block the entrance of other ions.

The dwell time is the time period when data is collected for a particular mass. If the dwell time is too short, the MS signal would be very noisy; and if the dwell time is too long, the sensitivity of the instrument would be dramatically reduced. The different dwell times evaluated during the study were 50, 100, 200, 300 and 400 ms. The instrument was tuned with 10 ppb In(NO₃)₃, and then a series of natural abundance Cr(VI) standard solutions (0.1, 0.2, 0.5, 1, 2, 5, 10 ppb) were injected into the IC-ICP-MS system which resulted in the above chromatography conditions being optimized. The signal of 0.1 ppb Cr(VI) at m/z = 50, 52 and 53 can only be clearly identified at the dwell time of 300 ms. Results indicate that the dwell time of 300 ms provides the best signal. Thus, the dwell time of 300ms was employed in the whole study.

The dwell time of 300 ms, with 10 ppb natural abundance Cr(VI), isotope-enriched ⁵³Cr(VI) solution and In(NO₃)₃ was used for tuning, respectively. The mono-valent ions were not evenly distributed around the ICP torch. The objective of the tuning procedure is to maximize the response of the instrument to a certain isotope. For Cr, ⁵²Cr is the most abundant isotope and is theoretically the optimal ion for tuning. However, ambient aerosol is a complex mixture, including various trace elements and carbon components (organic carbon and elemental carbon). Carbon can form ⁴⁰Ar¹²C⁺ and interfere with ⁵²Cr detection. Other aerosol components may form ¹H⁵¹V⁺, ¹²C⁴⁰Ca⁺, etc. to interfere with the detection of ⁵²Cr. Therefore, ⁵³Cr and natural

abundance In are expected to be the suitable elements for the purpose of tuning the instrument. The final ICP-MS operating conditions are presented in Table 3.

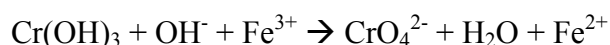
After tuning by $\text{In}(\text{NO}_3)_3$, natural abundance Cr(VI) (primarily ^{52}Cr), or isotope-enriched $^{53}\text{Cr}(\text{VI})$, a calibration curve ($R^2 = 0.999$) was created by introducing a series of natural abundance Cr(VI) standard solutions (0.1, 0.2, 0.5, 1, 2, 5, 10 ppb). A low concentration (0.5 ppb) standard of natural abundance Cr(VI) was then injected seven times, and the concentration of each injection was calculated based on the calibration curve. The standard deviation of the concentrations of the seven injections was calculated and three times of the standard deviation was defined as the detection limit. The analytical detection limit (ADL) for Cr(VI) was determined as 0.4 ppb (ng/mL), which is equivalent to 0.08 ng/m^3 air concentration for a sampling volume of 24 m^3 .

4.2 Effectiveness of Filter Cleaning Protocols

The results of the filter's background contamination after cleaning by the 4 different cleaning methods are presented in Table 4. All 4 procedures can effectively reduce the filter Cr(VI) and Cr(III) background. The Cr(VI) background was reduced from 5.84 ng to 1.12 ng and lower, and the Cr(III) background from 2.89 ng to 0.42 ng and lower. For a sampling volume of 24 m^3 , the background of Cr(VI) and Cr(III) after cleaning is equivalent to $< 0.05 \text{ ng/m}^3$ and $< 0.02 \text{ ng/m}^3$, respectively. Cleaning with EDTA solution can significantly reduce Cr background on the filters but it is very difficult to completely rinse off the EDTA. Any residue of EDTA on the filters will interfere with the measurement of Cr(VI) by ICP-MS detection. For cleaning with HNO_3 with sonication, some filters were broken during the sonication step. Thus, protocol A was chosen to clean the filters in this study. Protocol A consisted of soaking filters in a 10% nitric acid (HNO_3) cleaning solution overnight (~ 16 hours). The mean background level of Cr(VI) and Cr(III) after cleaning using protocol A is $< 0.05 \text{ ng/m}^3$ (equivalent to mass $< 1.12 \text{ ng}$) and $< 0.01 \text{ ng/m}^3$. If the mass of Cr(VI) background exceeded 1.12 ng, filters will be re-cleaned.

4.3 Selection of the Extraction Solution

A suitable extraction solution can provide a high extraction efficiency for Cr(VI), stabilize both Cr(VI) and Cr(III), and does not introduce interferences for the IC-ICP-MS analysis. In this study, the $\text{pH} = 4$ HNO_3 solution was selected for extracting Cr(VI) from ambient PM based on the following considerations. First, as stated earlier, HNO_3 does not interfere with the Cr(VI) detection by ICP-MS because nitrogen is the only extra atom (compared with H_2O) introduced into the IC-ICP-MS system and it does not form any polyatomic ions of $m/z = 50, 52$ or 53 with the major components of ambient aerosol or ICP carrier gas. Second, minimum conversion rates of Cr(VI) and Cr(III) are expected in the $\text{pH} = 4$ HNO_3 solution^[21]. The conversion rates between Cr(VI) and Cr(III) are affected by the acidity of the solution and co-existing chemical species in the solution^[13]. In previous studies, basic solutions ($\text{pH} = 8 - 14$) (e.g. NaOH) were used to extract Cr(VI) from various matrices^{[5][14][20]}. Although Cr(VI) might be stable in basic solutions, Cr(III) is likely to be converted to Cr(VI) under basic conditions with the existence of an oxidant (e.g. $\text{Fe}(\text{III})$, commonly observed in ambient PM), resulting in a measurement artifact of Cr(VI)^{[13][22]}.



In contrast, in the weak acidic environment, both Cr(VI) and Cr(III) should be stable^[13]. Although the oxidation of Cr(III) and the reduction of Cr(VI) could happen with the existence of Fe(III) and organic acids (commonly found in ambient PM) in a weak acidic solution, the reactions are UV light-induced^{[17][22][23][24]}. Under the laboratory condition, this photochemical inter-conversion mechanism is not expected to be significant. It has been recognized that Cr(VI) could be reduced by reductant agents under weak acidic conditions, such as Fe(II)^[21]. However, Buerge and Hug (1997)^[21] reported that the reaction between Cr(VI) and Fe(II) was pH dependent, with a minimal reaction rate around pH = 4. Thus, pH = 4 HNO₃ solution is expected to be the optimal extraction solution in which the inter-conversion of chromium species is minimal.

