

ERG No.: 0143.04.003
EPA No.: 68-D-00-264

Hexavalent Chromium Method Development

Final Report
Work Assignment 5-03

Prepared for:

Mr. James Homolya
Emissions, Monitoring and Analysis Division (C339-02)
Office of Air Quality Planning and Standards
US Environmental Protection Agency
Research Triangle Park, NC 27711

Prepared by:

Eastern Research Group, Inc.
1600 Perimeter Park Drive
Morrisville, NC 27560

September 30, 2005

DISCLAIMER

The information in this document has been funded wholly by the United States Environmental Protection Agency under Contract Number 68-D-00-264 to Eastern Research Group. It has not been subject to the Agency's peer and administrative review, and has not been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table of Contents

	<u>Page No.</u>
Executive Summary.....	5
1.0 Background.....	6
2.0 Introduction	7
3.0 Experimental Design.....	9
4.0 Results.....	11
5.0 Data Interpretation and Conclusions.....	22
6.0 Recommendations.....	23
7.0 References.....	24
Appendix A Hexavalent Chromium Standard Operating Procedure.....	25

List of Tables

<u>Table No.</u>	<u>Page No.</u>
1. Cellulose Filter Freezer Study.....	13
2. Interferant Check Study.....	14
3. Teflon Filter Freezer Study.....	16
4. Ambient Monitoring Study - Cellulose Filters.....	18
5. Spiked Teflon Filter Study (with rough polypropylene support).....	19
6. Teflon Filters Rural and Suburban Site Study.....	20
7. Comparison of Cr ⁶⁺ Recovery on Cellulose and Teflon Filters.....	22

Executive Summary

Hexavalent Chromium (Cr^{6+}) is a priority pollutant for the National Air Toxics Trends Stations (NATTS). Previous sampling and analysis for Cr^{6+} at NATTS has been problematic. High filter background concentrations are observed due to the increased sensitivity. Lower detection limits exacerbate the background contamination issue. Cellulose filters, typically used for the collection of Cr^{6+} may contain binders that can cause loss of Cr^{6+} . In addition, Cr^{6+} stability is affected by the pH of the filter extraction solution. For these reasons the sampling and analysis procedures used to monitor Cr^{6+} were evaluated to identify modifications that improve method performance and reduce bias in monitoring results. This report summarizes hexavalent chromium sampling and analysis method evaluation performed to investigate and correct ambient air monitoring procedures.

Experiments to evaluate and improve the hexavalent chromium sampling and analysis procedure included temporal stability assessments including:

- stability prior to sampling to simulate filter handling and set up in the field for 3 to 4 days prior to sampling,
- tests to simulate post sampling filter stability during sub-ambient storage and
- field comparison studies of potential method modifications to confirm improvements.

Stability studies were performed under controlled laboratory conditions on various coated and uncoated sampling filter media. Using the standard bicarbonate coated cellulose filters, the Method Quality Objectives stayed within control for the first two days. Other filter media had longer retention, but the field comparison studies showed the bicarbonate coated filters retained Cr^{6+} longer.

Initial field sampling with filter media that showed improved stability in the laboratory was performed in an urban and a rural location. Samples collected through a serial blank and spiked filter using a collocated sampler allowed investigation of stability of Cr^{6+} collected on uncoated

Teflon and bicarbonate impregnated filters. Method's bias and precision was determined from these controlled studies. Sampling was also performed during dry and rainy conditions. These initial ambient air samples allowed bias of humidity to be evaluated.

Field comparison studies were performed at five existing NATTS sites. These sites were selected based on recent history of measurable Cr⁶⁺ in their samples. Each site was sent standard bicarbonate coated cellulose and uncoated Teflon filters used in collocated air sampling. Results of the paired sample runs were used to compare the performance of both filter media. A preferred coating and sampling collection/storage methodology using bicarbonate coated cellulose filters was identified through these tests.

1.0 BACKGROUND

There are currently 188 hazardous air pollutants (HAPs), or Air Toxics (AT), regulated under the Clean Air Act (CAA) that have been associated with a wide variety of adverse health effects, including cancer, neurological, reproductive and developmental effects, as well as ecosystem effects. These air toxics are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population exposure to these air toxics as they occur in the environment. While in some cases the public may be exposed to an individual HAP, more typically people experience exposures to multiple HAPs and from many sources. Exposures of concern result not only from the inhalation of these HAPs, but also, for some HAPs, from multi-pathway exposures to air emissions.

