

US EPA ARCHIVE DOCUMENT

**Quality Assurance Project Plan for
Chromium (VI) Air Study
Kansas City, Kansas**

**U. S. EPA Region 7
Air Program
November 2011**



Stephanie Doolan, Program Lead
AWMD/APDB, EPA Region 7

11/07/2011

Date



Leland Grooms, Technical Lead
ENSV/ASRS, EPA Region 7

11/15/2011

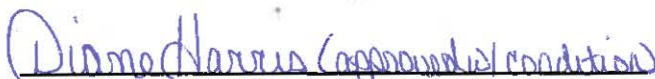
Date



Mark Smith, Chief
AWMD/APCO, EPA Region 7

11/7/11

Date



Diane Harris
Regional Quality Assurance Manager

11/28/2011

Date

RECEIVED
2012043

Table of Contents

A. Project Management	4
A3. Distribution List	4
A4. Project/Task Organization	4
A5. Problem Definition/Background	5
A6. Project/Task Description	8
A7. Quality Objectives and Criteria for Measurement Data	8
A8. Special Training Requirements/Certification	9
A9. Documentation and Records	9
B. Measurement/Data Acquisition	10
B1. Sampling Process Design	10
B2. Sampling Methods Requirements	11
B3. Sample Handling and Custody Requirements	11
B4. Analytical Methods Requirements	11
B5. Quality Control Requirements	12
B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements	12
B7. Instrument Calibration and Frequency	13
B8. Inspection/Acceptance Requirements for Supplies and Consumables	13
B9. Data Acquisition Requirements	13
B10. Data Management	13
C. Assessment/Oversight	14
C1. Assessments and Response Actions	14
C2. Reports to Management	14
D. Data Validation and Usability	15
D1. Data Review, Validation, and Verification Requirements	15
D2. Validation and Verification Methods	15
D3. Reconciliation with User Requirements	15

Appendix A

Figure 1 – Site Map & Proposed Air Sampler Location
Figure 2 – Air Modeling Results – Predicted Risk
Figure 3 – Air Modeling Results – Cr(VI) Predicted Concentration
Figure 4 – Air Sampler Detail

Appendix B

Eastern Research Group, Inc. Quality Assurance Plan

Appendix C

Standard Operating Procedure for Measurement of Hexavalent Chromium using the BGI PQ167R Low Volume Sampler, School Air Toxics Study, August 14, 2009

Appendix D

"Collection and Analysis of Hexavalent Chromium in Ambient Air," ERG, January 9, 2007

Appendix E

Region 7 Standard Operating Procedure No. 2314.06A, "Measurement of Hexavalent Chromium Using the BGI PQ167R Low Volume Sampler," November 7, 2011

A. Project Management

A3. Distribution List

Stephanie Doolan, Air Program Lead	AWMD/APDB, EPA Region 7
Leland Grooms, Technical Lead	ENSV/ASRS, EPA Region 7
Todd Phillips, Risk Assessment Support	ENSV/EAMB, EPA Region 7
Mike Jones, Analytical Contract Support	Office of Air Quality Planning Standards (OAQPS)
Julie L. Swift, Program Manager/Chemist	Eastern Research Group (ERG)
Miles Stotts, Air Program Lead	Kansas Department of Health & Environment (KDHE)

A4. Project/Task Organization

This project is being managed by the Air and Waste Management Division (AWMD), Air Planning and Development Branch (APDB), and administered by the Environmental Services Division (ENSV), Air Sampling and Services (ASRS) Branch, EPA Region 7. Field data collection, sample management, and reporting for the Chromium (VI) Air Study under this Quality Assurance Project Plan (QAPP) will be conducted by EPA Region 7. Air sample analysis will be conducted by Eastern Research Group, Inc. (ERG) under contract to the EPA's Office of Air Quality Planning and Standards (OAQPS) in Research Triangle Park, North Carolina.

EPA, Region 7

Stephanie Doolan, Program Lead
RCAP/AWMD (913) 551-7719

Responsibilities: Project management, laboratory coordination, and data validation and reporting

Leland Grooms, Technical Lead
EMWC/ENSV (913) 551-5010

Responsibilities: Receipt of sampling supplies, sample collection, shipment to laboratory, and data validation

Todd Phillips, Risk Assessment Support
ENSV/EAMB (913) 551-7438

Responsibilities: Developing site-specific action levels, sampling project design, technical support to program lead and field team

Mike Jones, Contract Officer Representative and Technical Support
OAQPS (919) 541-0528

Responsibilities: Contract fixed laboratory sample analyses, technical support

Julie Swift, Program Manager/Chemist
ERG (919) 468-7924

Responsibilities: Laboratory coordination including shipment of sampling supplies, sample management, quality assurance and data reporting

Miles Stotts
Kansas Department of Health and Environment
(785) 296-1615

Responsibilities: Act as a liaison with state regulatory agency.

