

Technical note

An on-line instrument for mobile measurements of the spatial variability of hexavalent and trivalent chromium in urban air

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Abstract

The Steam-Jet Aerosol Collector-long Pathlength Absorbance Spectroscopy (SJAC-LPAS), an on-line continuous instrument for mobile measurements of spatial distribution of water-soluble hexavalent and trivalent chromium in ambient aerosols, has been developed and is presented here. The system collects particles with the SJAC and analyzes the collected sample on-line using the diphenylcarbazide (DPC) colorimetric method. By using a Teflon AF (Amorphous Fluoropolymer) liquid core wave guide, the limit of detection has been significantly improved, allowing on-line measurements at ambient concentrations. The limit of detection for Cr(VI) is 0.2 ng m^{-3} . Water-soluble Cr(III) can also be measured by oxidizing it to Cr(VI) in a parallel line using hydrogen peroxide before the detection with the DPC method. The concentration of Cr(III) is then determined as the difference between the two lines (Cr(VI) and Cr(VI) plus Cr(III)). The instrument was specifically designed to be used on a mobile platform to study spatial distribution of the pollutant within a city on a scale of 100 m. Special attention was given to the time resolution and the stability of the instrument performance under driving conditions. The time resolution of the instrument is 15 s. At a typical driving speed of 30 km h^{-1} the instrument can detect variations in chromium concentration (“hot spots”) on the scale of about 150 m. The instrument has proven to operate reliably and capture temporal and spatial variability of Cr(VI) concentration during four mobile measurement campaigns in Wilmington, DE.

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1. Introduction

In the atmosphere chromium is primarily found in the airborne particulate matter (PM) in two valence states: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) (Kotas and Stasicka, 2000). Trivalent chromium is relatively nontoxic,

while hexavalent chromium is extremely harmful (Cohen et al., 1993; Singh et al., 1999) and is classified by the US Environmental Protection Agency (EPA) as a group A inhalation carcinogen (EPA, 1984). Because of these differences in the effects of Cr(III) and Cr(VI), speciation of chromium in ambient PM is vital for correct evaluation of aerosol toxicity.

Most sources of Cr(VI) are localized, originating from such activities as metal plating, dye and pigment manufacturing, cleaning of various metal

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parts in automobile and aircraft industry (Carlton, 2003; Paustenbach et al., 1991; Wang et al., 1999). It is thus possible that there are regions of elevated concentrations (“hotspots”) caused by the proximity of such activities. Characterization of such “hotspots” is critical for assessing population exposure on a neighborhood scale (of the order of 100 m). Such areas cannot be located and characterized by means of stationary monitoring. However, they can be identified and characterized by means of mobile sampling during which on-line instruments are placed on a vehicle and measurements are performed while driving mapping the spatial distribution (Bukowiecki et al., 2002; Weijers et al., 2004; Westerdahl et al., 2005).

Mobile measurements place a number of constraints on the instrumentation. They require a high time resolution: a spatial resolution of 100 m at a driving speed of 30 km h⁻¹ requires a time resolution of 10 s. The instrument needs to be sensitive enough to distinguish elevated concentrations above the background, which for Cr(VI) is often below 1 ng m⁻³ (Nriagu et al., 1988). The instrument also needs to be stable at the conditions of the driving, i.e. have minimum interference from the vibrations and acceleration/deceleration induced by the moving vehicle.

The common method for Cr(VI) in ambient aerosol involves filter sampling with the consequent analysis of the filter extract (e.g. US EPA methods 7196A and 0218.6). Extensive reviews of available methods can be found elsewhere (e.g. Ashley et al., 2003; Kotas and Stasicka, 2000). Filter measurements require long sampling times (usually 24 h),

which precludes them from being used on a mobile platform. Samanta et al. (2001) have reported a system for automated measurements of Cr(VI) in ambient aerosols, which uses a set of automatically washed filters to collect and extract aerosol species. The extract is pre-concentrated using an ion-exchange column and Cr(VI) is determined by flow-injection analysis. The detection limit of the system is 5 ng m⁻³. However, the time resolution (15 min) is still too low to be applicable for mobile measurements.