Current Government Performance Results Act (GPRA) commitments include a goal of reducing air toxics emissions by 75% from 1993 levels. This reduction in air toxics compounds in the ambient air should reduce significantly the risk to Americans of cancer and other serious adverse health effects caused by airborne toxics. Because of the limited tools to assess the impacts of these emissions on public health and the environment, reducing emissions is the focus used to meet GPRA goals. However, as new assessment tools are developed and begin to address the

risk associated with these emissions as required by the CAA, the GPRA goal may be modified to one that focuses on risk reductions associated with exposure to AT.

Hexavalent Chromium (Cr^{6+}) is a priority metal for the NATTS Program. To measure changes in ambient air Cr^{6+} concentration a method with lower detection limit and bias than existing methods is required.

2.0 INTRODUCTION

The method quality objectives (MQOs) that must be met for all data from EPA's National Ambient Air Toxic Trends Study (NATTS) are:

- Relative Percent Difference should not exceed ± 25 percent.
- Coefficient of Variation should not exceed ± 15 percent.

These quality objectives for the Cr^{6+} study are necessary to obtain the high degree of consistency and quality data required for the NATTS program. Previous sampling and analysis for Cr^{6+} at NATTS have identified a variety of issues that contribute imprecision and bias higher than the MQOs. Issues include filter contamination and storage stability, blank filter background, filter reactivity and extraction solution efficiency.

Direct application of the California Air Resources Board method for Cr^{6+} in ambient air did not meet the NATTS MQO requirements. ERG discussed these procedures with the California Air Resources Board (CARB) to determine if the modified method (modified CARB SOP 039)¹ being performed by ERG for the NATTS program is significantly different in comparison to the CARB program. Items discussed are listed below:

- CARB's development and history of the Cr^{6+} sampling:

- Started with Dionex in 87 or 88 to develop the Cr⁶⁺ analysis by Ion Chromatography (IC).
 - Worked with Research Triangle Institute (RTI) soon after to validate the method.
 - Used a PVC filter. RTI made an aerosol generator with LI as an internal standard and used the ratio to get the total Cr⁶⁺ collection efficiency.
 - Noticed that on PVC, HNO₃ acid in the atmosphere converts Cr⁶⁺ to Cr³⁺ (high HNO₃ in Los Angeles).
- The differences between CARB and ERG labs are:
 - ERG makes the sites collect the filters immediately after sampling (due to the loss of at least 20% after 1 day).
 - ERG uses a different analytical method, which allows us lower detection limits.
- Causes of bias identified by CARB and ERG:
 - There could be a possible HNO₃ (NO₂ to HNO₃) acid exposure (predominately on the west coast) and H₂SO₄ (SO₂ to H₂SO₄) acid exposure (predominately on the east) which could make the conversion on non-coated filters an issue.
 - If you let the filters sit too long, the air exposure to the bicarbonate on the filters could convert the Cr³⁺ to Cr⁶⁺.

High Cr⁶⁺ background concentrations are due to the filter manufacturing processes or contamination in storage. At low levels in ambient air, background contamination results in small differences in relatively equivalent values between measured and blank samples. Subsequent data interpretation is less confident.

Reactivity of cellulose filters toward Cr^{6+} is the result of binders that can cause a negative bias in these measurements. Negative bias was confirmed if the filter substrate is either too acidic (less than 9) or too basic (greater than 11). The filter extraction solution also affects the stability and recovery efficiency of the Cr^{6+} .

Since the MQOs were not being met through the direct application of the California Method for monitoring Cr^{6+} , a series of controlled experiments were performed to evaluate and improve the sampling and analysis procedure for Cr^{6+} in ambient air. Several of possible improvements to the Cr^{6+} sampling and analysis procedure were identified and described in the previous report entitled *MDL Study for the Low-Volume PM10 Method – NATTS Development*, for EPA Contract No. 68-D-00-264, delivered on January 26, 2005 including:

- Cellulose filters have the lowest levels of background chromium.
- The best extraction solution is deionized water.
- Washing the filters with acid, prior to impregnating them with sodium bicarbonate removes the background Cr^{6+} .
- There is not a difference in the recovery of Cr^{6+} from filters if they are frozen or held at ambient temperatures during the sampling period, as long as all samples are frozen before and re-frozen after sampling.