A5. Problem Definition/Background

The purpose of this Quality Assurance Project Plan (QAPP) is to describe the procedures to be used for outdoor air sampling for hexavalent chromium [Cr(VI)] at a location in Kansas City, Kansas, predicted by modeling to represent the highest risk for human exposure. Outdoor air sampling is to measure Cr(VI) concentrations in ambient air in a residential neighborhood downwind from the source of the Cr(VI) emissions, and to determine whether further action is necessary to protect human health and the environment.

The source of the Cr(VI) emissions is the CertainTeed wool fiberglass manufacturing facility at 103 Funston Road, Kansas City, Kansas, in what is commonly known as the "Fairfax District." During the rule revision of the Wool Fiberglass National Environmental Standards for Hazardous Air Pollutants (NESHAP), CertainTeed conducted a stack test in November 2010 for Cr(VI). The stack test data, validated by CertainTeed in February 2011, indicate that the facility emits approximately 840 pounds of Cr(VI) per year combined from two process stacks known as the "K1stack" and "K2 stack." OAQPS notified Region 7 of this information in June 2011. The Cr(VI) is believed to be emitted by the facility from the degradation of high-chrome refractory brick inside the furnaces that melt the silica and other substrates to form the fiberglass. Under high (3,000 degrees F) temperatures and a corrosive environment, the refractory brick degrades and Cr(VI), in the form of particulates, is emitted from the stacks that vent the kilns. By comparison, the next largest source of Cr(VI) in the wool fiberglass source category emits 56 lbs per year of Cr(VI).

Modeling was conducted by both OAQPS and Region 7 staff using AERMOD, EPA's preferred air dispersion model. Inputs to the model include five years of meteorological data (2006 – 2010) from Kansas City's Wheeler Airport, emissions data from the 2010 stack test conducted by CertainTeed, terrain and elevation data, and building and stack heights and dimensions to determine release heights of the Cr(VI) emissions and to evaluate potential "downwash" of contaminants from structures near the location the Cr(VI) is released. The outcomes of the model (Appendix A, Figures 2 and 3) indicate that the closest human receptors are in the Oak Grove Neighborhood to the southwest of the CertainTeed facility, that the Maximum Individual Risk (MIR) to the exposed population is approximately a 40-in-one-million (or 4×10^{-5}) cancer risk, and that the predicted maximum annual concentration averaged over five years (the number of years of meteorological data used to input the model) for Cr(VI) in the area of the Oak Grove Neighborhood is 2.4 nanograms per cubic meter (ng/m^3). For comparison, the EPA Air Program typically considers carcinogenic risks greater than 100-in-one-million (or 1×10^{-4}) to require further action. Based on EPA's Integrated Risk Information System (IRIS) database, the Region 7 toxicologists have recommended the following screening level for Cr(VI) listed in Table 1 below in outdoor air for a 70-year (e.g., lifetime) exposure.

Table 1. Cr (VI) Cancer Screening Levels¹

Risk Level	Screening Level (ng/m^3)	Modeled Concentration (ng/m^3) ²	Analytical Detection Level (ng/m^3)
100 in 1 Million	8	2.4	0.0039 ³
10 in 1 Million	0.8		
1 Million	0.08		

¹ - Assumes 70 year continuous exposure to outdoor (ambient) air

² - This value represents the modeled concentration at the closest human receptor.

³ - The Analytical Detection Limit listed is from the laboratory's Method Detection Limit (MDL) study which corresponds to 21.6 m^3 of air.

Table 2. Cr (VI) Non-Cancer Screening levels¹

Duration	Screening Level (ng/m^3)	Modeled Concentration (ng/m^3) ²	Analytical Detection Level (ng/m^3)
Chronic Exposure ($\geq 6 - 7$ years) ³	100	2.4	0.0039 ⁴

¹ - Assumes chronic/long-term continuous exposure. Generally applies to exposures greater than 6 to 7 years.

² - This value represents the modeled concentration at the closest human receptor.

³ - Source: EPA's Integrated Risk Information System (IRIS) chronic reference concentration (RfC) for particulates.

⁴ - The Analytical Detection Limit listed is from the laboratory's Method Detection Limit (MDL) study which corresponds to 21.6 m^3 of air.

Based on the predicted outcomes of the model and comparison with relevant human health screening criteria presented above, EPA intends to collect outdoor air data to confirm that the risk for the closest receptors does not exceed levels EPA has determined to be protective of human health. Note that for conservatism EPA is comparing the model predicted values for Cr(VI) to risk levels based on 70 years of continuous exposure. It is important to note that, based on available information, EPA believes that Cr(VI) emissions from the CertainTeed facility have only been elevated since 2004 when the facility reports that it re-bricked its furnaces with higher chrome content refractory brick.