Third, the pH value (pH = 4) of the HNO₃ extraction solution is similar to human lung fluid pH, especially for people with respiratory diseases^[24]. Therefore, the extraction method is more relevant to the bioavailability of Cr(VI) through inhalation exposure.

Finally, other extraction solutions, such as sodium bicarbonate buffer, potassium phosphate buffer, NH₄OH solution, and Mg(OH)₂ and NaOH solution^{[4][5][14]}, were used to extract Cr(VI) from soil and other matrices in previous studies. Most of those solutions were weak basic solutions. In addition to the concern of the oxidation of Cr(III) to Cr(VI) in the basic environment discussed above, most of the solutions interfere with the detection of Cr(VI) at m/z = 50, 52 and 53 by ICP-MS. Therefore, HNO₃ (pH = 4) was chosen as the extraction solution in this study.

4.4 Results for Extraction Stability and Efficiency

4.4.1 Optimal Extraction Time

The Cr(VI) concentrations versus extraction time are presented in Figure 2. As seen in Figure 2, the recovery was > 90% for the Cr(VI) spiked on the clean blank filter (Test 1) after 10 minutes of sonication which was similar to previous studies (9). A good recovery (~80%) was also obtained for the Cr(VI) spiked on the NIST 1648 particles at extraction time of 40 minutes (Test 2) but lower than the recovery from the filter only (Test 1), indicating that small portion (< 10%) of Cr(VI) was not recovered from the particle medium. In addition, the Cr(VI) concentration reached its plateau at 40 minutes for both spiked Cr(VI) (Test 2) and Cr(VI) from the NIST 1648 particles (Test 4), indicating the maximum extraction efficiency achieved at extraction time of 40 minutes at 60 °C. It is necessary to note that the recovery of Cr(VI) from the NIST 1648 PM cannot be determined because there is no certified value of Cr(VI) content for this material. The recoveries of Cr(III) that were spiked on both clean filters only and the NIST 1648 particles were very poor, mostly less than 5% (not shown in the figure). The low recovery of Cr(III) could be due to the poor solubility of Cr(III) at weak basic conditions. Most Cr(III) probably forms precipitation on the weak basic (NaHCO₃) pretreated filters.

The conversion rates between Cr(VI) and Cr(III) were also determined based on the Cr(III) concentrations in the extracts from Test 2 (spiked with only Cr(VI)), and the Cr(VI) concentrations in the extracts from Test 3 (spiked with only Cr(III)). Surprisingly, almost no Cr(III) was detected in the sample extracts in Test 2, although the recovery of Cr(VI) was only ~80%. The 20% loss of Cr(VI) was either due to the “loss” of Cr(VI) on the particles, or the conversion from Cr(VI) to Cr(III) or both. Given the low Cr(III) concentration detected in the

extracts, our results suggest that either the conversion from Cr(VI) to Cr(III) would be negligible, or if conversion occurred, the Cr(III) was not soluble and precipitated under our extraction conditions. In Test 3 (Figure 2), about 20% Cr(III) was converted to Cr(VI) during extraction. These results indicate that a portion of soluble Cr(III) can be converted to Cr(VI) under our extraction conditions.

4.4.2 Recovery and Inter-conversion of Cr Isotopes on Different Types of Particles

The inter-conversion rate and recovery data for the spiked isotopes on 3 different particles as well as on the blank filters are summarized in Table 5. The recovery and inter-conversion of Cr species on different types of particles were found to be similar to the above tests (Test 1 – 4). In summary, good recoveries were obtained for all 3 types of particles, ranging from 82% to 105%. The “conversion rate” from Cr(VI) to Cr(III) was below detection based on the ratio of the $^{53}\text{Cr(III)}$ and the spiked $^{53}\text{Cr(VI)}$. The low conversion rate of Cr(VI) to Cr(III) suggested that either the conversion is negligible or if conversion occurred, the Cr(III) was not soluble and precipitated under our extraction conditions. The recovery of $^{50}\text{Cr(III)}$ was low on all particles, less than 5% based on the ratio of the residual of the spiked $^{50}\text{Cr(III)}$ detected in the extract and the spiked $^{50}\text{Cr(III)}$. These results indicated that most $^{50}\text{Cr(III)}$ was precipitated in the conditions used in this study. The residue of Cr(III) in the extract resulted in 1% to 17% conversion from Cr(III) to Cr(VI), based on the ratio of detected $^{50}\text{Cr(VI)}$ and the spiked $^{50}\text{Cr(III)}$. It is necessary to note that these conversion rates represent the soluble fraction of Cr(III) that may transform to Cr(VI). Most Cr-III compounds in ambient air are insoluble^[9]. Cr(OH)_3 , which is somewhat soluble under typical atmospheric acidic condition, will precipitate at pH values of 3 and above. As stated early, the pH of the NaHCO_3 -pretreated filters ranged between 8-9, and the pH of our extraction solution is 4. Thus, Cr(OH)_3 is not expected to be soluble and thus will not convert to Cr(VI). Therefore, the conversion of Cr(III) to Cr(VI) observed in the lab tests probably is not expected to occur for Cr(III) associated with real ambient particles. In addition, the standard deviations were low (%RSD < 10%, Table 5) for all particle types, indicating a adequate precision of the newly developed method for the analysis of Cr(VI) in particles.

4.5 Method Accuracy

Table 6 shows the recovery of $^{52}\text{Cr(VI)}$ and the comparison of the measured Cr(VI) concentrations to the certified values. The concentration of Cr(VI) in SQC012 was detected at 135 ± 18.9 mg/kg, within the acceptable range of 64.0 to 170 mg/kg which is provided by the company. The recovery of Cr(VI) was 116%. The higher recovery might be due to analysis variability and or to the partial conversion from Cr(III) to Cr(VI), because it was found that there was a 17% conversion rate of Cr(III) to Cr(VI) for SQC012 particles. However, given Cr-III accounts for major fraction of Cr in soil, if the converted $^{50}\text{Cr-III}$ truly reflected the conversion of $^{52}\text{Cr(III)}$ to Cr(VI) in soil particles, the final recovery of $^{52}\text{Cr-VI}$ ought to be greater than 100%, which was not the case. Our results indicate that the conversion rate from $^{50}\text{Cr-III}$ to $^{50}\text{Cr-VI}$ determined by the spiking of soluble Cr(III) overestimates the conversion of Cr(III) to Cr(VI). Since most of the Cr(III) is present in an insoluble form in ambient PM and soil particles and the recovery of Cr(VI) was close to 100%, we think that the proportion of the measured Cr(VI) resulted from the conversion from Cr(III) to Cr(VI) is negligible in our experimental conditions. In summary, we concluded that our analysis method is suitable for the measurement of Cr(VI) in PM particles when the composition of PM is similar to SQC012 soil type.