3.0 EXPERIMENTAL DESIGN

Key elements used to perform the Cr^{6+} evaluation included:

1. Performing a stability study on coated filters spiked from a sodium bicarbonate (i.e., basic) Cr^{6+} solution. Previous stability studies were performed with Cr^{6+} spiked from deionized water which did not represent how samples are stabilized during field collections. All standards were prepared in a basic (sodium bicarbonate) solution to

ensure the spiked Cr^{6+} in this study was maintained at alkaline pH as it is in the collected ambient air samples. All of the filters were spiked at a low level (0.25 ng/mL or 0.12 ng/m³) because this value is typical of the ambient level measured in the air. After spiking, the filters were stored at ambient temperatures in a chromium free environment. Four spiked filters and a blank were stored 2, 3, and 4 days after preparation to determine the Cr^{6+} recovery. This simulates the field storage time experienced for ambient air measurements.

2. Evaluating the stability of Cr^{6+} on coated filters spiked with potentially interfering metal salts. A study performed by OSHA using Method ID-235 showed that Cr^{3+} , Fe^{2+} , and Mg^{2+} were possible interferences. These metals were added as water soluble salts with the Cr^{6+} spiking on laboratory recovery samples to represent potential analytical interference in field samples.
3. Comparing the recovery of various alternative filter media with bicarbonate coated cellulose. A variety of Teflon media was evaluated to determine if the rapid loss of Cr^{6+} observed with bicarbonate coated cellulose during field storage could be mediated. Teflon membrane, Teflon mat with smooth backed and rough backed polypropylene filter media were evaluated to determine if other filter compositions could provide more stable, easier to handle media.
4. Performing field sampling under controlled conditions to evaluate coated cellulose filter performance under a variety of ambient conditions. Ambient field tests using coated cellulose filters were performed to evaluate storage and handling procedures that minimize Cr^{6+} loss. Collocated samples were collected during rainy and dry days to evaluate the effect of humidity on the collection and recovery of Cr^{6+} . Sampling was accomplished by simultaneously collecting ambient air through blank and spiked filters. Samples were collected during dry and rainy weather. This allows the method's

accuracy and bias to be determined from under extremes in ambient conditions. Four spiked and blank collocated samples were collected on both dry and rainy days for a total of eight (8) samples to determine the 95% confidence level, 25 % PRD, and 15% CV for extremes in ambient humidity.

5. Field evaluation of various filter media. Sampling was performed through filters spiked with known quantities of Cr⁶⁺ under various ambient conditions. Samples were collected using single blank and spiked filters. Samples were collected sequentially through clean, blank and spiked filters. Using prefilters allowed determination of the method's bias from ambient air without interference from particulate. Samples were collected simultaneous with bicarbonate coated cellulose samples using a collocated sampler to allow comparison to the bicarbonate impregnated filters. This evaluation was a repeat of the experimental design used to perform field evaluation of the coated cellulose filter media.
6. Field sampling comparison of Teflon and coated cellulose filter media. The final comparison for selection of the best Cr⁶⁺ sampling techniques involved sending the best performing Teflon filters and bicarbonate coated cellulose filters to field sites for collocated sampling. NATTS sites with a history of Cr⁶⁺ in ambient air samples were selected for the study.

4.0 RESULTS

Results summarized in this report included ERG laboratory studies and field stability comparison studies involving participation of selected state monitoring agencies. Tests included temporal stability assessments prior to sampling to simulate filters set up in the field for 3 to 4 days prior to sampling and subsequent tests to simulate filter stability during subambient storage. These experiments developed and finalized the Cr⁶⁺ sampling and analysis method.

1. Stability Study

A filter stability study was performed on the cellulose filters to determine how long Cr^{6+} is stable on the coated cellulose filters. Two different sets of 4 filters were prepared. The first set was prepared, left at ambient temperatures, and on the specified days (Day 2, 3 or 4), the filters were analyzed. The second set was prepared, left at ambient temperatures, and on the specified days, the filters were placed in the freezer for analysis performed on Day 4. This study was set in this particular fashion to determine if the Cr^{6+} results were affected by either leaving them at ambient temperatures after sampling and/or how long the filters were frozen before analyzing. Blanks were prepared and analyzed for each sampling set and did not detect Cr^{6+} . This study is presented in the Table 1 below.

