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Improved Atmospheric Sampling of Hexavalent Chromium

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Abstract

Hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) are the primary chromium oxidation states found in ambient atmospheric particulate matter. While Cr(III) is relatively nontoxic, Cr(VI) is toxic and exposure to Cr(VI) may lead to cancer, nasal damage, asthma, bronchitis, and pneumonitis. Accurate measurement of the ambient Cr(VI) concentrations is an environmental challenge since Cr(VI) can be reduced to Cr(III) and vice versa during sampling. In the present study, a new Cr(VI) sampler (Clarkson sampler) was designed, constructed, and field tested to improve the sampling of Cr(VI) in ambient air. The new Clarkson Cr(VI) sampler was based on the concept that deliquescence during sampling leads to aqueous phase reactions. Thus, the relative humidity of the sampled air was reduced below the deliquescence relative humidity (DRH) of the ambient particles. The new sampler was operated to collect Total Suspended Particles (TSP), and compared side-by-side with the current National Air Toxics Trends Stations (NATTS) Cr(VI) sampler that is utilized in the United States Environmental Protection Agency (USEPA) air toxics monitoring program. Side-by-side field testing of the samplers occurred in Elizabeth, NJ during the winter and summer of 2012. The average recovery values of Cr(VI) spikes after 24 hour sampling intervals during summer and winter sampling were 57 and 72%, respectively, for the Clarkson sampler, while the corresponding average values for NATTS samplers were 46% for both summer and winter sampling, respectively. Preventing the ambient aerosol collected on the filters from deliquescing is a key to improving the sampling of Cr(VI).

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Keywords

Cr(VI); Sampler; TSP; NATTS; Recovery

INTRODUCTION

Cr(III) and Cr(VI) are the two common oxidation states of chromium in the environment. Cr(VI) is toxic and exposure to Cr(VI) may lead to cancer, nasal damage, asthma, bronchitis, pneumonitis, dermatitis and skin allergies (Barceloux, 1999; Park et al., 2004). In contrast, Cr(III) is a trace element essential for the proper function of living organisms (IETEG, 2005).

Meng et al. (2011) determined the soluble Cr(VI) concentration in ambient air of Paterson ($0.44 \pm 0.35 \text{ ng.m}^{-3}$) and Chester ($0.40 \pm 0.53 \text{ ng.m}^{-3}$), NJ, USA, which are an industrial city and a background site, respectively. Swietlik et al. (2011) performed ambient air sampling in Radom, Poland, and reported the average values for total Cr and Cr(VI) concentrations to be 25 and 6 ng.m^{-3} respectively. They determined the Cr(VI) to total Cr ratio to be 36%. A total of 1466 Cr(VI) measurements were conducted over 22 sites from January 2005 to December 2005 in the US (ERG, 2007). The concentration of soluble Cr(VI) ranged from 0.001 to 2.97 ng.m^{-3} , and the average Cr(VI) concentration was determined to be 0.044 ng.m^{-3} . The soluble and total Cr(VI) concentrations in ambient PM_{10} collected from 4 locations in New Jersey, i.e. Meadowlands, Elizabeth Traylor and Rahway (with mixed Cr emission sources), and Piscataway (a suburb area) were determined by Huang et al. (2013). In the locations with mixed Cr emission sources, the mean concentrations were 1.05 – 1.41 ng.m^{-3} (winter) and 0.99 – 1.56 ng.m^{-3} (summer) for total Cr(VI); 0.11– 0.19 ng.m^{-3} (winter) and 0.18–0.37 ng.m^{-3} (summer) for soluble Cr(VI). In Piscataway, the mean concentrations were 1.07 ng.m^{-3} (winter) and 0.99 ng.m^{-3} (summer) for total Cr(VI), 0.03 ng.m^{-3} (winter) and 0.12 ng.m^{-3} (summer) for soluble Cr(VI). Their results indicate that the ambient PM in these sampling locations contain soluble and insoluble Cr(VI) with insoluble Cr(VI) being most prevalent.

Table 1 reviews the total Cr and Cr(VI) concentrations as well as Cr(VI) to total Cr ratios determined in previous studies. Table 1 shows that Cr(III) comprises the majority of ambient chromium. Cr(VI) concentrations ranged from 0.001 (ERG, 2007) to 70 ng.m^{-3} (Mandiwana et al., 2006), and the average Cr(VI) to total Cr ratios varied from 1 to 30%.

ERG developed a sampler (Figure S1) (ERG, 2007) for the U.S. Environmental Protection Agency's National Air Toxics Trends Stations (NATTS) monitoring program to collect Total Suspended Particles (TSP). The sampler operates for 24 hours from midnight to midnight using a carbonate-impregnated cellulose filter (see Figure S1 in the supplemental material), and the samples typically remain in the sampler after the sampling interval. ERG (2007) has shown that when filters are left in the NATTS sampler for longer than 12–24 hours, conversion of Cr(VI) occurs. When filters are spiked with Cr(VI) solution and left in the field for 33 to 105 hours, the reduction in Cr(VI) mass values ranged from 30% to 58% (ERG, 2007).

Meng et al. (2011) found the average Cr(VI) recovery to be $57 \pm 9\%$ for the 24 hours sampling in Paterson, NJ and Chester, NJ using filters spiked prior to sampling. This recovery value was significantly lower than $67 \pm 23\%$ average Cr(VI) recovery for filters spiked after sampling.