For SRM 2701 particles, a lower recovery of Cr(VI) was obtained, with an average recovery of 51%. This may be due to different Cr oxidation forms in SRM 2701 and SQC012, i.e. a higher fraction of Cr(VI) in HNO₃ was insoluble. The conversion rate from Cr(III) to Cr(VI) was also low, suggesting more insoluble Cr(III) in these particles.

The Cr(VI) concentration in NIST PM was determined, with an average (SD) concentration of 1.75 ± 0.46 µg/g (equivalent to 0.02 ng/m³ in ambient particles for a sampling volume of 24 m³). More samples are needed to confirm the Cr(VI) value in NIST PM since it is not a certified Cr(VI) material. Additional samples will be analyzed during the next USEPA funded project "Evaluation of two analytical methods and two sampling trains for the measurement of hexavalent chromium in ambient air" USEPA grant # XA 97247301-0.

4.6 Stability during Storage

Stabilities of the chromium species during storage for both clean filters (NaHCO₃ pre-treated) and NIST PM were evaluated. Both isotope species (⁵⁰Cr-III and ⁵³Cr-VI) were spiked on clean filters (filter only sample in Table 7) and filters pre-coated with NIST1648 PM (NIST1648 sample in Table 7). The storage time ranged from 1 to 111 days for filter only samples and 1 to 95 days for the NIST PM samples. The results are presented in Table 7 and Figures 3-4. For Cr(VI), nearly all samples had recovery rates of Cr-VI > 80% and conversion rate < 5%. These results indicated that Cr-VI is very stable when stored at -15°C in a freezer. For Cr(III), the recovery was lower than 10% for 22 of 24 samples tested,. Also, nearly all samples had conversion rates (Cr-III to Cr-VI) from 0% to 20%, and no significant increase of conversion rate was observed during the storage process up to 3 months for both types of samples.

4.7 CEF Test Results

The recovery and conversion rates of Cr(VI) and Cr(III) under different testing conditions are presented in Table 8. No significant loss of Cr(VI) was found on the control samples (CA-L in Table 8) or filter samples that sampled clean air for 24 hours. For the other testing conditions, except when SOA particle samples were exposed to ozone, the recoveries of Cr(VI) and Cr(III) were found to be similar on both particles. Except for the condition of SO₂, the recovery of Cr(VI) on DPM was > 80% under all conditions, 75% for SOA with ozone and > 80% for SOA under all other conditions. The recovery of Cr(VI) was low for both types of particles when exposed to SO₂, with an average of ~40%. No significant effects of temperature or humidity on the stability of chromium species on DPM were observed under the conditions tested in this study. By pulling clean air through SOA particles under high T/RH, higher conversion rate ($15.2 \pm 1.34\%$) from Cr(III) to Cr(VI) were found compared with room T/RH. The recovery of Cr(VI) was similar, with an average (SD) of $97.4 \pm 3.94\%$ under high T/RH. The results indicated that the oxidation from soluble Cr(III) to Cr(VI) might occur under high T/RH on the SOA particles. Similarly, a higher conversion rate (13.10 ± 2.42) from Cr(III) to Cr(VI) than for the control sample was found by pulling air with NO₂ through SOA particles. These results suggest that NO₂ may react with some organics in SOA without light inside the chamber to produce some free radicals, which could promote oxidation of soluble Cr-III.

The recovery of Cr(III) is low at less than 5% for both types of particles under all test conditions. These results indicate that most of the Cr(III) was precipitated once it was spiked on the basic filter under our extraction conditions. A small amount of Cr(III) was found to be

converted to Cr(VI). The conversion rate from Cr(III) to Cr(VI) was between $6.01 \pm 1.33\%$ to $15.2 \pm 1.34\%$ on SOA particles and $4.25 \pm 0.71\%$ to $5.22 \pm 1.12\%$ on DPM particles under the different test conditions. These results suggested that the liquid environment and organic composition of SOA might promote the oxidation from Cr(III) to Cr(VI).

4.8 Field Evaluation Results

The ambient Cr(VI) and Cr(III) concentrations (mean $\pm$ SD) and corresponding meteorology data are summarized in Table 9. The recovery and conversion rates of Cr species are present in Table 10.

The method detection limit (MDL) was determined based on the field blanks (n=10). The MDL was 0.09 ng/m^3 , which was a significant improvement over the MDL of 0.16 ng/m^3 which was obtained during UCAMPP. The method precision also improved, with an average %difference determined from the duplicate samples (n=33) of $17\% \pm 12\%$, while the average %difference(SD) obtained from the UCAMPP was $23\% \pm 18\%$.

The recovery of $^{53}\text{Cr(VI)}$ on field control samples was found to be lower than that of lab control samples ($\sim 100\%$) in both seasons. When comparing the recovery between winter and summer, the recovery in summer ($68 \pm 7\%$) was found to be significantly lower than in winter ($78 \pm 13\%$). These results suggest that Cr(VI) decays during storage at warmer temperatures. The recovery of $^{53}\text{Cr(VI)}$ which was spiked before sampling was lower than that of field control samples and samples that were spiked after sampling. There was no significant difference in Cr(VI) recovery between field control and after sampling spikes. These results suggest that the sampling process can affect the stability of Cr(VI), and the pre-treated filter can preserve Cr(VI) collected on the filters that were stored at -15°C .

The recovery of $^{50}\text{Cr(III)}$ was very low $<3\%$ on all particle samples, indicating Cr(III) precipitated on the weak basic treated filter, as discussed earlier. We did not observe significant differences in conversion rates from Cr(VI) to Cr(III) or Cr(III) to Cr(VI) between all sample types, suggesting that there are no effects from the ambient particles on interconversion.

The ambient Cr(VI) in both seasons was detected, and no significant differences were observed between winter ($0.03\text{-}0.26 \text{ ng/m}^3$) and summer seasons (non-detectable to 0.21 ng/m^3 , Table 9). More tests are needed to examine seasonal variation because during UCAMPP, it was observed that the summer concentrations were higher than in the winter.