Table 1. Cellulose Filter Freezer Study

Sample	Date Analyzed	Analyzed - not frozen (Set 1)		Date Analyzed	Frozen before analyzed (Set 2)	
		Relative Percent Difference (Bias)	Coefficient of Variation		Relative Percent Difference (Bias)	Coefficient of Variation
Freezer set 1	8-Mar	1.7		11-Mar	9.0	
Freezer set 2		7.4			0.08	
Freezer set 3		3.8			--	
Freezer set 4		4.0			--	
AVERAGE		4.2	2.5		4.5	6.2
Day 2 - 1	8-Mar	25		11-Mar	39	
Day 2 - 2		13			18	
Day 2 - 3		24			26	
Day 2 - 4		17			21	
AVERAGE		20	7.1		26	12
Day 3 - 1	9-Mar	30		11-Mar	42	
Day 3 - 2		35			44	
Day 3 - 3		33			39	
Day 3 - 4		17			48	
AVERAGE		29	11		43	6.5
Day 4 - 1	11-Mar	58		11-Mar	49	
Day 4 - 2		56			35	
Day 4 - 3		48			52	
Day 4 - 4		100			68	
AVERAGE		66	12		51	28

Note: All Filters were spiked with Cr⁶⁺ at 0.25 ng/mL on March 7, 2005

As shown, the Cr⁶⁺ begins to degrade after 24 hours at ambient temperatures. If the sample is analyzed immediately after sampling (Day 2), the RPD is lower (20%, Set 1) as opposed to freezing for 3 days before analysis (26%, Set 2). The loss of Cr⁶⁺ continues through the 4 days the study was conducted (Set 1), showing a 20% RPD on Day 2, analyzed the day after they were collected, to 66% on Day 4. For the filters that were immediately frozen on the specified days, the loss of Cr⁶⁺ reduced from 26% on Day 2 to 51% on Day 4. As represented by the CV for each day (with the exception of Day 4, Set 2), all results in each set is relatively close, showing

that the values that were obtained were consistent.

2. Interferant Check Study

An interferant check study was performed on the cellulose filters. Three filter sets (4 filters in each set) were spiked with 1 ng/mL of iron (Fe), trivalent chromium (Cr³⁺), and Magnesium (Mg). These filters were also spiked with 1 ng/mL of Cr⁶⁺. One set was left as a blank check and did not detect Cr⁶⁺ during the analyses. The results are presented in Table 2 below. As shown, none of these elements posed as interferences during the analysis of Cr⁶⁺ (based on the required relative percent difference (RPD) of 25% and the coefficient of variation (CV) of 15% criterion).

Table 2. Interferant Check Study

Filter Description	Date Analyzed	Results (ng/mL)	% Recovery	RPD (Bias)	CV
Trivalent Cr Spiked Filters					
Filter 1	9-Mar	1.0986	109.86	9.86	
Filter 2		1.0471	104.71	4.71	
Filter 3		1.0878	108.78	8.78	
Filter 4		1.0862	108.62	8.62	
AVERAGE		1.0799	107.99	7.99	2.09
Iron Spiked Filters					
Filter 1	9-Mar	1.0777	107.77	7.77	
Filter 2		0.9861	98.61	1.39	
Filter 3		0.9816	98.16	1.84	
Filter 4		0.7649	76.49	23.51	
AVERAGE		0.9526	95.26	8.63	13.93
Magnesium Spiked Filters					
Filter 1	9-Mar	1.0882	108.82	8.82	
Filter 2		0.9407	94.07	5.93	
Filter 3		1.0945	109.45	9.45	
Filter 4		1.0879	108.79	8.79	
AVERAGE		1.0528	105.28	8.25	7.11

Note: All Filters were spiked with Cr⁶⁺ at 0.25 ng/mL on March 9, 2005

3. Comparing the Recovery of Various alternative Filter Media

Because of the quick conversion of Cr^{6+} on cellulose filter paper, another stability study was conducted on Teflon filter paper. The Teflon filter paper had the lowest background during the first phase of this study (EPA Contract No. 68-D-00-264., WA 4-05), but because of its hydrophobic nature, this media did not appear to be ideally compatible. The Teflon filter paper used was a polypropylene rough-backed filter paper. Table 3 presents the stability study conducted on the Teflon media.