We present here an instrument for measurements of Cr(VI) in ambient air that has been specifically designed to meet the requirements of mobile measurements. It should be noted, that the main value of mobile measurements is in locating areas with concentrations elevated relatively to the city average, i.e. detecting concentration differences within a city. Therefore, most attention is directed to characterization of the instrument’s ability to detect differences in ambient concentration on a small scale, and less to the absolute accuracy of the instrument.

2. Experimental

2.1. Aerosol sampling and collection

The schematic of Steam-Jet Aerosol Collector-long Pathlength Absorption Spectroscopy (SJAC-LPAS) system is shown in Fig. 1. Ambient aerosol is collected with the Steam-Jet Aerosol Collector (SJAC) (Khlystov et al., 1995). The air is sampled at a rate of 16.7 l min⁻¹ through a Teflon-coated

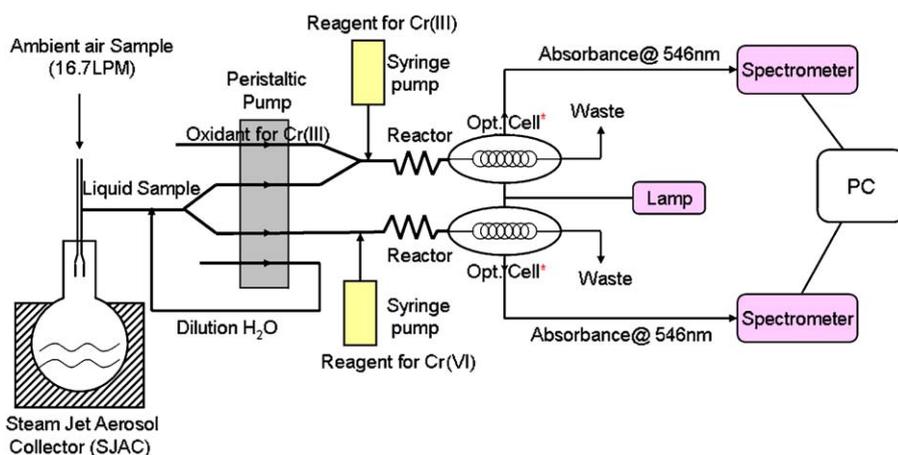


Fig. 1. General schematic of SJAC-LPAS system for measurements of hexavalent and trivalent chromium in ambient aerosol. The use of Cr(III) line is optional. The SJAC is described in detail in Khlystov et al. (1995).

PM_{2.5} cyclone (URG Inc., Chapel Hill, NC). The SJAC operates by injecting steam into the sampled air stream, which causes water vapor to condense on the sampled aerosol particles. Particles grow due to water condensation to a size of at least 1 μm in diameter and are collected by a cyclone. The SJAC quantitatively collects particles down to a few nanometers in diameter (collection efficiency 99%) (Khlystov et al., 1995). The collected liquid containing dissolved aerosol species is continuously pumped out with an eight channel Dynamax RP-1 (Rainin Instrument Co., Emeryville, CA) peristaltic pump and is directed to the LPAS-CFA, where the concentration of Cr(VI) is determined.

2.2. LPAS-CFA system

The LPAS-CFA system uses the well established diphenylcarbazide (DPC) colorimetric method (Allen, 1958). Liquid core waveguide (LCW) optical cells have been used to increase the sensitivity of colorimetric methods (Lei et al., 1983) and have been successfully applied to Cr(VI) determination with the DPC method (Li et al., 2003; Yao and Byrne, 1999). A LCW provides long optical pathlength by constraining light propagation within a liquid medium which has a higher refractive index (RI) than the surrounding solid tubing (Lei et al., 1983). Teflon AF-2400 (DuPont), has an RI of 1.29 and many of the desirable chemical properties of Teflon (Altkorn et al., 1997).

