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Mr. Michael Jones  
Emissions, Monitoring and Analysis Division (C339-02)  
Office of Air Quality Planning and Standards  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

Dear Mr. Jones:

I have enclosed a copy of the paper we recently presented for "Collection and Analysis of Hexavalent Chromium in Ambient Air". We presented this paper at the NEMC in Washington, DC (August, 2006), and the QA Region 6 Conference, in Dallas, TX (October, 2006).

If you have any questions or comments, please call me at (919) 468-7924.

Sincerely,

*Julie L. Swift*

Julie L. Swift  
Senior Program Manager

cc: Dennis Mikel, EPA

# Collection and Analysis of Hexavalent Chromium in Ambient Air

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## ABSTRACT

Hexavalent chromium ( $\text{Cr}^{6+}$ ) is one of the top four pollutants of concern in the EPA National Air Toxics Trends Stations (NATTS) Program. The Environmental Protection Agency (EPA) worked in conjunction with Eastern Research Group (ERG) to improve the California Air Resource Board (CARB) Method 039 for  $\text{Cr}^{6+}$  monitoring. Attempts to sample and analyze  $\text{Cr}^{6+}$  at NATTS with improved sensitivity uncovered challenges in the sampling procedures. Issues with background contamination on filters and stability of field samples were the most important contributors to bias and imprecision. Different filters and filter preparations were studied to minimize background  $\text{Cr}^{6+}$  on filters. A standardized method for media preparation and storage will be discussed. A stability study was performed to determine the best storage conditions to maintain  $\text{Cr}^{6+}$  stability with less than 30 Relative Percent Difference (RPD). The stability of  $\text{Cr}^{6+}$  was also evaluated using collocated samplers with spiked and blank filters. Data, using improvements to the  $\text{Cr}^{6+}$  sampling and analysis procedure for the NATTS, will be presented to show the recent history of  $\text{Cr}^{6+}$  recovery from field samples.

## INTRODUCTION

Chromium is a natural constituent of the earth's crust and is present in several oxidation states. Trivalent chromium ( $\text{Cr}^{3+}$ ) is naturally occurring, environmentally pervasive and a trace element in man and animals. Hexavalent chromium is anthropogenic from a number of commercial and industrial sources. It readily penetrates biological membranes and has been identified as an industrial toxic and cancer substance. Hexavalent chromium is a known inhalation irritant and associated with respiratory cancer. Exposure occurs primarily in the chrome plating and anodizing process, and emissions from chromate treated cooling towers.

## METHOD DEVELOPMENT

Previous sampling and analysis studies for  $\text{Cr}^{6+}$  at NATTS have shown a variety of issues including filter contamination and storage stability issues. High filter background concentrations are due to manufacturing processes or contamination in storage. Background contamination results in small differences between measured and blank values, which make data interpretation at low concentrations less confident.

### Determining the Sampling Media

Four types of filter media were examined to determine which performed best in terms of background contamination and stability. These filters were prepared using the CARB Standard

Operating Procedure (SOP) 039 to determine if the chromium leaching off the filters at ambient temperatures would cause contamination. The filters used in this study were:

- Cellulose;
- Binderless Quartz;
- Teflon<sup>®</sup>; and
- Polyvinyl Chloride (PVC).

The results of this study show that the best media is the cellulose filters. The Teflon<sup>®</sup> filter results are questionable because the coating solution does not adhere to these filters. The results for all of the filters are presented in Table 1 below.

Table 1: Chromium Filter Background Contamination – Assessing the Filter Media

Sample Name	Filter Media Concentrations (total ng)			
	Cellulose	Binderless Quartz	PVC	Teflon <sup>®</sup>
Day 0 – 1	Not Detected	8.42	2.43	0.320
Day 0 – 2	Not Detected	6.95	2.03	0.370
Day 0 – 3	Not Detected	8.22	3.00	0.400
Day 6 – 1	Not Available	21.9	Not Available	Not Available
Day 6 – 2	Not Available	47.7	Not Available	Not Available
Day 6 – 3	Not Available	28.3	Not Available	Not Available
Day 12 – 1	1.44	Not needed	15.9	0.430
Day 12 – 2	1.12	Not needed	14.6	ND
Day 12 – 3	0.760	Not needed	14.4	ND

ERG treated the cellulose filters selected from initial evaluation of filter media in an attempt to reduce the background below the detection limit of the analysis method. Filters were cleaned with nitric acid to remove hexavalent chromium prior to filter preparation before sampling. Once cleaned, hexavalent chromium was not detected on any unspiked filters. Recovery on spiked filters was from 92 to 100 percent. Based on these results, the acid washed filters are determined to have no associated chromium contamination.