Table 3. Teflon Filter Freezer Study

Sample	Date Analyzed	Analyzed - not frozen (Set 1)		Date Analyzed	Frozen before analyzed (Set 2)	
		Relative Percent Difference (Bias)	Coefficient of Variation		Relative Percent Difference (Bias)	Coefficient of Variation
Freezer set 1	23-Mar	7.2				
Freezer set 2		16				
Freezer set 3		15				
Freezer set 4		6.2				
AVERAGE		11	5.7			
Day 2 - 1	24-Mar	5.3				
Day 2 - 2		7.2				
Day 2 - 3		7.0				
Day 2 - 4		0.22				
AVERAGE		4.9	6.2			
Day 3 - 1	25-Mar	24		25-Mar	8.4	
Day 3 - 2		10		2.6		
Day 3 - 3		18		18		
Day 3 - 4		52		4.9		
AVERAGE		26	36		8.4	7.8
Day 4 - 1	26-Mar	5.2				
Day 4 - 2		11				
Day 4 - 3		13				
Day 4 - 4		10				
Day 4 - 5		6.4				
AVERAGE		9.8	2.9			

NOTE: For Table 1 and 3, results listed in **bold** are outside the required relative percent difference (RPD) of 25% and the coefficient of variation (CV) of 15%.

As shown, Cr⁶⁺ spiked on Teflon filters is more stable than spikes on bicarbonate coated cellulose filters. The Cr⁶⁺ recoveries ranged from 88 to 109%, RPD from 4.9 to 26% and CV's from 2.9 to 36. A spiking error seems indicated in the Day 3 studies. Results of samples immediately analyzed compared to samples held for the requisite sampling time showed acceptable recoveries. It is difficult to add an aqueous spike to a Teflon filter than it is to add it to a cellulose filter. The spike has a tendency to roll off the filter before it is completely dried, which can explain the difference in recovery results for Day 3. Because of the limited number of filters available, only one set of filters were frozen before analyzed as presented on Day 3.

4. Ambient Field Tests with Coated Cellulose Filters

The sampling site for collocated spiked filters was determined and the collocated samples were collected. For the first study, all sample sets collected the following filters:

- One filter unspiked. (Sample)
- One filter spiked at 0.25 ng/mL. Total spiked amount in a 21.6 m³ sample (10 mL final preparation volume) is 0.12 ng/m³. This value is 10 times the current detection limit, but is assumed an approximate average of samples collected in the field. (Spike)
- One trip blank (stored in cooler during sampling period). (Trip Blank)
- One filter spiked at 0.25 ng/mL and left in the filter container. This filter was stored in the freezer while the samples were taken to the field. It was taken out of the freezer right before analysis. (Matrix Spike)

All samples were analyzed the day after collection. The results are presented in Table 4 below. All passive and trip blank samples did not detect any hexavalent chromium. It should be noted, however, that the recoveries are slightly better during cold, wet days.

Table 4. Ambient Monitoring Study – Cellulose Filters

Sample Set	Conditions				RPD	% Recovery
	Sample Volume (m ³)	Humidity	Temperature	Comments		
1	21.57	88% (58% - 96%)	48.8°F (44.1°F - 57.9°F)	Rain	28	72%
Matrix Spike - 1					3.2	103%
2	21.66	81% (38% - 100%)	41.3°F (37°F - 59°F)	Rain	6.4	94%
Matrix Spike - 2					4.0	96%
3	21.7	76% (37% - 100%)	37.8°F (34°F - 42.1°F)	Overcast to Clear	73	27%
Matrix Spike - 3					9.1	109%
4	21.7	42% (24% - 61%)	35.3°F (27°F - 45°F)	Mostly Cloudy to Clear	58	42%
Matrix Spike - 4					0	100%

NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25% and the coefficient of variation (CV) of 15%.