Before entering the LPAS-CFA system, the collected sample is diluted with a constant flow of double-deionized water to ensure sufficient flow for Cr(VI) and Cr(III) analysis. It should be noted that the Cr(III) line is optional and the detection limit for Cr(VI) can be improved by switching off the Cr(III) line, in which case no dilution is needed. The diluted sample then passes through a debubbler. The bubble formation in the system is further prevented by using an exit restriction to increase backpressure. The flow after the debubbler is divided equally for the Cr(VI) and Cr(III) analysis. A computer-controlled syringe pump (Versa 6, Kloehe Ltd., Las Vegas, NV) is used for reagent delivery. Super-serpentine mixer (1/16 "OD and 0.030" ID, 2 m long, GlobalFIA Inc., Fox Island, WA) is used for mixing and reacting the sample with the DPC reagent. The serpentine mixer has a minimal axial dispersion, which is an important factor for a fast instrument response.

The sample is then directed to the LCW optical cell. The design of the LCW cell follows that described elsewhere (Yao and Byrne, 1999). A 5 m long Teflon AF-2400 tubing (0.031 "OD and 0.008" ID, Random Technologies, San Francisco, CA) is used as the LCW. Two optical fibers (200 and 600 μm) are used to connect the cell to a LS-1 Tungsten Halogen Light Source and a USB2000 Miniature Fiber Optic spectrometer (all from Ocean Optics, Dunedin, FL). Absorbances at the detection wavelength of 546 nm and the non-absorbing wavelength of 700 nm are used to calculate chromium concentration, with the non-absorbing wavelength serving to compensate for any eventual drifts in the signal.

The setup for the Cr(III) analysis is similar to that for Cr(VI) analysis except that the liquid sample is oxidized by adding a solution of hydrogen peroxide (Andersen, 1998) and directing the flow through a 1 m long super-serpentine mixer before mixing it with the DPC reagent. Cr(III) concentration is then determined as the difference between the two lines.

2.3. Reagents and standards

All solutions were prepared with double deionized water and using analytical grade reagents. 1,5-diphenylcarbazide (Alfa Aesar, Ward Hill, MA), acetone, NaOH, K₂Cr₂O₇, CrK(SO₄)₂ (all from Fisher, Pittsburgh, PA), H₂O₂ (Acros Organics, Geel, Belgium), were obtained as indicated. Trace-metal grade sulfuric acid was obtained from EM Science (Darmstadt, Germany). The following reagent compositions were used. The DPC solution was prepared by dissolving 0.167 g of the reagent in 100 ml of acetone and then mixed with 1.67% H₂SO₄ solution in 1:1 volume ratio. 0.1% H₂O₂ solution was prepared by diluting 0.143 ml of H₂O₂ with 0.1 M NaOH solution to 100 ml.

3. Results and discussion

3.1. Calibration and limit of detection

The analytical part of the system was calibrated using Cr(VI) and Cr(III) standard solutions. The absorbance signals for both Cr(VI) and Cr(III) have linear relationship with chromium concentration (Fig. 2). The limit of detection (LOD) for the Cr(VI) and Cr(III) aerosol measurements, defined as three times the standard deviation of the blank (reagents + deionized water) measured in laboratory

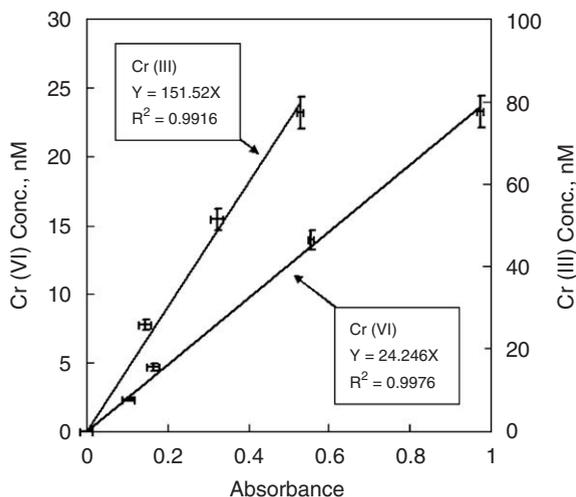


Fig. 2. Calibration curves of Cr(VI) and Cr(III) standard solutions.

conditions, is 0.19 ng m^{-3} for Cr(VI) and 1.9 ng m^{-3} for Cr(III). When the system is running on a moving vehicle, the vibrations and frequent acceleration/deceleration caused by the driving affect the system stability. Data obtained from a moving vehicle showed a larger standard deviation, and thus a higher LOD of 0.48 ng m^{-3} for Cr(VI). If the Cr(III) line is switched off, the LOD for Cr(VI) under driving conditions is lowered to 0.24 ng m^{-3} , because no dilution is required to provide a sufficient flow to the detector.