### ***Temporal Stability Study***

A temporal study was performed on cellulose and Teflon filters because of the low recovery of background Cr<sup>6+</sup> in the background contamination study. To determine if the preferred filter preparation method would interfere with recovery of Cr<sup>6+</sup> samples, 32 bicarbonate coated cellulose and 32 Teflon filters were prepared and spiked. All filters were spiked with 2.5 total ng Cr<sup>6+</sup> and placed on the laboratory countertop. The experimental design for each filter media included:

- Four spiked filters were analyzed the day they were spiked and four were placed in the freezer.
- Four spiked filters were analyzed the day after spiking (Day 2) and four were placed in the freezer.
- Four spiked filters were analyzed two days after spiking (Day 3) and four were placed in the freezer.
- Four spiked filters were analyzed three days after spiking (Day 4) and four were placed in the freezer.

Table 2 shows the spiked filter results.

Table 2: Cr<sup>6+</sup> Filter Stability Study

Spiked Samples	Cellulose Filters		Teflon Filters	
	Average Concentration (total ng)	Percent Recovery	Average Concentration (total ng)	Percent Recovery
<b>Stored at Room Temperature</b>				
Day 1	2.17	87 ± 3%	2.05	89 ± 5%
Day 2	2.20	88 ± 4%	2.25	98 ± 6%
Day 3	2.28	91 ± 3%	2.27	99 ± 35%
Day 4	1.93	<b>77 ± 10%</b>	2.53	110 ± 3%
<b>Stored at -18°C</b>				
Day 1	2.62	105 ± 3%	NA	NA
Day 2	2.66	107 ± 3%	NA	NA
Day 3	2.74	109 ± 7%	2.46	108 ± 8%
Day 4	2.58	103 ± 7%	NA	NA
Day 7	2.75	110 ± 8%	NA	NA
Day 8	2.54	102 ± 4%	NA	NA
Day 9	2.57	103 ± 1%	NA	NA
Day 10	2.60	104 ± 4%	NA	NA
Day 11	2.71	108 ± 2%	NA	NA
Blanks	ND	NA	ND	NA

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

One of the purposes of this study is to determine whether it is feasible to have the filters stored in the field for more than one day after sampling. The cellulose filters stored at room temperature had a reduced recovery from 87 percent on Day 1 to 77 percent on Day 4. The recoveries for the Teflon filters stored at room temperature varied from Day 1 to Day 4 by approximately 15 percent. Once the cellulose filters were stored at -18°C before analysis, however, the percent recovery varied 102 to 110 percent. Because only one set of Teflon filters was frozen for the stability study, limited data is available for conclusions; however, the recovery for Day 3 is 108 percent. This study shows that the cellulose filters would need to be recovered within 1 day to determine the best recovery, whereas the Teflon filter could be recovered up to 4 days without

any significant loss. Also, once frozen, the  $\text{Cr}^{6+}$  can be considered stable and can be left on the cellulose filters for up to 11 days.

### ***Interfering Element Check***

Possible interfering compounds were added to the filters and to determine if there were any positive or negative interference when analyzing for  $\text{Cr}^{6+}$ . All filters were spiked with 10 total ng of  $\text{Cr}^{6+}$ . Four separate sets of filters were spiked with 10 total ng of  $\text{Cr}^{3+}$ , Fe, and Mg. All recoveries were within  $95\% \pm 13\%$ , indicating that these elements do not pose any interference for the analysis of  $\text{Cr}^{6+}$ .

### **Method Validation**

Field studies were performed to validate the filter preparation and storage study determined acceptable under laboratory conditions.

### ***Cr<sup>6+</sup> Sample Stability Study***

In order to determine the stability of a sample in field before retrieval, filters were spiked and left in the field for up to 4 days. All filters were spiked with 2.5 total ng  $\text{Cr}^{6+}$ . Filters were installed on a line in the field. Four filters were prepared for each batch of samples and are shown in Figure 1.