5. Field test of alternative filter media.

In order to compare cellulose to the Teflon filters, a study to reproduce the sampling performed on the cellulose filters was formulated. This study is presented in Table 5 and is described below:

- Teflon Set 1 through 3 followed same procedures as the cellulose study (spiked at 0.25 ng/mL),
- Teflon Set 4 through 7 collected using a slower flow at 8 L/min (spiked at 0.25 for 4 and 5, 0.5 ng/mL for 6 and 7),
- Teflon Set 8 and 9 collected at 15 L/min with a particulate filter before the spiked filter (spiked at 0.25 and 0.5 ng/mL respectively),
- Teflon Set 10 and 11 collected using an ozone scrubber cartridge (used for TO-11A sampling) that would take out ozone as well as particulate).

Table 5. Spiked Teflon Filter Study (with rough polypropylene support)

Sample Set	Setup	RPD	% Recovery
Teflon Set 1	Standard conditions at 15 L/min	24	76%
Teflon Set 2		64	36%
Teflon Set 3		4.0	96%
Teflon Set 4	Flow at 8 L/min	1.2	101%
Teflon Set 5		83	17%
Teflon Set 6		9.0	109%
Teflon Set 7		60	41%
Teflon Set 8	Collected a particulate filter before spiked filter	1.9	98%
Teflon Set 9		5.6	94%
Teflon Set 10	Collected using an ozone scrubber before spiked filter	13	113%
Teflon Set 11		6.3	94%

NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25% and the coefficient of variation (CV) of 15%.

Cr⁶⁺ was not detected in any of the passive samples. Sample volume for all samples was 21.6 m³ ± 2 m³. Sample conditions during these sample dates are listed below:

- Average humidity is 90%, with a low of 65% and a high of 100%;
- Average temperature is 60°F, with a low of 53.6°F and a high of 70°F;
- The weather conditions were from overcast to rainy, however mostly sunny and clear.

Because the Teflon recovery in the preliminary field tests looked promising, two sampling locations were selected, one rural and one suburban. The rural site was located in the country near the woods 8 miles from Chapel Hill, NC and 8 miles from Pittsboro, NC. The suburban site chosen was located within one block from a Middle School and two blocks from Highway 55. The results of the study performed on these new Teflon rough polypropylene coated filters are presented in Table 6 for the rural and suburban sites.

Table 6. Teflon Filters Rural and Suburban Site Study

Sample Set	Measurable Precipitation	RPD	CV
RURAL LOCATION			
Rural Dry 1	No	7.2	13
Rural Dry 2		15	
Rural Dry 3		2.8	
Rural Dry 4		20	
Average		11	
Rural Wet 1	Yes	21	13
Rural Wet 2		1.9	
Rural Wet 3		11	
Rural Wet 4		5.7	
Average		10	
SUBURBAN LOCATION			
Suburban Dry 1	No	7.8	14
Suburban Dry 2		26	
Suburban Dry 3		6.7	
Suburban Dry 4		32	
Suburban Dry 5		24	
Average		13	
Suburban Wet 1	Yes	5.1	7.0
Suburban Wet 2		3.7	
Suburban Wet 3		9.0	
Suburban Wet 4		6.1	
Average		6.0	

All Method Blanks and Extraction Blanks were non-detects.

All Method Spikes and Laboratory Control Spikes were in control limits (80 – 120% recovery).

All sample volumes were 21.6 m³ (±10%).

These rural and suburban results show good recovery of collecting Cr⁶⁺ in rural or urban areas. These collections, however, were done on filters that were spiked with a liquid, which formed a salt on the filter. Spike reproducibility was consistent with the other media tested under laboratory conditions. The method spikes prepared and held for analysis show a wide range of

recoveries from 76 to 107% recovery, 5 to 24 RPD. The recovery results for the method spikes are consistent with the uncertain ability to spike the filters with consistent amounts of Cr⁶⁺. As shown in Figure 1, the sample spikes (spiked filters that had ambient air pass through) are statistically within range of the average method spike, method spike duplicates.

6. Field sampling comparison of Teflon and coated cellulose filter media

The optimal way to confirm the performance using the Teflon filters is collecting collocated sets of cellulose and Teflon filters. ERG has sent five different NATTS sites the standard cellulose and Teflon filters as a means to evaluate the performance of the Teflon filters. These sites were selected based on recent history of Cr⁶⁺ in their samples. The results are presented in Table 7.

