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Research Project Summary
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Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air

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Abstract

The overall goal of this study was to develop a sensitive and reliable method for the measurement of ambient airborne hexavalent chromium [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 trivalent chromium [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/m^3; 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 (O_3), sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) in ambient air; and 5) to evaluate the developed method in the field during summer and winter seasons.

Good method sensitivity was obtained with a method detection limit of 0.09 ng/m^3. This is close to the minimal risk level (MRL) of 0.083 ng/m^3, 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 pairs) for lab duplicates and 12% (N=33 pairs) for field duplicates. Cr(VI) was found to be very stable during storage for up to 3 months at -5°C.

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 of 78±13%. The recovery of Cr(VI) was lower in summer than in winter, with an average recovery of 68±7%.

The conversion from Cr(VI) to Cr(III) was negligible number. A small fraction of soluble Cr-(III) spiked on the filter converted to Cr-(VI), with conversion rates ranging from 0%-20%. As discussed in Section 4.4.2 of the final report, 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.

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. SO_2 was found to be the most significant pollutant that can cause reduction of Cr(VI) on both fresh diesel particles (DPM) and secondary organic aerosols (SOA). In the presence of SOA, a small reduction of Cr(VI) was also found when particles were exposed to O_3, NO_2 or high T/RH number. A higher conversion rate of Cr(III) was also observed for exposure to NO_2 and high T/RH. The effects from those factors were negligible for DPM. 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 in ambient particles is usually higher in the summer. In addition, the results suggest that NO_2 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.

Introduction

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 trace element for human health. 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]. Cr(VI) compounds have been listed as one of the 187 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).

There is an EPA method for the measurement of Cr(VI) in ambient air (http://www.epa.gov/ttn/amtic/airtox.html) by the IC/UV approach. However, this method cannot quantify the potential inter-convention between Cr(III) and Cr(VI) which is important due to the potential inter-convention between Cr(III) and Cr(VI) during sampling (particle characteristics, temperature, humidity and co-pollutants), sample processing and analysis [3][4][5][6][7]. In order to simultaneously quantify the inter-conversion between chromium species during sampling, processing and sample analysis, the combination of the isotope spike technique and Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS) is required.

Methods

Optimization of the IC/ICPMS

The mobile phase, ionic strength of the mobile phase, flow rate and dwell times of the IC-ICPMS were tested under various conditions for the most effective conditions to detect and separate Cr(VI) and Cr(III), improve sensitivity and reduce detection level.

Extraction stability and efficiency were determined by testing extraction solution under different conditions.

Reduction of Cr(VI) background levels on blank filter

Four different cleaning solutions/ procedures were tested. All cleaned filters were dried in a nitrogen environment before being pretreated with sodium bicarbonate solution and dried in a nitrogen environment. The pretreatment helps to preserve Cr(VI) collected during sampling or spiked during laboratory experiments.

Recovery and interconversion of chromium species

Extraction efficiency, recovery and interconversion rates were evaluated using isotope spikes on NIST 1648 particles (no certified chrome species) and two certified soil materials, SQC012 and SRM2701.

Characterization of factors that potentially impact stability of Cr(VI)

Both $^{50}Cr(III)$ and $^{53}Cr(VI)$ were spiked on pre-collected fresh particles {either Diesel Particulate Matter (DPM) or Secondary Organic Aerosols (SOA)} to monitor the interconversion of chromium species aged under different conditions in the controlled environment facility (CEF). CEF conditions included clean air, air containing SO_2, O_3, and NO_2, at 20ºC and 40% relative humidity (RH), high temperature (31 ºC) and humidity (68%, the highest RH that could be achieved in the CEF).

Field Evaluation

The field evaluation was conducted in Rahway NJ for 7 days in both summer (late August 2008 to September 2008) and winter (February 2009 to early March 2009).

Results

Optimization of the IC/ICPMS

The optimal mobile phase was determined to be a weak HNO_3 solution, a flow rate of 1.25 mL/min and a dwell time of 300 ms.

An extraction solution of pH=4 HNO_3 solution was selected because it doesn't interfere with the IC-ICPMS analysis, minimal interconversion is expected, and a pH value of 4 is similar to human lung fluid pH. Optimal extraction conditions were sonication at 60°C for 40 minutes.

Reduction of Cr(VI) background levels on blank filter

The most effective cleaning procedure was soaking the filters in a 10% nitric acid solution overnight then rinsing with DI water until the pH of the filter matched the pH of DI water.

Recovery and interconversion of chromium species

Good recoveries of Cr(VI) were obtained for all three particle types (82%-105%). The conversion of Cr(VI) to Cr(III) was below the method's detection level. There was a low conversion rate of Cr(VI) to Cr(III) suggesting that conversion was negligible. There was low recovery of Cr(III) indicating that C(III) was not soluble under the analytical conditions.

Characterization of factors that potentially impact stability of Cr(VI)

SO_2 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 O_3, NO_2 or high T/RH number. A higher conversion rate of Cr(III) was also observed for exposure to NO_2 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 NO_2 may serve as an oxidant for ambient Cr(III) under dark conditions.

Field Evaluation

The method detection limit (MDL) was determined to be 0.09 ng/m^3. Method precision was 17%±12%. Recovery in summer was lower than in winter suggesting that Cr(VI) decays under summer conditions. Recovery of Cr(III) was low. No significant differences in conversion rates occurred. No significant seasonal differences were observed. Increases in wind speed corresponded to a decrease in Cr(VI) concentrations.

Discussion and Conclusion

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 MDL of 0.09 ng/m^3. This is similar to the minimal risk level (MRL) of 0.083 ng/m^3, 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. Cr(VI) was found to be very stable during storage for up to 3 months. Cr(VI) in ambient particles which were collected during the winter was found to be relative stable during the entire measurement process, however, the recovery of Cr(VI) was lower in summer than in winter.

The specific mechanisms behind the Cr transformation are far from being understood, and require further study.

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