Figure 1. Field Cr<sup>6+</sup> Sample Stability Study



The filters were left for 33 hours – 24 hours (based on 1 day) plus 9 hours (needed for sample retrieval). All samples were analyzed on the day the samples were recovered, as presented in Table 3.

Table 3: Cr<sup>6+</sup> Filter Stability Study – Sample Stability (Cellulose Filters)

Spiked Samples in Field	Average Concentration (total ng)	Percent Recovery	Average Relative Percent Difference (RPD)	Coefficient of Variation (CV)
<b>Spiked and placed in Freezer after Days presented and analyzed after sample pickup.</b>				
33 Hours	1.76	<b>70%</b>	30% ± 6%	8%
57 Hours	1.27	<b>51%</b>	49% ± 6%	13%
81 Hours	1.19	<b>48%</b>	53% ± 4%	9%
105 Hours	1.05	<b>42%</b>	58% ± 5%	11%

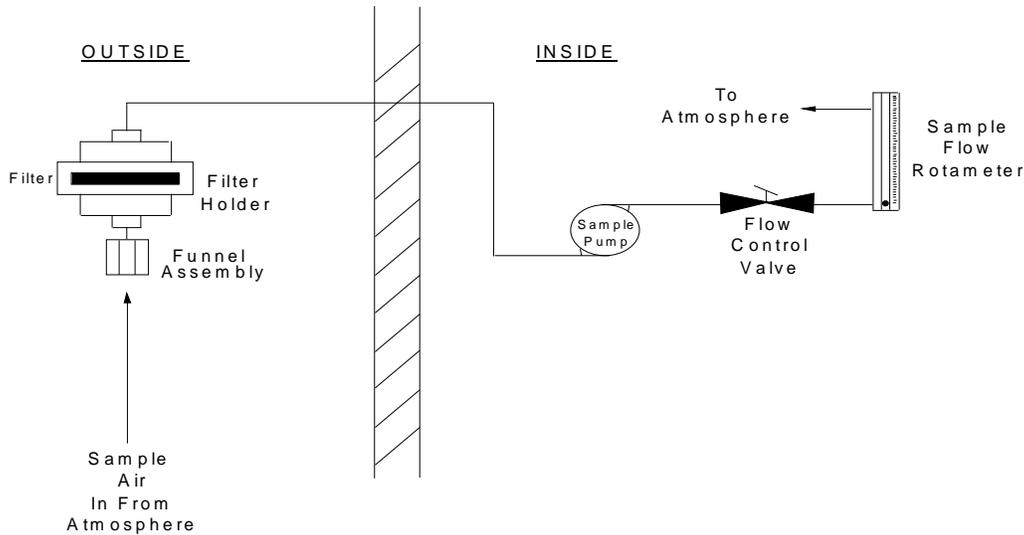
NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%.

The purpose of this study was to determine whether it is practical to leave the cellulose filters in the field for more than one day after sampling. The cellulose filters stored in the field had reduced recoveries from 70 percent for 33 hours (24 hours + 9 hours for recovery) to 42 percent for 105 hours (24 hours times 4 days + 9 hours for recovery). This study shows that the cellulose filters would need to be recovered within 1 day in order to allow the best recovery possible. Once frozen, however, the Cr<sup>6+</sup> can be considered stable and can be left on the cellulose filters for up to 11 days (as presented in Table 2).

### *Cr<sup>6+</sup> Sampling Study*

To continue evaluating the preparation and stability of these filters, a field sampling study was performed. A hexavalent chromium sample is collected by pulling ambient air through the prepared filter at a known flow rate for a period of 24 hours. The hexavalent chromium sampling system is designed to automatically perform a 24-hour filter collection and is automated using a digital timer to initiate sample collection at a flow rate of 15 Lpm. The prepared filter assembly is attached to the inlet of the probe, and the funnel is attached to the inlet of the filter assembly. At the end of the 24-hour collection period, the filter assembly containing the exposed filter is removed from the sampler. The Teflon rod stock plugs are reinserted into the inlet and outlet. Figure 1 presents a standard Cr<sup>6+</sup> sampling layout.