The corresponding values for Cr(III) conversion were reported to be $17 \pm 9\%$ and $11 \pm 5\%$, for filters spiked prior to sampling and after sampling, respectively. Their results suggest that $\sim 10\%$ of the Cr(VI) and $\sim 6\%$ of the Cr(III) were converted during sampling. Huang et al. (2013) studied chromium stability during sampling (NATTS sampler) using the method of filter-spiked prior to and after sampling such that reduction of Cr(VI) occurred during summer and winter. However, sampling had no significant influence on the Cr(III) oxidation. Tirez et al. (2011) determined the Cr(VI) recovery to be $75 \pm 39\%$, and the Cr(III) conversion was $1.7 \pm 1.2\%$ during sampling in Flemish region of Belgium. These previous results regarding chromium reduction and oxidation during sampling indicate that in general, there is conversion of Cr(VI) to Cr(III) during sampling. However, since Cr(III) is much higher in concentration than Cr(VI) in ambient PM, even a small conversion of Cr(III) to Cr(VI) can lead to a substantial positive bias in Cr(VI) measurements. The observed Cr(VI) and Cr(III) conversion in previous studies are attributed to the conversion during sampling, filter storage, extraction and analysis. The differences in the reported Cr(VI) recovery and Cr(III) conversion among previous studies could be also due to differences in the type of filters, analytical and filter extraction methods.

The conversion of Cr(VI) during sampling could be the result of deliquescence of the collected ambient particulate matter that provides aqueous reaction media, and subsequent reactions with organic matter, SO₂, and other reductants (Huang et al., 2013; Amouei Torkmahalleh et al., 2012; Grohse et al. 1988). Under typical atmospheric conditions, the RH varies over the 24 hour sampling period. It may exceed the deliquescence relative humidity (DRH) at least two times during the 24 hours sampling periods commonly employed: after sunset and early in the morning. Once the relative humidity (RH) reaches or exceeds the DRH of the ambient particulate matter (76%) (Amouei Torkmahalleh et al., 2012), conversion of Cr(VI) can occur even if the relative humidity subsequently drops below the DRH. The conversion of Cr(III) during sampling could be attributed to the reaction of Cr(III) with dissolved Mn (Seigneur & Constantino, 1995; Nico and Zasoski, 2000), water soluble organic carbons (WSOC) that contain secondary organic aerosol (SOA) (Huang et al., 2013) and also reactions with gaseous oxidants such as O₃ and particle-bound reactive oxygen species (ROS) (Amouei Torkmahalleh et al., 2013; Werner et al., 2006).

The reported Cr(VI) concentrations and Cr(VI) to total Cr ratios in previous studies may have been biased by the Cr(VI) reduction and Cr(III) oxidation during sampling, filter storage, filter extraction and analysis.

The goal of the current study was to design, construct, and test a new Cr(VI) sampler (Clarkson sampler), and compare the recovery of Cr(VI) using the Clarkson sampler with the NATTS sampler. The new sampler preserves Cr(VI) by reducing the humidity of the ambient air during sample collection to avoid deliquescence and slightly cooling the ambient air during summer.

EXPERIMENTAL METHODS

Clarkson Cr(VI) Sampler

The Clarkson Cr(VI) sampler was designed such that the sampling filters remain dry ($RH < 76\%$) during the sampling and post sampling intervals. To keep the filter dry, the RH of the air passing through the sampling filter was maintained below $76 \pm 2\%$, the deliquescence relative humidity (DRH) of the ambient particles reported by Amouei Torkmahalleh et al. (2012). The dry filter should slow the reduction reactions of Cr(VI) with ambient particles by preventing aqueous Cr(VI) chemistry so only solid-gas and solid-liquid reactions can occur (Amouei Torkmahalleh et al., 2013; Huang et al., 2013). Thus, a clean and dried air flow was added to sampled air in an FRM sampler (Rupprecht and Patashnick Model 2000H) equipped with TSP inlet (Figure 1). The clean air is also cooled to 10°C in the summer to decrease the temperature of the sampled air to slow Cr(VI) reactions on the filter. The clean air is warmed to 10°C in the winter to decrease the relative humidity. The FRM sampler pump draws air through two paths, the clean air and the ambient air paths.

The sampling flow rate was adjusted to 15 LPM, and clean air was introduced into the sampler at 5 LPM. The TSP sampler was operated from 00:00 to 24:00. The ambient air flow was controlled by a solenoid valve installed between the sampler inlet and the clean air inlet. The valve was controlled by the sampler's controller. The solenoid valve is normally closed. The controller provides a signal to open the valve at 00:00 and close the valve at 24:00. In the subsequent period, the clean air flow rate increased to 15 LPM with the pump continuously pulling air through the filter/dryer/cooler system.

To provide dry air, filtered air was forced through a mechanical dryer (Model No: D18IN, Ingersoll Rand, USA) to provide initial water removal. The air stream leaving the dryer was divided into four paths, each of them entered the drier enclosure (DE) of each Clarkson sampler. However, the mechanical dryer is required to operate even one Clarkson sampler because of the amount of water that needs to be removed from the air in hot and humid weather.