We also examined the effects of other environmental factors, i.e. wind, temperature and co-air pollutants, on the stability of Cr species. The results are presented in Figures 5 - 9. As shown in Figure 5, Cr(VI) concentrations tended to be lower with increased wind speed, indicating that wind played a significant role in diluting Cr(VI) concentrations. No significant effects of temperature or other co-pollutants on Cr(VI) concentrations were observed. However, the findings are based on limited sample size and range of factors examined, thus, more tests are needed to examine those factors on the stability of Cr species.

4.9 Comparison of the Field Study Evaluation Results with Lab Test Results

Comparing the results from the field work to that of the DPM and SOA in the CEF tests and NIST1648 in the lab tests, we found that the recovery of $^{53}\text{Cr-VI}$ was much lower

(50~80%) in fresh ambient PM than those from the DPM and SOA (80~90% except for SO₂) and NIST PM (>85%). The conversion from ⁵⁰Cr-III to ⁵⁰Cr-VI was a higher (10~30%) in the field evaluation than those from the CEF tests (0~10%) and the lab tests with NIST1648 (~5%). Additionally, the recovery of Cr(VI) and the conversion rate of Cr(III) to Cr(VI) caused by exposure to single co-air pollutant (O₃, SO₂, NO₂) was generally lower than those in the field tests, albeit the levels of co-air pollutants in CEF were much higher than the usual ambient conditions

The results suggest that chemical composition and physical properties of the fresh ambient PM are different from DPM, SOA and NIST1648. For instance, NIST 1648 PM contains aged particles collected from St. Louis, MO in the 1970s but the PM collected from Rahway contains both fresh and aged particles. Thus, the chemical constituents, such as Fe(II) and organic acids which may lead to the reduction of Cr(VI), could be different between the two types of particles. In addition, the oxidation states of the chemical species on the fresh aerosols are often lower than the aged particles and thus have higher potential leading to the reduction of Cr(VI). Further, the size fraction (< 60 μm) and therefore the surface properties of NIST 1648 PM are different from the Rahway samples (PM₁₀), which may also affect the stability of Cr(VI). In the CEF test, the air sampled with filters was purified air, which is different from the ambient air that contains various types of air pollutants. The smaller change caused by a single co-air pollutant indicates that single gas phase co-air pollutants, except for SO₂, do not play a significant role in promoting ambient Cr interconversion. However, the synergic effect of these co-air pollutants and components in PM is probably responsible for the more significant interconversion in ambient conditions.

5. SUMMARY AND CONCLUSIONS

A comprehensive study was conducted to develop and evaluate a method to quantify Cr(VI) in ambient air. Good method sensitivity was obtained with a method detection limit of 0.09 ng/m³. This is similar to the minimal risk level (MRL) of 0.083 ng/m³, which allows for the estimation of risk from exposure to Cr(VI) in ambient air. Good precision was also achieved in both lab and field evaluations, with an average %difference for the duplicate samples of < 10% (N=10 of lab duplicates) and 12% (N=33 pairs of field duplicates), respectively. Cr(VI) was found to be very stable during storage for up to 3 months. With this newly developed method, Cr(VI) on ambient particles which were collected during the winter was found to be relative stable during the entire measurement process, with an average recovery > 69%, however, the recovery of Cr(VI) was lower in summer than in winter. Thus, in order to preserve Cr(VI) and reduce the potential Cr transformation during sample collection, a cooling system is needed. This is one of the goals of the new USEPA funded method comparison project "Evaluation of two analytical method and two sampling trains for the measurement of hexavalent chromium in ambient air", i.e. evaluate the stability of Cr(VI) in the newly developed sampler that includes a cooling system.

The conversion from Cr(VI) to Cr(III) was negligible. A small fraction of soluble Cr-III was found on different particle types, with a conversion rate ranging from 0%-20% during the storage process at -15°C. As discussed in Section 4.4.2, considering most Cr(III) in ambient

particles are not soluble in our experimental conditions, the artifacts resulting from the conversion of Cr(III) to Cr(VI) are not expected to be significant. A multiple-laboratory comparison will be implemented as part of the new method comparison project to verify the developed method. Further, it would be very helpful to develop a certified Cr(VI) ambient particulate matter standard reference material so the recovery and inter-conversion rates could be verified. Development of a standard reference material may be an additional outcome of the new method comparison project, although not specifically part of the proposed work plan.

The factors, including aerosol type and composition, relative humidity, temperature, ozone, sulfur dioxide and nitrogen dioxide, that may affect the stability of Cr species were investigated under dark controlled environmental conditions. SO₂ was found to be the most significant pollutant that can cause reduction of Cr(VI) on both DPM and SOA. In the presence of SOA particles, a small reduction of Cr(VI) was also found when particles were exposed to O₃, NO₂ or high T/RH. A higher conversion rate of Cr(III) was also observed for exposure to NO₂ and high T/RH. The effects from those factors were negligible for DPM particles. These results indicate that Cr(VI) collected from ambient air during summer may be less stable than particles samples collected in winter because the fraction of SOA is usually higher in the summer. In addition, the results suggest that NO₂ may serve as an oxidant for ambient Cr(III) under dark conditions. The specific mechanisms behind the Cr transformation are far from being understood, and require further study.

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TABLES

Table 1: Test condition CEF

Experiment ID	Tested Environmental factor	Condition ^a	# of Sampling Filters ^b	
			SOA	DPM
1	NO ₂	NO ₂ =150 ppb	4	3
2	Ozone	Ozone=100 ppb	4	3
3	SO ₂	SO ₂ =160 ppb	4	3
		SO ₂ =50 ppb	4	0 ^c
5	Clean air	Clean air	3	3
6	High T and H	T=88F, RH=68%	3	3
7	Control Filters (CA)	Freezer	7	5

^a T=68F, RH=40% was set under experiment 1-5.

^b Sample filters with DPM/SOA particles were spiked with 50 µl 2 ng/ml ⁵³Cr (VI) and 50 µl 2 ng/ml ⁵⁰Cr(III).

^cSince no effects were found for Cr(VI) spiked on the DPM when exposed to 160 ppb SO₂, no further tests were conducted for Cr(VI) spiked on DPM at the SO₂ of 50 ppb condition.