Figure 1. Cr<sup>6+</sup> Sampler Layout



### ***Cr<sup>6+</sup> Sampling Study – Cellulose Filters***

A sampling site was chosen for the initial study which included a collocated sampler loaded with either spiked or unspiked filters. For the initial study, each sample sets collected the following cellulose filters:

- One filter unspiked. (Background Sample)
- One filter spiked at 2.5 total ng. Total spiked amount in a 21.6 m<sup>3</sup> sample is 0.12 ng/m<sup>3</sup>. This value is 10 times the current detection limit, but is assumed an appropriate average result from samples collected in the field. (Spike)
- One trip blank (stored in cooler during sampling period). (Trip Blank)
- One filter spiked at 2.5 total ng 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 immediately 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 had no detectable hexavalent chromium. The recoveries of spiked samples are slightly better during cold, wet days.

Table 4: Ambient Monitoring Study – Cellulose Filters

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

NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%. MS = Matrix Spike

The cellulose filters showed varying recoveries on the samples taken. Two of the 8 spiked filters recovered under 70%, with a total average recovery at 80%.

#### *Cr<sup>6+</sup> Sampling Study – Teflon<sup>®</sup> Filters*

A comparison study was performed to reproduce the sampling completed on the cellulose filters. 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 2.5 total ng),
- Teflon Set 4 through 7 collected using a lower flow rate at 8 L/min (spiked at 2.5 total ng for 4 and 5, 5.0 total ng for 6 and 7),
- Teflon Set 8 and 9 collected at 15 L/min with a particulate filter before the spiked filter (spiked at 2.5 and 5.0 total ng, 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 (spiked at 2.5 total ng).

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

Sample Set	Setup	RPD	% Recovery
Teflon Set 1	Standard conditions at 15 L/min	<b>24</b>	76%
Teflon Set 2		<b>64</b>	<b>36%</b>
Teflon Set 3		4.0	96%

Sample Set	Setup	RPD	% Recovery
Teflon Set 4	Flow at 8 L/min	1.2	101%
Teflon Set 5		<b>83</b>	<b>17%</b>
Teflon Set 6		9.0	109%
Teflon Set 7		<b>60</b>	<b>41%</b>
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%.

The Teflon also showed varying recoveries. Three of the 11 spiked filters recovered under 70%, with a total averaged recovery at 80%. This indicated a close comparison of the Teflon to the cellulose filter  $\text{Cr}^{6+}$  collection.

### *Cr<sup>6+</sup> Sampling Study – Interferants*

In order to distinguish other possible interferants, another set of experiments were performed:

- Volume Check - the rate of collection was too high by reducing the overall sample volume to 11.5 m<sup>3</sup>,
- Particulate Check - the particulate reacted with the  $\text{Cr}^{6+}$  to reduce it to  $\text{Cr}^{3+}$  by having a Teflon filter inline before the spiked filter, and
- Ozone Check – ozone reacts to oxidize other agents that could reduce the  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ .

As presented in Table 6, the  $\text{Cr}^{6+}$  recovery was not affected by changing any of these parameters (volume, particulate and ozone).

Table 6: Physical interferants check for  $\text{Cr}^{6+}$  sampling.

Sample	Spiked in total ng	Results in total ng	Percent Recovery
Volume Check – collected at 11.5 m <sup>3</sup> (instead of standard 21.6 m <sup>3</sup> )			
Run 1	2.5	2.53	101%
Run 2	5.0	5.45	109%
Particulate Check – collected particulate before ambient air crossed spiked filter			
Run 1	2.5	2.45	98%
Run 2	5.0	4.72	94%
Ozone Check – scrubbed ozone and particulate before ambient air crossed spiked filter			
Run 1	2.5	2.82	113%
Run 2	5.0	4.68	94%

### ***Comparison Sampling using Cellulose and Teflon Filters***

The optimal way to confirm the performance using either filter is to collect collocated sets of cellulose and Teflon filters. ERG 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 Cr<sup>6+</sup> in their samples. The results are presented in Table 7 below.