Each DE included two 47 mm cellulose filters, two HEPA filter capsules, a membrane dryer (Thermo Fisher Scientific, USA), a chiller/heater (TE Technology; model CP-065), two needle valves, a vacuum pump, and a vacuum pressure gage. The chiller/heater cooled the air in the summer, and heated the air during winter. The set point of the chiller/heater was 10°C , and the actual working temperature was $10 \pm 0.5^{\circ}\text{C}$. The temperature reached approximately 5 and 15°C during winter and summer, respectively, at the end of the line, before mixing with ambient air. The needle valve was used to adjust the clean air flow rate as needed. The membrane dryer removed the water from the air flow. To prevent water saturation in the dryer, a counterflow purge air driven by 24 ± 1 in Hg pressure drop was applied continuously across each dryer. The vacuum pump was used to provide purge air flow in the dryer. The purge air was passed through the cellulose filter and a HEPA filter capsule before entering the dryer. The needle valve was used to adjust the flow rate of the purge air to 0.5 LPM (Figure 1). Abrasion-Resistant Gum rubber tubing (1/4" ID, 1/2" OD, 1/8" wall thickness) was used in the clean air path and the tubing was insulated by semi-flexible polyethylene foam rubber (McMaster Carr) to minimize the temperature drop.

Because of heat transfer across the clean air line, the temperature of the clean air slightly deviated from the cooler/heater set point. Figures S2 and S3 show the FRM sampler with TSP inlet and DE connected to the sampler. The relative humidity and the temperature of the ambient air and clean air were continuously monitored using a temperature and relative humidity sensor (iButton, Maxim).

Sampling Filters—Cellulose filters were used because they have low chromium background concentrations (ERG, 2007). Cellulose filters spiked with Cr(VI) solution and then frozen showed no Cr(VI) reduction for up to 11 days at -18°C (ERG, 2007). The cellulose filters were leached overnight in 10% nitric acid solutions to remove any chromium contamination. The filters were washed with ultrapure water, and dried overnight in a clean bench. The pH of the filters was measured using pH indicator paper, and found to be between 5 and 6. To prepare basic cellulose filters, the acid washed filters were impregnated with 500 mL of a 0.12M sodium bicarbonate solution. The filters were dried in a clean bench producing filters with pH values between 9 and 10 (ERG, 2007).

Isotopic Spiking—Solutions of isotopically enriched Cr(III) (Chromium (III) Nitrate, $\text{Cr}(\text{NO}_3)_3$) and Cr(VI) (Potassium Dichromate, $\text{Cr}_2\text{K}_2\text{O}_7$) standards were purchased from Applied Isotope Technology, and refrigerated at 4°C . $^{53}\text{Cr}(\text{VI})$ and $^{50}\text{Cr}(\text{III})$ isotopes were spiked on the filters to simultaneously monitor the oxidation and reduction of Cr(III) and Cr(VI) respectively, using IC/ICPMS (Ion Chromatography (IC) coupled with Inductively Coupled Plasma Mass Spectrometry (ICPMS)).

Cr(VI) standard was spiked on the filters to determine Cr(VI) recovery using ICUV (Ion Chromatography Ultra Violet) for positive control study that was performed during field (summer) sampling campaign. All unspiked filters including field and laboratory blank filters were analyzed using ICUV.

Spiked filters were placed in a laminar flow clean bench for 10 minutes to dry and then stored in a freezer at -20°C . All of the frozen filters were then dried in vacuum desiccators before being used for sampling to remove any possible absorbed water.

Analytical Methods—To determine Cr (VI) concentration using IC/ICPMS (Thermo X-series, MA) analysis, a CS5A ion exchange column (Dionex IonPac, 250×4.0 mm, $5 \mu\text{m}$ size) was employed. The sample delivery system consisted of High Performance Liquid Chromatography (HPLC), a Spectrosystem peristaltic pump, and a quartz spray chamber with a Conikal concentric glass nebulizer. Collision cell technology (CCT) was used to reduce polyatomic interferences such as $^{52}\text{ArC}^+$ and $^{53}\text{ClO}^+$. The instrument was optimized daily using a Thermo A25 Tune solution. External calibration curves were generated using a blank and Cr(VI) standards of 0.2, 0.5, 1, 2, 5 and 10 ng/mL. The Method Detection Limit (MDL) (40. CFR 136, Appendix B) was determined as 0.042 ng/mL. The mean of the blank filter extract was 0.004 ng/mL ($n=4$), which was below the MDL. Relevant HPLC parameters and analytical conditions for HPLC-ICP-MS are given in Table S1 (supplemental material).

To determine the concentration of Cr(VI) using ICUV analysis, Cr(VI) is separated by ion chromatograph (IC) using an anion exchange analytical column (AS7, Dionex) with a supporting guard column (NG1, Dionex), and reacted using a post-column derivatization module with diphenylcarbohydrazide (DPC) to form a complex that can be detected at 530 nm with a visible detector.

The conversion of Cr(VI) to Cr(III) cannot be directly compared from IC/ICPMS analysis to ICUV analysis. The samples are extracted using an acidic solution when prepared for IC/ICPMS, and a slightly basic solution when prepared for ICUV analysis.

Data Analyses—The relative standard deviations (RSD) of Cr(VI) recovery and Cr(III) conversion were calculated as the ratio of the standard deviation of the group of data to average of the data. Data for samples with more than two repetitions are presented as average $\pm$ standard deviation while data from duplicated samples are presented as average $\pm$ relative percent difference (RDP). Variability is defined as “absolute (value of sample 1 – value of sample 2) / average (value of sample 1 and value of sample 2)”.

One way ANOVA and two-way ANOVA analyses were used for statistical comparisons in campus and field studies, respectively.