Table 2: Sample types and the factors that were examined

Sample type	Abbreviation	Factors Examined
Lab Blank	LB	Filter background
Field Blank	FB	Field trip background
Lab Control	CA-L	Storage factor on the blank filters
Field Control	CA-F	Storage factor in the field for blank filters
Samples with Isotopes Spiked Before sampling	BS	1. Sampling factors; 2. Particle effect during process
Samples with Isotopes Spiked after sampling	AS	Storage factor on the particles
Samples with no Isotopes Spiking	PM	For the determination of Cr(VI) in ambient PM

Table 3. ICP-MS operating conditions during Cr speciation analysis

Torch	VG Quartz
Nebulizer	Concentric
R.F.Power	1450 W
Reflected power	1.6 W
Sample delivery rate	1.0 mL/min
Sampler cone	Nickel, 1.0 mm orifice
Skimmer	Nickel, 0.7 mm orifice
Dwell Time	300 ms
Acquire Time	4 min
Cooling Argon Gas	12 L/min
Auxiliary Argon Gas	0.88 L/min
Nebulizer Argon gas	0.99 L/min
Target Isotopes	^{50}Cr , ^{52}Cr , ^{53}Cr , ^{115}In

Table 4. Level of Cr(VI) and Cr(III) on blank filter after different cleaning protocol*

Protocol	Method	⁵² Cr(VI) (ng)		⁵² Cr(III) (ng)	
		Mean	SD	Mean	SD
A	HNO ₃	1.12	0.23	0.27	0.24
B**	HNO ₃ +Sonication	1.03	N/A	0.42	N/A
C	EDTA	0.14	0.14	0.05	0.08
D	EDTA +HNO ₃	1.00	0.3	0.05	0.05
Commercial filter	No cleaning	5.84	0.56	2.89	1.34

* The sampling volume was taken as 24m³. Triplicates were measured in each condition.

** One filter was broken in the cleaning procedure and no SD was obtained.

Table 5: Conversion and recovery rate for tests with different particles (%)

Particle type (N=3)	Recovery (%)				Conversion (%)			
	$^{50}\text{Cr(III)}$		$^{53}\text{Cr(VI)}$		$^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$		$^{53}\text{Cr(VI)}$ to $^{53}\text{Cr(III)}$	
	Average	SD	Average	SD	Average	SD	Average	SD
CA-L	4.87	0.52	90.1	3.0	1.48	0.19	0.30	0.42
NIST1648	1.22	0.54	84.5	0.5	3.69	1.33	ND	ND
SQC012	0.96	0.40	106	9	16.72	6.31	ND	ND
SRM2701	0.29	0.08	82.3	6.6	1.72	0.35	ND	ND

- The recoveries of $^{53}\text{Cr(VI)}$ for the 3 SQC012 and SRM2701 samples that were spiked with isotope were corrected for the $^{53}\text{Cr(VI)}$ from the soil material based on the isotope ratio of 52 and 53 and the certified $^{52}\text{Cr(VI)}$ values.
- ND: non-detectable

Table 6. The concentration and recovery of Cr(VI) on different types of particles

Particle type	Number of Samples	⁵² Cr(VI) (ng/g)			⁵² Cr(VI) Recovery(%)*	Relative error (%)
		Mean	SD	RSD(%)		
NIST1648	12	1.75	0.46	26	NA	NA
SQC012	12	135	18.9	14	116	16
SRM2701	12	2.81	0.56	20	51	-49

*recovery was calculated as extracted Cr(VI) /Cr (VI) certified value. The certified Cr(VI) level is 116.96±17.66 and 5.51±0.32 ng/g for SQC012 and SRM2701(1:100 diluted) respectively.

Table 7. Summary of stability results for lab control samples and NIST1648 samples

Sample type	storage time (day)	Recovery (%)		Conversion (%)	
		$^{50}\text{Cr(III)}$	$^{53}\text{Cr(VI)}$	$^{50}\text{Cr(III)} \rightarrow ^{50}\text{Cr(VI)}$	$^{53}\text{Cr(VI)} \rightarrow ^{53}\text{Cr(III)}$
Filter Only	1	4.9	108	15.4	ND
	2	3.1	83.7	5.7	0.6
	4	5.6	97.0	12.0	0.2
	7	4.9	90	1.5	0.3
	8	12.6	107.0	10.7	0.4
	12	0.0	98	4.5	ND
	13	5.0	100	15.7	0.6
	15	0.5	95.7	1.0	ND
	17	3.57	91	6.6	1.6
	78	2.4	86.0	34.2	0.6
	84	3.0	96	6.7	ND
	92	1.0	85.0	16.2	1.6
	97	3.2	98	3.3	0.4
	104	1.1	100	15.5	0.8
	106	0.4	92.0	14.8	0.4
	111	2.6	90	3.2	1.2
NIST1648 samples	1	5.5	92.6	6.6	0.2
	3	1.3	90.7	4.6	ND
	6	1.2	85.2	3.7	ND
	8	20.5	96.5	35.6	12.4
	16	0.6	93.1	2.8	ND
	32	3.5	91.6	3.3	0.4
	59	3.4	89.4	1.8	0.2
	95	0.7	90.5	3.8	ND

Table 8. Summary of CEF test results^a

Tested factor	Recovery (%) ^b				Conversion (%) ^b			
	⁵⁰ Cr(III)		⁵³ Cr(VI)		⁵⁰ Cr(III) to ⁵⁰ Cr(VI)		⁵³ Cr(VI) to ⁵³ Cr(III)	
	DPM	SOA	DPM	SOA	DPM	SOA	DPM	SOA
CA-L	3.64±2.82	3.16±2.11	97.0±7.5	100±7	1.88±0.64	6.02±2.63	1.50±1.03	0.79±0.47
Clean air	1.72±0.32	2.04±0.37	92.3±5.6	85.7±5.9	4.25±0.71	6.02±0.54	0.43±0.31	1.04±0.65
NO ₂	2.48±0.28	2.47±0.28	86.2±1.9	95.2±4.9	5.22±1.12	13.10±2.42	1.54±0.60	2.18±1.24
SO ₂	1.35±1.13	1.76±0.65	40.8±3.5	41.9±6.8	4.97±3.00	6.78±1.66	2.41±1.67	2.63±0.46
O ₃	3.31±2.51	2.97±0.98	97.1±1.1	75.2±5.5	4.60±0.64	6.01±1.33	1.98±0.46	3.39±1.85
High TH	4.34±0.65	2.29±0.07	91.3±2.2	97.4±3.9	4.94±0.17	15.2±1.34	1.30±0.06	1.99±0.47

^aThe concentration of NO₂, SO₂ and O₃ was 150, 160 and 100 ppb, respectively. The temperature was set as 68 °F and RH at 40% except high TH which temperature and RH were set as 88°F and 68% with clean air pull through.