Table 7: Comparison of Cr<sup>6+</sup> Recovery on Cellulose and Teflon Filters

<b>Site</b>	<b>Total # of Samples</b>	<b>Cellulose Concentration Higher (&gt;30% RPD)</b>	<b>Similar Results on Cellulose and Teflon (±30% RPD)</b>	<b>Teflon Concentration Higher (&gt;30% RPD)</b>
Boston, MA	3	100%	0%	0%
Detroit, MI	5	80%	20%	0%
Seattle, WA	4	25%	75%	0%
Tampa, FL	5	80%	0%	20%
Washington, DC	4	75%	0%	25%
Average	4	72%	19%	9%

Note: Sampling was conducted from June to August 2005.

This table shows the total number of samples collected at each site and compares the Cr<sup>6+</sup> recoveries of the cellulose to the Teflon filters. For example, the site in Detroit sampled 5 sets of collocated filters (one cellulose and one Teflon filter) during the same sampling period. One of these filter sets had similar recoveries on the cellulose and Teflon filters, and the other 4 filter sets had higher Cr<sup>6+</sup> recoveries on the cellulose filters. The lower recovery on the Teflon filters could be due to other reducing agents in the ambient air that would convert the Cr<sup>6+</sup> to Cr<sup>3+</sup>. This is prevented on the cellulose filters because of the sodium bicarbonate coating. In Seattle, WA, the air stream is blown from the west, off the Pacific Ocean. Because of the lower interference from mobile and emission sources, the difference between the cellulose and Teflon filters is minimal. The other 4 sites (Boston, Detroit, Tampa, and Washington, DC) are in highly populated areas where these emissions could reduce the Cr<sup>6+</sup> significantly. Based on the results of this sampling study, ERG determined that collection on the acid washed, sodium bicarbonate coated cellulose filters would recover the Cr<sup>6+</sup> more efficiently for real-world ambient samples.

### **FIELD SAMPLE RESULTS FOR HEXAVALENT CHROMIUM**

Twenty-two National Monitoring Program (NMP) sites collected Cr<sup>6+</sup> samples from January 2005 to December 2005. Some monitors were placed near the centers of heavily populated cities (e.g., Chicago, IL and Detroit, MI), while others were placed in moderately populated areas (e.g., Madison, WI and Hazard, KY). Hexavalent Chromium concentrations measured during this time varied significantly from monitoring location to monitoring location. The proximity of the monitoring locations to different emissions sources, especially industrial facilities and heavily traveled roadways, often explains the observed spatial variations in ambient air quality.

Table 8 presents the frequency of detects, maximum value, minimum detected value, median, and average.

Table 8: Analytical Results for samples collected between January 2005 and December 2005.