Clarkson Campus Study

Basic pH filters were spiked with 10 ng Cr(VI) and 20 ng Cr(III). Four FRM samplers were used either for the NATTS samplers or were assembled for the Clarkson samplers. The samplers were operated simultaneously using spiked basic cellulose filters prepared a day before the sampling day, from November 2010 to February 2011. Sampling was performed with flow rates of 15 L min⁻¹ on the roof of an academic building on the Clarkson University campus in Potsdam, NY. After sampling, the filters were transferred to petri dishes, and stored in a freezer at -20°C until analysis.

To examine the precision of the four Clarkson samplers on Cr(VI) recovery and Cr(III) conversion, four samplers were operated simultaneously for 24 hours, and the sampling was repeated for four days to collect a total of 16 filters.

NATTS and Clarkson samplers were operated side-by-side to compare the performance of both types of the samplers to recover Cr(VI). The experiments were performed by operating two Clarkson samplers and two NATTS samplers simultaneously with 15 LPM flow rate. The comparison was made on two different days to duplicate the study. Overall, four filters were collected per sampler type.

Field Study

Field sampling was conducted at the New Jersey Department of Environmental Protection (NJDEP) air toxics monitoring site in Elizabeth, NJ. The site is downwind from a number of potential sources of hexavalent chromium emissions, and is located adjacent to interchange 13 on the New Jersey Turnpike (Figure 2). The site has power, and is easily accessible by field sampling crews 24 hours/day, seven days/week. A total of eight samplers (four Clarkson samplers and two dual-channel NATTS samplers) were deployed in the field for

the sampling at average flow rates of 13.1(NATTS) and 15.2 (Clarkson) LPM. To minimize potential airflow interferences, the collocated samplers were placed at least one m apart from each other at the monitoring site, but close enough to ensure that there were no significant differences (<20%) in the collected PM mass by the samplers. The mass precision tests were conducted for four rounds, from August 1, 2011 to August 4, 2011. The sampling was performed 14 ± 1 LPM for 24 hours on Teflon filters, with no Cr spiking. The sampled filters were kept in petri dishes in a weighing room (20 ± 2 °C and $35 \pm 5\%$) at least 24 hours until gravimetric analysis. The mass of the filters before and after sampling were monitored using a micro balance to determine the collected PM mass.

During the sampling campaign, field blank samples were placed in all samplers for 24 hours, and, then, were collected with field samples to store in the freezer until analyses. After sample collection, the field and field blank samples were shipped overnight to the designated laboratories for analysis by mail on dry ice (without weekend delivery). Accordingly, laboratory blank samples were shipped from either ERG or Rutgers University laboratories to the designated laboratories. Samples were kept at -20°C in freezers at each laboratory until analysis. Samples were analyzed by each laboratory soon after receipt.

Tables S2 and S3 (supplemental material) present the details of field samples during winter and summer 2012, respectively. Tables S4 and S5 (supplemental material) show the sampling information for field and laboratory blank samples during winter and summer sampling campaigns, respectively. Rounds 5 and 6 in Table S3 are considered as positive control study.

Winter and summer sampling were performed in January 2012 (eight rounds) and June 2012 (six rounds), respectively. During winter sampling, in each round, eight samplers (four Clarkson and four NATTS samplers) were operated side by side except round 1. During round 1, six samplers including four Clarkson samplers and two NATTS samplers were operated. Day 1 pickup represents 24 hours sampling plus the subsequent overnight field storage period, and Day 3 pickup refers to 24 hours sampling plus subsequent 48 hours and an overnight field storage period. During the winter sampling, sample analysis was performed by ICUV at Clarkson University, Rutgers University and ERG, and also by IC/ICPMS at Clarkson University and Rutgers University, under the same sampling and analysis conditions per analytical method. All recovery and conversion calculations were made using the determined concentrations by IC/ICPMS.

During summer sampling, four NATTS and three Clarkson samplers (one sampler had failed) were operated side by side. Rounds 3 and 4 were designed to monitor Cr(VI) recovery and Cr(III) conversion using IC/ICPMS while rounds 5 and 6 (positive control study) were performed to monitor only the Cr(VI) recovery using ICUV. During summer campaign, sample analysis was performed by ICUV at ERG and IC/ICPMS at Rutgers University.

Table S6 (supplemental material) shows the method detection limit (MDL) for each analytical method at each laboratory.

Ambient Cr(VI) concentration was defined as the mass of the collected Cr(VI) after 24 hours sampling divided by the sampling volume. For Laboratory and field blank samples, the Cr(VI) concentration was estimated by the mass of the determined Cr(VI) divided by the average sampling volume (20.2 m³ for winter sampling and 20.5 m³ for summer sampling) during the sampling period. The precision in sampling flow rate was higher for Clarkson samplers compared to NATTS samplers.

RESULTS and DISCUSSION

All of the laboratories analyzed Quality Assurance /Control (QA/QC) samples before field sampling as well as during field campaign to ensure the accuracy for each method at each laboratory. All of the laboratories showed acceptable results for Cr(VI) and Cr(III) audit samples during winter sampling. During summer sampling, Clarkson laboratory as well as Rutgers University laboratory (for ICUV method) did not show acceptable results, and thus, were not included for analyses. Audit samples were prepared and distributed by an independent third party (Wibby Environmental, Golden, CO) as well as by the three laboratories.