^bThe methods of how each type of sample were prepared are presented in Table 2, and the number of samples for each type is presented in Table 1

Table 9. ^{52}Cr and meteorology data in each sampling day

Season	sampling date	sample number	T (°F)	Wind spd (mph)	PM ($\mu\text{g}/\text{m}^3$) ^a	O ₃ (ppb) ^d	NO ₂ (ppb) ^d	SO ₂ (ppb) ^d	$^{52}\text{Cr(VI)}$ (ng/m ³)	$^{52}\text{Cr(III)}$ (ng/m ³)
Winter	FB	7							0.10±0.05	0.02±0.02
	2/9/2009	5	40.9	0.5		6.4	43.7	8.5	0.26±0.02	0.01±0.01
	2/11/2009	6	51.5	12.2		28.8	7.9	0.6	0.03±0.01	ND
	2/16/2009	6	34.0	1.7		19.5	23.3	2.1	0.14±0.03	ND
	2/18/2009	6	41.0	6.3	14.25	14.8	20.6	5.1	0.09±0.01	ND
	2/23/2009	6	29.4	4.6	6.04	27.1	15.6	4.7	0.14±0.02	ND
	2/25/2009	6	38.7	0.8	32.21	9.0	39.3	11.0	0.10±0.02	ND
	3/2/2009	6	21.2	4.6	8.71	28.1	13.8	1.5	0.11±0.02	ND
Summer	FB	3							0.03±0.02	0.02±0.01
	08/20/2008	2	74.2	1.1		28.5	20.5	1.9	0.19	0.01
	08/25/2008	4	72.4	1.2		27.3	12.5	0.5	0.17±0.06	ND
	09/03/2008	4	80.7	1.9		38.9	16.9	3.7	0.05±0.05	ND
	09/08/2008	4	70.1	2.0		27.3	15.5	2.3	0.21±0.12	0.01±0.01
	09/15/2008 ^b	4			7.67	12.7	14.3	0.7	0.12±0.14	ND
	09/17/2008	4	67.4	2.5	15.67	31.8	18.6	0.8	ND	ND
	09/22/2008	4	63.5	2.5	19.33	13.0	19.5	0.8	0.07±0.04	ND

a. PM concentration was monitored by loading Teflon filters in one cartridge, some days lacked of the data because the cartridges were used for other purpose.

b. The meteorology data missed on 09/15/2008 due to the failure of met station

c. All chromium data has been FB subtracted.

d. The concentration of co-air pollutants was obtained from the local air quality monitor station in Bayonne, NJ, which is closest to Rahway.

Table 10. The recovery and inter-conversion rate data in field study

Season	Sample	Number	Recovery (%)		Conversion (%)	
			$^{50}\text{Cr(III)}$	$^{53}\text{Cr(VI)}$	$^{50}\text{Cr(III)}$ to $^{50}\text{Cr(VI)}$ ^a	$^{53}\text{Cr(VI)}$ to $^{53}\text{Cr(III)}$
Winter	BS	14	0.89±1.23	69±18	20.8±9.16	2.05±0.97
	AS	14	2.14±1.39	82±18	11.4±5.95	2.13±1.43
	CA-F	7	2.41±1.79	78±13	17.0±4.99	0.62±0.86
	CA-L	6	7.02±2.96	100±6	13.9±2.03	0.20±0.28
Summer	BS	13	0.24±0.24	51±17	19.1±6.79	0.17±0.18
	AS	13	0.30±0.17	64±10	27.2±7.18	0.20±0.17
	CA-F	4	0.77±1.03	68±7	21.9±6.21	0.37±0.25
	CA-L	7	1.23±0.66	100±11	19.6±6.79	0.77±0.47

^aThe conversion rate of Cr(VI) to Cr(III) may not truly reflect real conversion due to either incomplete extraction or precipitation of $^{53}\text{Cr(III)}$ that was converted from $^{53}\text{Cr(VI)}$.

FIGURES

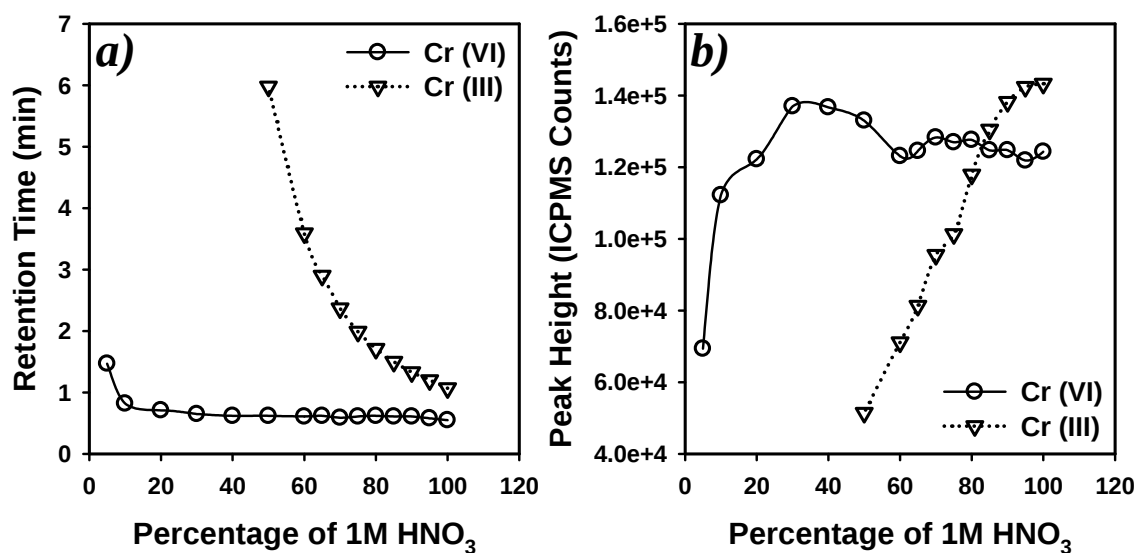


Figure 1. The retention time (a) and peak height (b) of Cr(VI) and Cr(III) (20 ppb respectively) as a function of HNO₃ acidity (at a flow rate of 1.25 mL/min)