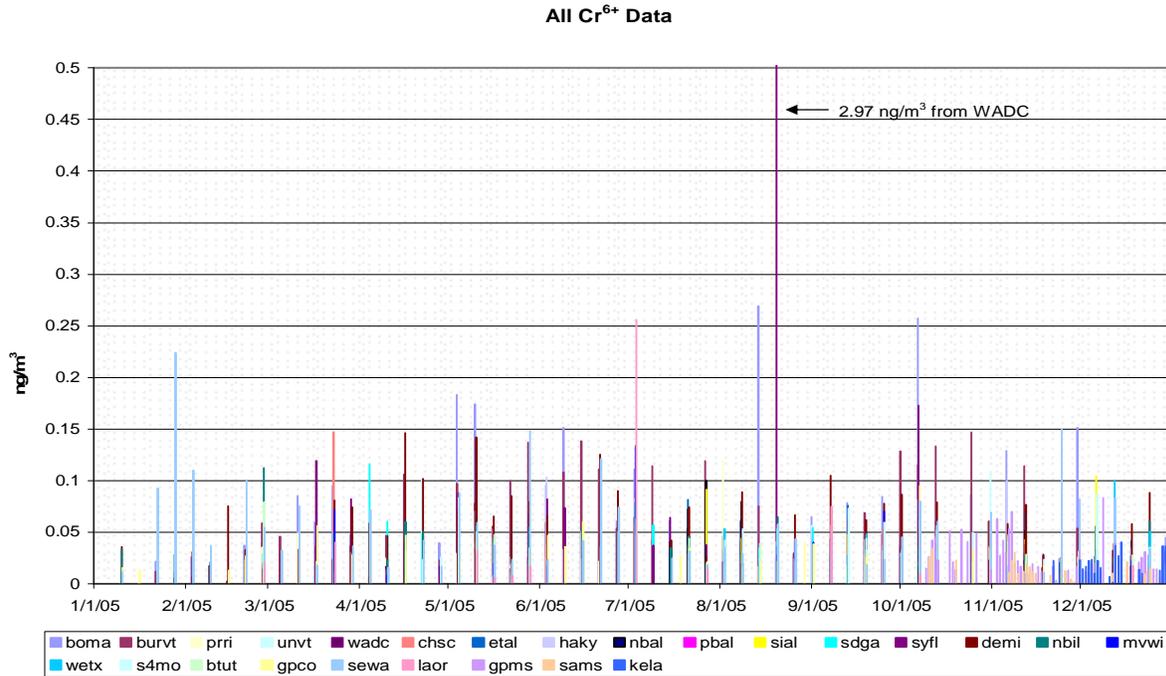
Sites	% Frequency	Maximum Value (ng/m <sup>3</sup> )	Minimum Value (ng/m <sup>3</sup> )	Median (ng/m <sup>3</sup> )	Average (ng/m <sup>3</sup> )
Roxbury, MA	78%	0.269	0.017	0.048	0.071
Burlington, VA	80%	0.147	0.003	0.054	0.065
Providence, RI	100%	0.119	0.006	0.023	0.028
Underhill, VT	32%	0.101	0.005	0.027	0.034
Washington, DC	54%	2.970	0.010	0.026	0.156
Chesterfield, SC	40%	0.147	0.006	0.024	0.034
Birmingham, AL (site 1)	73%	0.081	0.020	0.041	0.049
Hazard, KY	43%	0.103	0.011	0.029	0.036
North Birmingham, AL	67%	0.100	0.016	0.046	0.050
Providence, AL	50%	0.026	0.004	0.019	0.016
Birmingham, AL (site 2)	56%	0.104	0.029	0.044	0.052
S. Dekalb Co., GA	100%	0.116	0.010	0.039	0.039
Tampa, FL	56%	0.134	0.007	0.032	0.042
Detroit, MI	85%	0.146	0.006	0.066	0.066
Chicago, IL	67%	0.112	0.006	0.031	0.036
Madison, WI	48%	0.132	0.008	0.022	0.032
Austin, TX	85%	0.100	0.016	0.035	0.040
St. Louis, MO	71%	0.109	0.015	0.036	0.041
Bountiful, UT	100%	0.079	0.004	0.027	0.030
Grand Junction, CO	68%	0.095	0.002	0.027	0.030
Seattle, WA	86%	0.224	0.010	0.042	0.053
La Grande, OR	100%	0.256	0.005	0.017	0.034
Kenner, LA	55%	0.040	0.001	0.022	0.021
Gulf Port, MS	65%	0.083	0.003	0.020	0.025
Stennis Airport, MS	33%	0.034	0.002	0.014	0.015
Average	67%	2.970	0.001	0.032	0.044

A total of 1,466 Cr<sup>6+</sup> measurements were detected at the 22 NMP sites from January 2005 to December 2005. Two hundred and thirty of these were taken at three sites during the clean up after Hurricane Katrina. Of the 1,466 Cr<sup>6+</sup> measurements, 67% of these results were detects and 9% of these concentrations were below the MDL. The average Cr<sup>6+</sup> concentration was 0.044 ng/m<sup>3</sup>.

Data from the NMP sites is presented in Figure 2. The highest concentration was taken at

Washington, DC, at 2.97 ng/m<sup>3</sup>. The samples taken for Katrina were collected on a 1-in-1 schedule starting October 10, 2005. Hexavalent chromium results at Katrina monitoring sites were similar or slightly lower than other sites in the program.

Figure 2: Analytical Cr<sup>6+</sup> Results for samples collected between January 2005 and December 2005.



## DATA QUALITY CONTROL AND ASSURANCE

Precision of the analytical and sampling technique was determined using the analysis of collocated sampling episodes. A collocated sample (i.e., a sample collected simultaneously with the primary and collocated sample using separate sampling systems) provides information on the potential for sampling variability. ERG was not able to perform replicate analyses because the final sample instrument injection volume did not allow the replicate analyses. Method spikes were analyzed, however, and give an acceptable range of 80-120% recovery. The collocated results were compiled from sites sampling in the NMP from January 2005 through December 2005.