The ratio of the measured ⁵³Cr(VI) mass in the sample extract subtracted from the portion of ⁵³Cr(VI) in the ambient air divided by the spiked ⁵³Cr(VI) mass was defined as “recovery” of ⁵³Cr(VI) when IC/ICPMS was used for analysis. Likewise, The ratio of the measured natural Cr(VI) mass in the sample extract subtracted from the portion of natural Cr(VI) in the ambient air divided by the spiked Cr(VI) standard mass was defined as “recovery” of Cr(VI) when ICUV was used for analysis. The conversion of ⁵⁰Cr(III) to ⁵⁰Cr(VI) was defined as the measured mass of ⁵⁰Cr(VI) in the sample extract subtracted by the portion of ⁵⁰Cr(VI) in the ambient air divided by the spiked ⁵⁰Cr(III) mass. To estimate the mass of ⁵⁰Cr(VI) and ⁵³Cr(VI) in the ambient air, the determined mass of ⁵²Cr(VI) using IC/ICPMS was corrected by the abundance isotopic ratio of each chromium isotope.

Campus Study

Evaluation of the Membrane Dryer—This section examines the performance of the DE in drying the clean air as all of the data presented in this section were obtained when the mechanical dryer was off. The pressure of the purge air strongly affects the intensity of the drying by the membrane dryer. Increasing the pressure drop of the purge air decreases the relative humidity of the clean air. Therefore, the pressure of the purge air was adjusted at the lowest possible pressure (24 in Hg vacuum), maintained by the vacuum pump.

The Clarkson sampler efficiently reduced the RH of the clean air below 30% during 24 hours sampling (Figure 3), even during the early morning around 3 a.m. when the ambient RH reached 94%. The average temperature for the ambient air and the clean air were 5.1 ± 1.2°C and 5.0 ± 1.3°C, respectively.

The RH of the clean air increased as its flow rate increased to 15 LPM (Figure 4). During the post sampling period, the increase in the clean air flow rate decreased its residence time inside the membrane, and, thus at constant ambient RH, purge air flow rate and membrane

pressure drop, the RH of the clean air increased compared to the sampling period (Figure 4). The RH of the clean air was below 60% during the most humid condition when the RH of the ambient air exceeded 85%. During the post sampling time, the sampling filter faced only the clean stream with a RH value below 76% indicating that the Clarkson sampler will keep the filter dry during the post sampling period.

Evaluation of Final RH—To examine the RH of ambient air after mixing with the clean air produced by the mechanical and membrane dryers, an experimental study was conducted with the Clarkson sampler during summer. In this study, the RH of the clean air, ambient air and the ambient air passing through the filter were monitored simultaneously for 24 hours (Figure 5). The final RH after mixing was below the DRH of ambient particles indicating that the Clarkson sampler design works to reduce RH.

During winter sampling, the clean air was slightly heated by the heater to reduce its RH. However, heating the clean air increases the ambient temperature by 1°C after mixing. This change in temperature is negligible and should not affect the collection of the particulate matter on the filter.

Campus Sampling—The samplers showed good precision (< 20%), in particular for Cr(III) conversion (Table 2). Sampling during a windy day (round 2) resulted in higher Cr(VI) recovery (over 95%) compared to the rainy day (round 3). This result is in agreement with our recent finding showing that relative humidity plays an important role in the reduction of Cr(VI) during sampling (Amouei Torkmahalleh et al., 2012). During a rainy day, the average and maximum humidity values were found to be higher compared to a windy day. During round 1, the ambient RH exceeded the DRH for only six hours, and during round 2, the ambient RH never exceeded the DRH (data not shown). During round 3, the ambient RH exceeded the DRH of ambient particles for approximately 16 hours (data not shown). The difference in the Cr(VI) recovery between rounds 2 and 3 was determined to be statistically significant ($P=0.014$).

The average and maximum temperature values were lower in round 3 compared to round 2 (Table 2). Round 3 with the lower temperature that slows Cr(VI) conversion resulted in lower recovery compared to round 2. This result suggests that the role of humidity might be more important than the role of temperature for the temperature range of this study. It is assumed that the difference in collected PM mass among different sampling events is low such that the Cr conversion is not biased by this difference. The data presented by Swietlik et al. (2011) show the importance of humidity in Cr(VI) to total Cr ratio in the atmosphere. For example, sampling at the same location in Radom, Poland but different days showed Cr(VI) to total Cr ratio to be $27.6 \pm 15.5\%$ ($N=3$) at cold and humid atmosphere (average $T=3-6^{\circ}\text{C}$, average $\text{RH}=90\%$, $\text{PM concentration} = 116.5 \mu\text{g.m}^{-3}$ and $\text{Cr}_{\text{total}} \text{ concentration} = 14.3 \pm 2.5 \text{ ng.m}^{-3}$) and $38.3 \pm 5.7\%$ ($N=3$) at mildly hot and dry weather (average $T=22-25^{\circ}\text{C}$, average $\text{RH}=57\%$, $\text{PM concentration} = 100.0 \mu\text{g.m}^{-3}$ and $\text{Cr}_{\text{total}} \text{ concentration} = 15.3 \pm 2.3 \text{ ng.m}^{-3}$).

Cr(III) conversion was found to be consistent with higher precision independent of metrological conditions. Oxidants such as ozone and reactive oxygen species (Amouei Torkmahalleh et al., 2013; Huang et al, 2013) can oxidize Cr(III) to Cr(VI).

Side-by-side comparison between NATTS and Clarkson samplers showed no statistical difference in the Cr(VI) recovery. The average Cr(VI) recovery values after 24 hours sampling were determined to be 87 ± 2 (N=4) and 89 ± 13 (N=4) for Clarkson and NATTS samplers, respectively. The Clarkson samplers had better precision compared to NATTS samplers. Potsdam, NY is a clean rural area where PM mass concentrations are low providing little to react with spiked Cr(VI) during campus sampling. Therefore, it was expected there would be no difference in the Cr(VI) recovery between the two sampling trains.