Table 7. Comparison of Cr⁶⁺ Recovery on Cellulose and Teflon Filters

Site	% RPD Range	Cellulose Higher
Seattle, WA	-28.7 to -4.3%	One filter set had a detect on a cellulose filter, but nothing was detected on the Teflon filter. The 3 other sampling sets had similar results on both Cellulose and Teflon. Teflon was always slightly higher.
Washington, DC	Not Applicable	One filter set had a detect on Teflon, but nothing was detected on the Cellulose filter. The 3 other sampling sets had detects on the Cellulose but nothing was detected on the Teflon filters.
Tampa, FL	-55.31%	One filter set had a higher result on the Teflon filter. The other 4 sampling sets had detects on Cellulose but nothing was detected on the Teflon filters.
Detroit, MI	-0.65 to 114%	One filter set had similar results on the cellulose and Teflon filters. One set had ~50% higher and another had ~114% higher on the cellulose filter. Two other sets had detects on the cellulose but nothing was detected on the Teflon filters.
Boston, MA	Not Applicable	Three out of 3 filter sets had detects on the cellulose but nothing on the Teflon filters.

Note: Sampling was conducted from June to August 2005.

5.0 DATA INTERPRETATION AND CONCLUSIONS

Analysis of sodium bicarbonate coated cellulose filters spiked with known concentrations of Cr⁶⁺ demonstrated acceptable recoveries if the samples are recovered as soon as possible after sampling ends. Results of collocated Teflon and bicarbonate coated cellulose filters showed cellulose superior to Teflon for Cr⁺⁶ retention and recovery.

Hexavalent chromium is a strong oxidizer that reacts with certain filter media and with components in the ambient air like nitrous oxide and sulfur dioxide that can be easily oxidized. Hexavalent chromium is stabilized with alkaline bicarbonate coated on collection media. While at

least one type of Teflon filter backed with polypropylene demonstrated acceptable recovery of Cr^{6+} under controlled laboratory conditions, the same filter did not perform as well as bicarbonate coated cellulose in actual ambient collocated conditions.

Bicarbonate coated cellulose present several handling issues including a requirement to acid wash filters to reduce interference and a requirement to freeze samples immediately after sampling to reduce Cr^{6+} loss. The results of this study continue to support use of cellulose filters for NATTS Cr^{6+} sampling. Teflon filters do not collect and retain the Cr^{6+} as efficiently as cellulose possible due to the stabilizing effect of the bicarbonate coating on the cellulose. Reducing agents in the ambient air seem to be converting the Cr^{6+} to Cr^{3+} . Attempts to coat Teflon filter media with aqueous bicarbonate have not been unsuccessful. Since Teflon filters can not currently be coated, they do not have the buffer coating (sodium bicarbonate) to stabilize the Cr^{6+} on the filter when reducing agents, such as acid gases, also are in the ambient air.

6.0 RECOMENDATIONS

Based on the results of this study, ERG recommends continuing the sample collection using the sodium bicarbonate coated cellulose filters. However there are certain preservation procedures that must be followed before acceptable sample results can be obtained. These procedures are presented below:

- The filters must be acid washed before coating them with the sodium bicarbonate, or the Cr^{6+} background inherent in the filter production may interfere with the analysis results. Acid washed filters do not affect the length of sample collection.
- Samples must be retrieved from the field within one day after the sample has been collected or a Cr^{6+} negative bias (loss) will occur (up to 20% on the first day).
- All samples must be frozen immediately after collection to reduce the risk of Cr^{6+} loss.

The sampling and analytical methodology modifications that improve Cr^{6+} monitoring

procedures are described in a National Laboratory Accreditation Counsel (NELAC) format SOP. A copy of the Standard Operating Procedure for the Determination of Hexavalent Chromium in Ambient Air Analyzed by Ion Chromatography (IC) is presented in Appendix A.

7.0 REFERENCES

1. California Air Resources Board, Standard Operating Procedure MLD-039, "Extraction and Analysis of Hexavalent Chromium by Ion Chromatography", Monitoring and Laboratory Division, March, 2002, Revision Number 3,
<http://www.arb.ca.gov/aaqm/sop/summary/summary.htm>

Appendix A

Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air Analyzed By Ion Chromatography (IC)