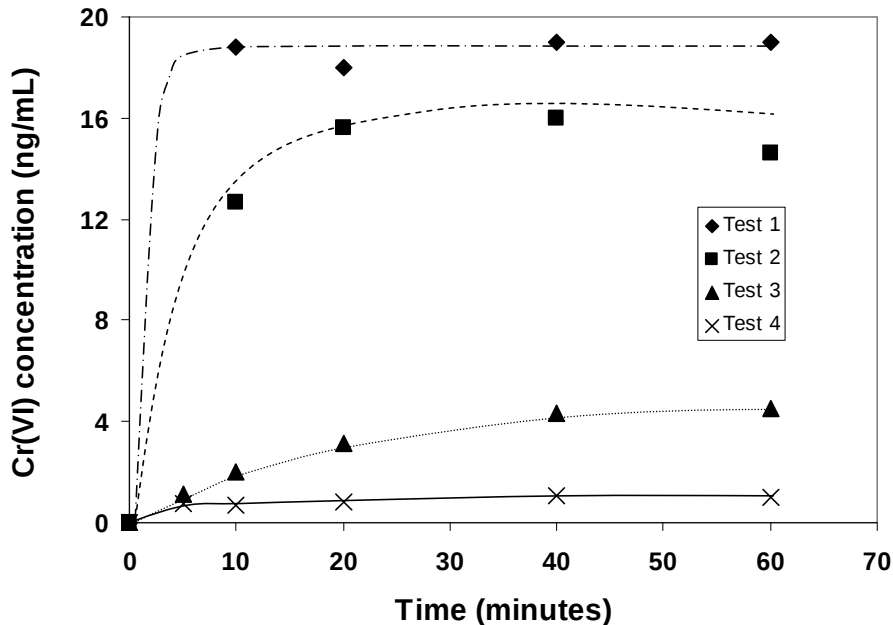


Figure 2. The Cr(VI) concentration in 40 mL HNO₃ solution (pH=4) measured at different extraction time. Test 1: the pre-cleaned and pre-treated filter spiked with 0.8 μ g Cr(VI); Test 2: 10mg NIST 1648 spiked with 0.8 μ g Cr(VI); Test 3: 10mg NIST 1648 spiked with 0.8 μ g Cr(III); and Test 4: 10 mg NIST 1648 only.