Field Study

Overall, both types of the samplers showed a good precision individually, in each sampling day (Table S7). Also, the precision among all eight samplers on each sampling day was found to be $14 \pm 5\%$ that is better than the acceptable range ($<20\%$).

Cr(VI) Concentration—The average (N=61) Cr(VI) concentrations during the laboratory and field blank study for winter and summer sampling campaigns were below the analytical MDL (Table S6). The very low Cr(VI) concentrations suggests that no chromium contamination was introduced by the samplers, sampling filters, and during the analyses. However, for some samples, IC/ICPMS analysis showed chromium background contamination that could cause the results to be biased.

The average $^{53}\text{Cr(VI)}$ recovery and $^{50}\text{Cr(III)}$ conversion for the laboratory blank samples (N=8) were determined to be $102.8 \pm 9.1\%$ and $3.0 \pm 2.4\%$. The average $^{53}\text{Cr(VI)}$ recovery and $^{50}\text{Cr(III)}$ conversion for the winter field blank samples (N=4) were $113.5 \pm 27.2\%$ and $14.0 \pm 15.0\%$, respectively, on day1 pickup. One sample with 153% Cr(VI) recovery and 36% Cr(III) conversion among those field blank samples, markedly increased the standard deviation values. The average $^{53}\text{Cr(VI)}$ recovery and $^{50}\text{Cr(III)}$ conversion for the winter field blank samples (N=6) were determined to be $88.2 \pm 8.7\%$ and $8.5 \pm 3.5\%$, respectively, on day3 pickup. The average $^{53}\text{Cr(VI)}$ recovery and $^{50}\text{Cr(III)}$ conversion for the summer field blank samples (N=2) were $77.0 \pm 0.1\%$ and $6.0 \pm 0.0\%$, respectively, on day1 pickup. The average $^{53}\text{Cr(VI)}$ recovery and $^{50}\text{Cr(III)}$ conversion for the summer field blank samples (N=2) were found to be $67.0 \pm 0.04\%$ and $11.5 \pm 0.08\%$, respectively, on day3 pickup. Decreases in Cr(VI) recovery values were observed for summer and winter field blank samples when the blank filters were left in the field for 3 days compared to 1 day field blank samples. Also, spiked field blank filters showed lower Cr(VI) during summer compared to winter demonstrating the negative effect of temperature on Cr(VI) recovery.

Unceta et al. (2010) stated that reduction of Cr(VI) can occur by reaction of Cr(VI) with the polymeric materials used in sampling filters such as cellulose and glass during Cr(VI) sampling. In addition, filter holders may add to Cr(VI) conversion as a results of the presence of plasticizers materials. However, the high recovery of Cr(VI) in the laboratory blank samples as well as winter filed blank samples at day1 pickup imply very low impact

of cellulose filter and filter holder on Cr(VI) conversion. This observation is in agreement with findings of Huang et al. (2013).

Twenty four hour samples showed no statistically significant differences between Cr(VI) concentrations determined by NATTS and Clarkson samplers for each campaign (Table 3). The observed ambient Cr(VI) concentration during our winter and summer sampling campaigns in Elizabeth, NJ was much less than previous findings (Table 1). The average ambient Cr(VI) concentrations, $0.03 \pm 0.01 \text{ ng.m}^{-3}$ (summer) and $0.02 \pm 0.01 \text{ ng.m}^{-3}$ (winter), determined in this study are lower than the average Cr(VI) concentration of 0.044 ng.m^{-3} determined over 22 locations in the US (ERG, 2007). The difference in the total Cr(VI) concentrations between the current study and previous investigations could also be due to difference in analytical methods. The results of this study show statistically higher levels of Cr(VI) concentration during the summer sampling compared to the winter sampling ($P = 0.0003$) at Elizabeth, NJ.

Cr(VI) Recovery and Cr(III) Conversion—All of the data reported in this section were obtained using IC/ICPMS analysis unless otherwise stated.

(1) Cr(VI) Recovery—The average Cr(VI) recovery on day 1 for Clarkson sampler during summer and winter sampling periods were found to be 57.1 ± 0.2 and $71.8 \pm 4.9\%$, respectively, while the corresponding average values for NATTS samplers were 46.0 ± 1.6 and $46.2 \pm 10.8\%$ for the summer and winter sampling campaigns, respectively (Table 4). The average Cr(VI) recovery at day 3 for Clarkson sampler during summer and winter sampling were found to be 43.9 ± 17.6 and $72.3 \pm 4.3\%$, while the corresponding average values for NATTS samplers were 32.4 ± 2.1 and $33.9 \pm 7.6\%$ for the summer and winter sampling programs, respectively. No statistically significant difference was observed between day 1 and day 3 for both samplers during winter sampling campaign. This result could be due to the low ambient temperature during winter. During summer sampling, a statistically significant difference ($P = 0.038$) was observed between day 1 and day 3 Cr(VI) recovery for the both samplers. The reduction in Cr(VI) recovery between day 1 to day 3 was found to be 23 and 30% for Clarkson and NATTS samplers during summer, respectively. The statistical analyses of the results revealed that Cr(VI) recovery by Clarkson sampler was greater compared to NATTS sampler during winter sampling for both day 1 and day 3 pickup ($P < 0.001$), while no statistical difference was observed during summer. Only two filters were sampled during summer by Clarkson sampler so these results may not truly reflect its performance. The results from positive control study that were obtained using ICUV analysis showed that the average Cr(VI) recovery values by Clarkson and NATTS samplers were found to be 75.5 ± 0.3 and $17.8 \pm 15.8\%$, respectively.