3.3. Response time

The time resolution of the instrument was tested by observing the signal change in response to a step change in chromium concentration. Due to the time needed to transfer the sample from the point of collection to the optical cell, there is a considerable delay before a change in signal is detected. The delay times (as defined by the time difference between the input concentration change and the 50% change of the signal) are 8 min 30 s for the Cr(VI) line and 9 min 57 s for the Cr(III) line, reproducible to within 3 s. During the mobile measurements this delay is accounted for by correcting the sampling times by the appropriate delay values. To assure accurate correction, the clocks of the on-board global positioning system (GPS) and the SJAC-LPAS data acquisition are synchronized to a second before each measurement.

Due to the mixing processes in the system, a step change in the input concentration appears as an S-shaped curve. The system response function, which is the system response to an infinitely sharp pulse input (δ -signal) can be found by differentiating the S-shaped response curve with respect to time. The time resolution of the instrument was assessed by convoluting the response function with a rectangular pulse function of different duration representing a plume. Our objective was to be able to observe plumes having a concentration at least two times higher than the background. System responses to plumes of different duration are shown in Fig. 3. Due to the mixing processes in the instrument the plume signals are smeared out. When the plume duration is 15 s or longer, the signal due to the plume can be distinguished from the noise of the background (the instrument noise is 10% of the measured concentration). Time resolution of 15 s corresponds to a spatial resolution of about 150 m, if measurements are made at a driving speed of 30 km h^{-1} .

3.4. Field deployment

The SJAC-LPAS system has been installed on the Duke University mobile laboratory equipped with a GPS along with a set of other instruments and successfully deployed within the enhanced Delaware air toxics assessment study (EDATAS) during four 1-week campaigns held near downtown Wilmington,

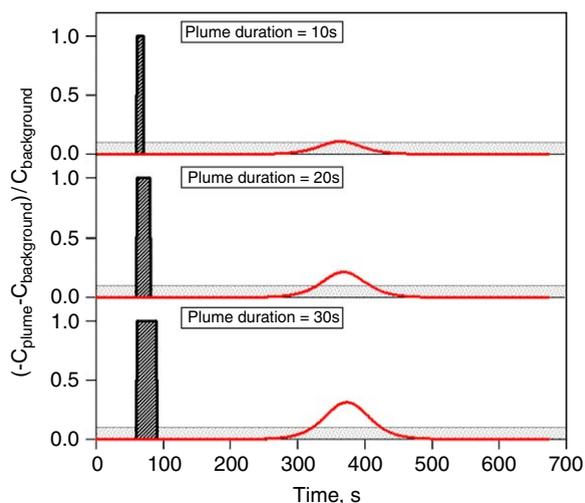


Fig. 3. Modeled system response to plumes of different duration. The Y-axis shows increase in concentration relatively to background concentration ($(C_{\text{plume}} - C_{\text{backgr}}) / C_{\text{backgr}}$). The grey area represents the noise level.

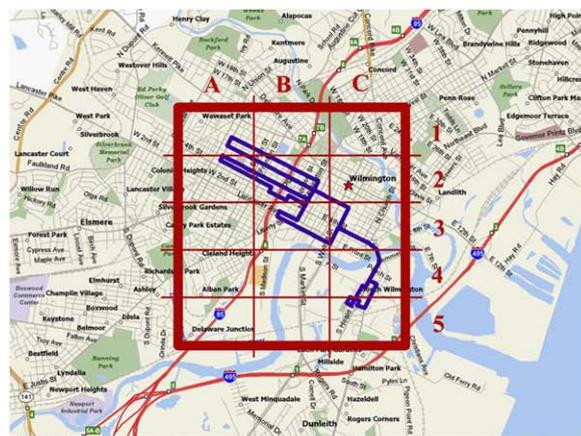
DE. Measurements were made while driving on a specifically designed route passing through several residential neighborhoods. The main objectives of the deployment were to evaluate the SJAC-LPAS system performance for measuring Cr(VI) in ambient aerosols, to characterize the temporal and spatial variability of the pollutants on a neighborhood scale, and to provide detailed fine-scale data for model evaluation with 1 km grid resolution.