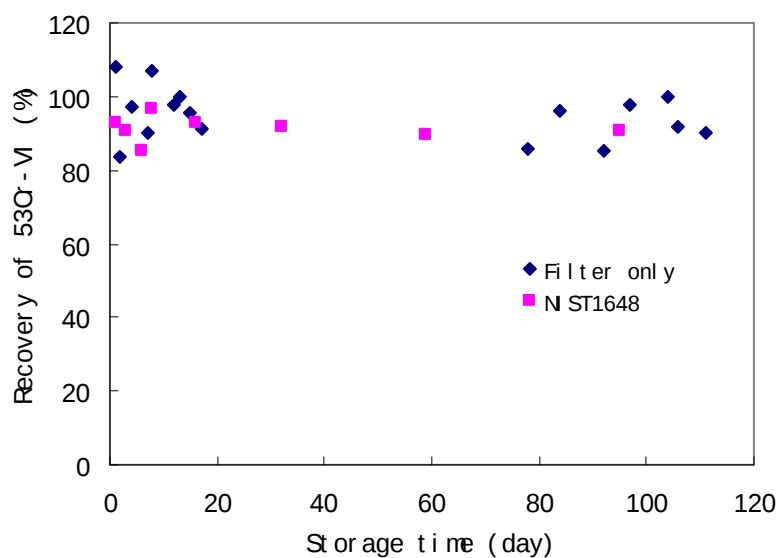


Figure 3. The stability of Cr-VI during storage process

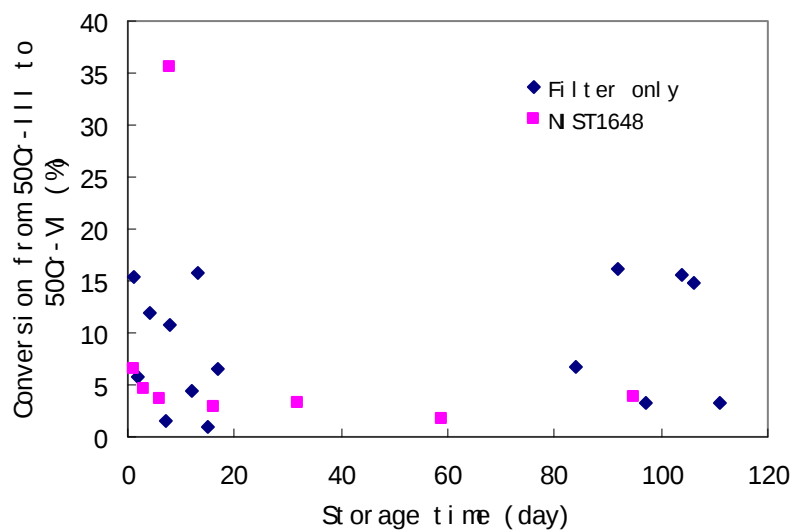


Figure 4. The stability of Cr-III during the storage process

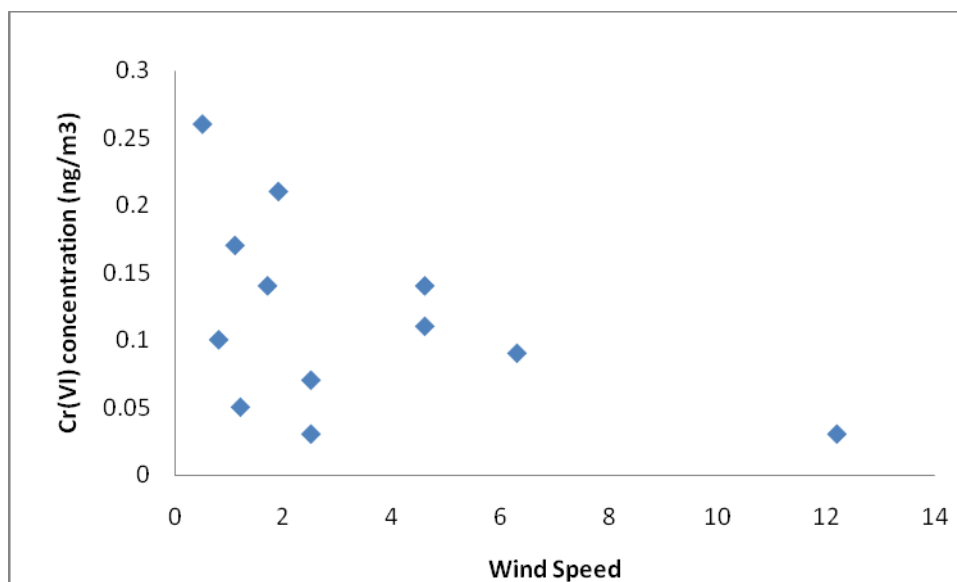


Figure 5. Scatter plot of Cr(VI) and the wind speed

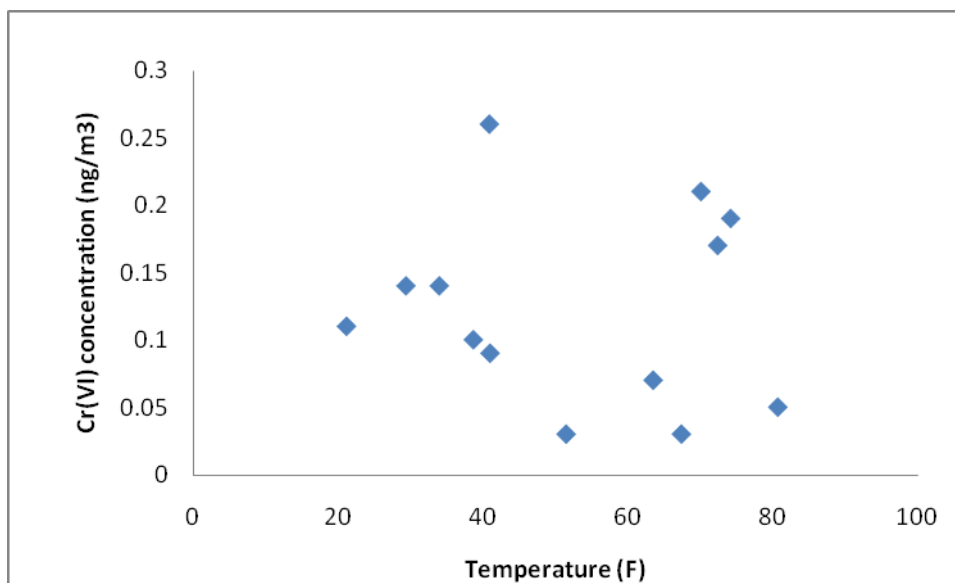


Figure 6. Scatter plot of Cr(VI) and the temperature

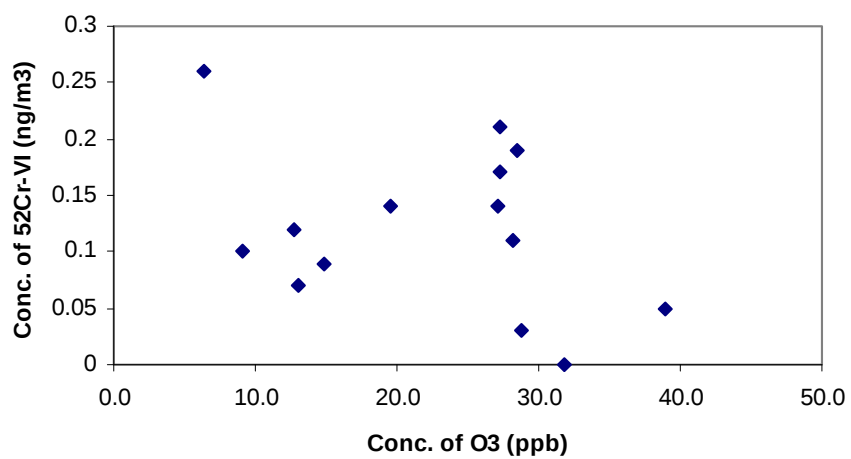


Figure 7. Scatter plot of Cr(VI) and the ambient O₃ level

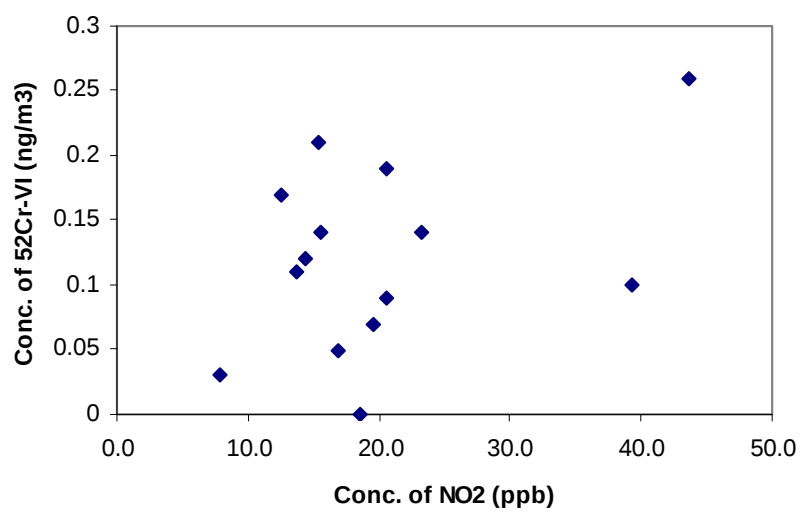


Figure 8. Scatter plot of Cr(VI) and the ambient NO₂ level

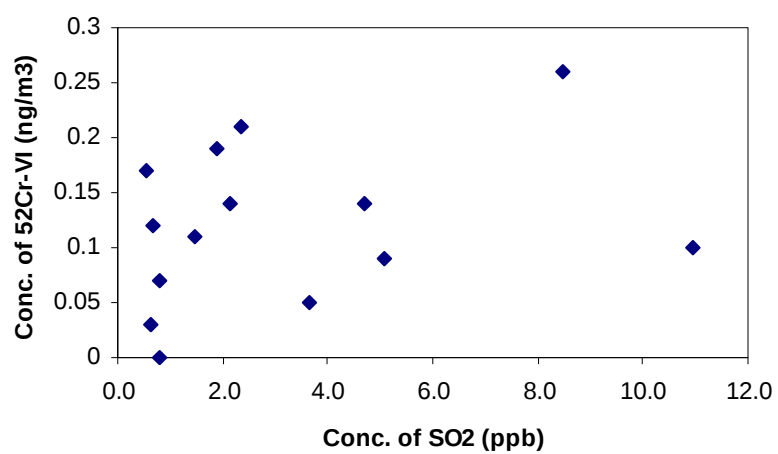


Figure 9. Scatter plot of Cr(VI) and the ambient SO_2 level