The improvement in Cr(VI) recovery by Clarkson samplers indicates that drying was influential in preserving Cr(VI) during sampling. Clarkson samplers keep the filters dry until the end of the post sampling period to prevent deliquescence of ambient particles while NATTS samplers may experience deliquescence of ambient particles resulting in the conversion of Cr(VI).

(2) Cr(III) Conversion—The average Cr(III) conversion on day 1 for the Clarkson sampler during the summer and winter sampling periods were determined to be 8.6 ± 0.2 and $12.7 \pm 2.1\%$, respectively while the corresponding average values for NATTS samplers were 5.1 ± 0.8 and $8.4 \pm 5.9\%$ for the summer and winter sampling, respectively. However, only duplicate samples were taken for Clarkson samplers during summer campaign to determine the Cr(III) conversion on day 1.

The average Cr(III) conversion by day 3 for the Clarkson sampler during summer and winter sampling campaigns were found to be 10.6 ± 2.0 and $9.2 \pm 2.0\%$, respectively, while the corresponding average values for NATTS samplers were 9.8 ± 1.4 and $2.8 \pm 1.8\%$, respectively. Statistically significant differences were observed between day 1 and day 3 for the both samplers during winter sampling ($P = 0.008$). The observed lower Cr(III) conversion by day 3 compared to day 1 during winter sampling could be due to reconversion of $^{50}\text{Cr(VI)}$ during post sampling period. The Cr(III) conversion during summer at day 3 was statistically higher compared to day 1 for both samplers ($P = 0.004$). The statistical analyses of the results of both sampling seasons showed statistically significant differences between the two samplers ($P = 0.017$ for summer and $P = 0.003$ for winter). The observed conversion of Cr(III) to Cr(VI) during field sampling could be the results of the either of following cases:

1-Limited deliquescence of soluble Cr(III) salts such as $\text{Cr(NO}_3)_3$ that deliquesce at 52% (Amouei Torkmahalleh et al., 2012) as the Clarkson samplers keeps the ambient RH below 76% and not necessarily below 52%.

2-Solid-gas and solid-liquid reactions of soluble Cr(III) with potential oxidants in the atmosphere (Amouei Torkmahalleh et al., 2013) available during field sampling that result in the formation of soluble Cr(VI).

This study investigated the concentration and conversion of soluble Cr(VI) since the methods for the filter extraction and conversion monitoring are applicable only for soluble Cr(V). Huang et al. (2013) showed that insoluble Cr(VI) constitutes the majority of the total ambient Cr(VI). No conclusions can be obtained regarding the concentration and conversion of insoluble Cr(VI) during sampling in the present study.

See and Balasubramanian (2008) found insoluble Cr in indoor PM. Chromium speciation in indoor environments would be an interesting topic for future study. In particular, outdoor origin particles in indoor environment could be important sources of Cr(VI) since they accounts for major part of indoor particles.

The availability of the soluble and insoluble Cr(III) in the ambient PM samples depends on the source of the chromium. However, there are studies that showed that insoluble Cr(III) dominates the ambient Cr(III) in PM. A field test conducted by Huang et al. (2013) showed that soluble Cr(III) in ambient PM of the sampling locations was negligible, and, thus, the Cr(III) conversion is expected to be insignificant for these soluble Cr species. This conclusion was also reached by Tirez et al., (2011) and Werner et al., (2007). Insoluble Cr(III) was reported to be inert under the temperature and pH of the filter extraction process in this study (Huang et al., 2013). Thus, the observed conversion of Cr(III) during the field

study of this dissertation that was obtained from the conversion of soluble spiked Cr(III) does not reflect the conversion of Cr(III) in ambient PM during sampling. This conclusion suggests that the conversion of ambient Cr(III), which is one of the major challenges for the measurement of Cr(VI) using the current filter extraction procedure may be a concern only if the insoluble Cr(III) such as $\text{Cr}(\text{OH})_{3(s)}$ converts to soluble Cr(VI) such as $\text{CrO}_4^{-2}(\text{aq})$ in the presence of gaseous and particle oxidants.

CONCLUSIONS

Drying the filter during sampling of Cr(VI) below DRH of ambient particles is a key to improving the sampling of Cr(VI). Drying slows the chemistry of chromium by preventing the system from forming an aqueous phase through deliquescence. The Clarkson Cr(VI) samplers were designed and constructed based on this principle. Even though only a small amount of samples were collected, the Clarkson Cr(VI) samplers showed better Cr(VI) recovery compared to the current NATTS Samplers during sampling at Elizabeth, NJ. Because of the low chromium concentrations found during the field sampling in NJ, a study performed where Cr(VI) concentrations may be higher would allow a better evaluation of Clarkson samplers. However, based on the limited results presented here, it appears likely that the current NATTS sampling system is systematically underestimating the ambient concentrations of Cr(VI) in ambient PM. The extent of this underestimation depends on the fraction of soluble Cr(VI) as well as the handling practices for the collection of the samples from the samplers following the sampling period. There is thus a need for serious consideration of upgrading the current samplers that incorporate the drying and cooling that were included in the Clarkson samplers to provide better sampling and preservation of the collected PM to produce more accurate estimates of the population exposure to Cr(VI).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Clarkson Cr(VI) sampler – The arrows show the direction of ambient air flow

Figure 2.
Sampling location at Elizabeth, NJ

Figure 3.