The collocated data is presented in Relative Percent Difference (RPD). The RPD expresses average concentration differences relative to the average concentrations detected during collocated analyses. The RPD is calculated as follows:

$$RPD = \frac{|X_1 - X_2|}{\bar{X}} \times 100$$

Where:

$X_1$  is the ambient air concentration of a given compound measured in one sample;

$X_2$  is the concentration of the same compound measured during collocated analysis; and

$\bar{X}$  is the arithmetic mean of  $X_1$  and  $X_2$ .

As this equation shows analyses with low variability have lower RPDs (and better precision), and analyses with high variability have higher RPDs (and poorer precision). The RPD method quality objective for all data from the NMP is 25 percent. The overall data average RPD result for 2005 was 17%, which is within the 25% target. Table 9 presents the collocated data results.

Table 9: Collocate Statistical Data Results (January 2005 to December 2005).

Site ID	# of Collocates	Median (RPD)	Average (RPD)	Percent Standard Deviation
Roxbury, MA	6	10%	14%	12%
Burlington, VA	11	6%	18%	35%
Providence, RI	6	21%	<b>35%</b>	47%
Underhill, VT	6	0%	5%	6%
Washington, DC	4	1%	9%	16%
Chesterfield, SC	6	0%	12%	0%
Hazard, KY	5	0%	6%	0%
North Birmingham, AL	1	0%	0%	0%
Providence, AL	1	0%	0%	0%
Birmingham, AL (site 2)	1	0%	0%	0%
S. Dekalb Co., GA	2	<b>41%</b>	<b>41%</b>	0%
Tampa, FL	5	0%	18%	29%
Detroit, MI	5	16%	14%	13%
Chicago, IL	3	18%	14%	12%
Madison, WI	4	16%	16%	17%
Austin, TX	1	<b>33%</b>	<b>33%</b>	0%
St. Louis, MO	4	4%	8%	11%
Grand Junction, CO	5	0%	10%	22%
Seattle, WA	6	10%	<b>32%</b>	55%
Gulf Port, MS	7	<b>27%</b>	<b>27%</b>	25%
Stennis Airport, MS	1	19%	19%	0%
Kenner, LA	4	17%	<b>35%</b>	43%
Average	4	8%	17%	16%

## CONCLUSIONS

Based on the results of this study, ERG concludes Teflon filters do not collect the  $\text{Cr}^{6+}$  more efficiently than cellulose. Reducing agents in the ambient air seem to be converting the  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  and the filter media must stabilize and protect the  $\text{Cr}^{6+}$  from these reducing agents. The Teflon filters do not have the buffer coating (sodium bicarbonate) to stabilize the  $\text{Cr}^{6+}$  on the filter when reducing agents are present (such as acid gases).

ERG laboratory's detection limit for acrolein is  $0.012 \text{ ng/m}^3$  (experimentally determined using 40 CFR, Part 136 procedures) which is lower than the cancer and noncancer health risk threshold concentration. Based on the results of this study, sample collection using the sodium bicarbonate coated cellulose filters is recommended. There are certain preservation procedures that must be followed before acceptable sample results should be reported, including:

- The filters must be acid washed and rinsed before coating them with the sodium bicarbonate to prevent  $\text{Cr}^{6+}$  background. Using this method however, does not lengthen the collection or storage hold time.
- All samples must be retrieved from the field one day after the sample has been collected to prevent  $\text{Cr}^{6+}$  negative bias (loss) (up to 20% on the first day).
- All samples must be frozen after collection to reduce the risk of  $\text{Cr}^{6+}$  loss.

Analysis of sodium bicarbonate coated cellulose filters containing known concentrations of  $\text{Cr}^{6+}$  demonstrated acceptable recoveries, if the samples are recovered as soon as possible after sampling ends.

ERG has determined that this modified method shows consistent recovery for  $\text{Cr}^{6+}$  over time throughout the country. The collocated sample recoveries meet the method quality objectives set by the EPA for the NATTS program, however there does seem to be limitations on sample recovery for loading filters outside of the controlled laboratory conditions.

## ACKNOWLEDGMENTS

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