The field measurements demonstrated that the SJAC-LPAS is suitable for mobile measurements of chromium species in the ambient aerosols. Although the ambient Cr(VI) concentration was within the measurable range, the concentration of water-soluble Cr(III) was usually below the LOD. Therefore, the instrument was mostly run measuring Cr(VI) only (the Cr(III) line was switched off) to decrease the detection limit for Cr(VI).

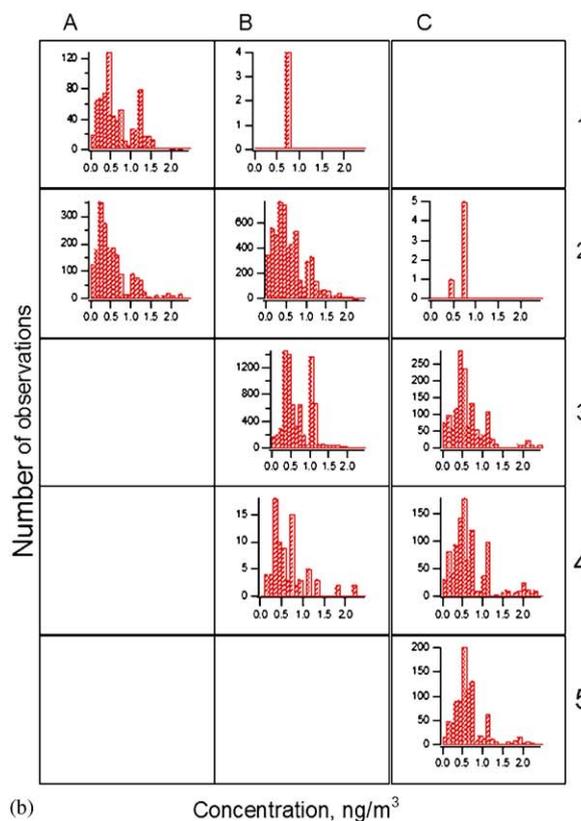
Fig. 4 shows the sub-grid variability distributions measured during the summer campaign of EDATAS. Each grid is 1 km \times 1 km. The plots for each grid represent histograms showing the number of observations as a function of the observed concentration in ng m^{-3} . This demonstrates the capability of the instrument to detect and quantify the variability between and within the grids, which can be used for verification of air quality models and for better assessment of the exposure of an urban population to hexavalent chromium compounds on a neighborhood scale. A detailed analysis of the data will be presented in a forthcoming paper.

4. Conclusions

The steam jet aerosol collector–long pathlength absorbance spectroscopy (SJAC-LPAS), an automated near real-time instrument for hexavalent chromium and water-soluble trivalent chromium in ambient aerosol has been developed for application on a mobile platform. The system collects particles into liquid water and analyzes the collected sample with diphenylcarbazide (DPC) colorimetric method using a Teflon AF liquid core waveguide. The LOD of the system is 0.2 ng m^{-3} for Cr(VI) and 1.9 ng m^{-3} for Cr(III). The system can capture the variability of chromium concentration on the time scale of 15 s. During four field campaigns the instrument has proven to be a useful tool for detecting and quantifying spatial variability within a city on a 100 m scale.



(a)



(b)

Fig. 4. (a) A map of Wilmington, DE showing the driving route and the grid used to calculate sub-grid variability distributions. Each grid is 1 km \times 1 km. (b) Sub-grid variability distributions of Cr(VI) concentration observed during the summer intensive campaign. The histograms show the number of observations as a function of Cr(VI) concentration in ng m^{-3} .

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