RH variations for the ambient air and the clean air during 24 hours, purge air pressure =24 in Hg vacuum, purge air flow rate =0.5 LPM, the clean air flow rate =5 LPM

Figure 4. RH variations for the ambient air and the clean air during 24 hours, purge air pressure =24 in Hg vacuum, purge air flow rate =0.5 LPM, the clean air flow rate =15 LPM

Figure 5.
RH variations for the ambient air, the clean air, and the ambient air mixed with the clean air

Table 1

Total Cr and Cr(VI) concentration values as well as Cr(VI) to total Cr ratio reported in previous studies

Reference	Total Cr (ng.m ⁻³)	Cr(VI) (ng.m ⁻³)	Cr(VI) ratio (%)	Location
Puxbaum (1991)	1–40			non-polluted area
Krystek and Ritsema (2007)		20	1–20	close to a foundry
Mandiwana et al., (2006)		20–70		ferrochrome smelter
Nowak and Kwapulinski (1991)	30			heavy industry region
Bem et al. (2003)	5			central part of Poland
Nowak and Kwapulinski (1991)	2000			in the vicinity of a power plant
Talebi (2003)	27	7	25	Isfahan, Iran
Zereini et al. (2005)	16.3			Frankfurt, Germany
Fernández et al. (2000)	7.1			Seville, Spain
Utsunomiya et al. (2004)	2.7			Detroit, USA
Richter et al. (2007)		5		Santiago, Chile
Nusko and Heumann (1997)		1	25	Regensburg, Germany
Khlystov and Ma (2006)		0.5		Wilmington, USA
Li et al. (2002)		0.1–1.3		Sydney Basin, Australia
Metze et al. (2004)			1–20	city area
Bell and Hipfner, (1997)			20	Ontario
Borai et al. (2002)	19–6842		20–30	Alexandria and Cairo, Egypt
Tirez et al. (2011)	34–96	1.2–5.2	2.6–3.5	Near and far from an anthropogenic source, Flemish, Belgium
Hagendorfer et al., (2007)		0.04–0.23	1	Vienna, Austria

The $^{53}\text{Cr(VI)}$ recovery and $^{50}\text{Cr(III)}$ conversion determined by four Clarkson samplers (precision study)- campus study

Table 2

Sampling Round	Cr(VI) Recovery (Average $\pm$ STD)- RSD	Cr(III) Conversion (Average $\pm$ STD)- N=4)-RSD	Ambient RH, (Average $\pm$ STD)- Highest RH	Ambient Temp., (Average $\pm$ STD)-, Highest Temp.	Event
1	95.1 $\pm$ 8.54% (N=4)- (%8.9)	11 $\pm$ 0.20% (N=4)- (% 1.81)	59.6 $\pm$ 19.5%, (92.62%)	15.3 $\pm$ 10.8 °C, (33.66 °C)	no wind- no rain
2	101 $\pm$ 6.44% (N=4)- (%6.34)	11 $\pm$ 0.35% (N=4)- (%3.14)	42.1 $\pm$ 23.4%, (71.46%)	18.6 $\pm$ 10.1 °C, (36.06 °C)	windy
3	85.6 $\pm$ 2.20% (N=4)- (%2.57)	9.3 $\pm$ 1.2% (N=4)- (% 12.87)	68.2 $\pm$ 21.6%, (87.46%)	10.3 $\pm$ 4.68 °C, (21.91 °C)	rainy

Table 3

Ambient Cr(VI) concentration determined in this study- field study

Sampler Type	Day	Summer	Winter
		Cr(VI) (ng.m ⁻³) (N)	Cr(VI) (ng.m ⁻³) (N)
NATTS	1	0.03 ± 0.01 (11)	0.02 ± 0.01 (9)
Clarkson	1	0.03 ± 0.01 (5)	0.02 ± 0.01 (6)
Average	1	0.03 ± 0.01 (16)	0.02 ± 0.01 (15)

Table 4

Average Cr(VI) recovery and Cr(III) conversion determined by Clarkson and NATTS samplers- field study- All data are presented as average $\pm$ standard deviation except data for Clarkson sampler during summer as well as positive control that are presented as average $\pm$ variability.

Sampler Type	Winter % Cr(VI) Recovery (N)	Winter % Cr(III) Conversion (N)	Day	Summer % Cr(VI) Recovery (N)	Summer % Cr(III) Conversion (N)	Positive Control Study (N)
NATTS	46.2 $\pm$ 10.8 (4)	8.4 $\pm$ 5.9 (4)	1	46.0 $\pm$ 1.6 (4)	5.1 $\pm$ 0.8 (4)	17.8 $\pm$ 15.8 (4)
	33.9 $\pm$ 7.6 (6)	2.8 $\pm$ 1.8 (6)	3	32.4 $\pm$ 2.1 (4)	9.8 $\pm$ 1.4 (4)	NA
Clarkson	71.8 $\pm$ 4.9 (4)	12.7 $\pm$ 2.1 (4)	1	57.1 $\pm$ 0.2 (2)	8.6 $\pm$ 0.2 (2)	75.5 $\pm$ 0.3 (2)
	72.3 $\pm$ 4.3 (5)	9.2 $\pm$ 2.0 (5)	3	43.9 $\pm$ 17.6 (4)	10.6 $\pm$ 2.0 (4)	NA