In the initial phase of outdoor air sampling, EPA plans to collect multiple rounds of samples to determine the outdoor air concentration of Cr(VI) in the Oak Grove Neighborhood area, and to compare actual concentrations to the human health screening levels and predicted results of the model listed in Tables 1 and 2 above. Because wind direction and speed, relative humidity, and outdoor temperature can greatly affect the results of outdoor air sampling, EPA will initially collect samples at a frequency of one sample per every three days (1/3) from both of the collocated samplers for a period of six months. At the end of six months, EPA will evaluate the initial results and determine whether the frequency of sampling needs to be adjusted, the sampling needs to be continued, and if the number and location of samplers is appropriate. If the initial data indicate the need to adjust the sampling regime, this QAPP will be revised accordingly.

A public hearing and availability session is being planned for November 2011 to discuss the proposed Risk and Technology Review for Wool Fiberglass facilities, the new standards for Cr(VI) emissions from the CertainTeed facility, the results of EPA's risk modeling, and the plan to conduct this study to gather actual outdoor air data for Cr(VI) in the area of highest predicted risk for human receptors.

The former Garland Park Landfill is the selected location for sampling because it lies within the same contours for MIR and Cr(VI) concentration as the nearest residences, e.g., a measured concentration at the landfill is representative of Cr(VI) that may be measured at nearby residences. The former landfill site is open so that there are no obstructions from trees or buildings between samplers and the CertainTeed stacks emitting the Cr(VI), and it is fenced to limit access and tampering with the air samplers. Figure 1 in Appendix A depicts the proposed location of the air samplers. The Unified Government of Wyandotte County and Kansas City, Kansas, the current owners of the landfill property, have agreed to grant access for the sampling. At this time, discussions are occurring to determine whether electrical power for the samplers can be arranged or if the samplers will need to be powered by marine cycle batteries. Electrical power is preferable to battery power if possible due to the consistency in the power source, especially during cold winter months.

December 5, 2011

Analytical work will be performed by ERG, Inc., a contractor to OAQPS for air sample analysis. The laboratory's QAPP is provided as Attachment B. The analytical SOP for the specific analysis for Cr(VI) is proprietary; however, a copy will be made available to the Region 7 RQAM upon request. The analytical method for Cr(VI) is based on the California Air Resources Board (CARB) Method 039 and the paper provided as Appendix D titled, "Collection and Analysis of Hexavalent Chromium in Ambient Air," transmitted from ERG to Mike Jones, EPA OAQPS, in a letter dated January 9, 2007.

A6. Project/Task Description

The project is designed to:

- Measure concentrations of Cr(VI) in ambient air in areas where human exposures may occur;
- Assess whether exposure to Cr(VI) concentrations in outdoor air exceed human health risk-based criteria; and
- Determine whether further action is necessary.

To determine if exposure poses a potential human health risk, data will be compared with the risk-based screening levels presented in Tables 1 and 2 above, for cancer and non-cancer risks, respectively.

The data from this study will be submitted by the contract laboratory, ERG, to Mike Jones, EPA OAQPS, and Stephanie Doolan, EPA Region 7. If the average results for Cr (VI) over the first six months are found to exceed risk-based screening criteria listed above in Tables 1 and 2, further action may be deemed necessary. Further action could include, but is not limited to, additional sampling, an investigation of other possible sources of Cr (VI) in the surrounding area, and regulatory options, including enforcement, to reduce Cr (VI) emissions from the facility.

A7. Quality Objectives and Criteria for Measurement Data

By following the QAPP, the ERG contract statement of work, the EPA SOP, and the laboratory quality assurance plan, the quality objectives of this air sampling and analysis plan are to provide valid data of known and documented quality such that:

- Data will be collected in a manner to result in an accurate average annual 24-hour concentration of Cr(VI) in outdoor air;
- Data will be collected for comparison with risk based screening levels based on chronic/long-term exposure;
- Data will be used to determine the need for possible future actions; and
- Samples will be representative of seasonal and temporal variability of local meteorological conditions and operating conditions at the facility.

December 5, 2011

The data quality indicators to be used are identified below. Note that field collection best practices are detailed within the sampling SOP and methodology provided in Appendices C and E, and criteria for measurement data are embedded within the analytical methods.

- Representativeness will be addressed by collecting, analyzing, and reporting the data as described in this document, the attached SOP, and the analytical method.
- Comparability will be addressed by collecting, analyzing, and reporting the data as described in this document, the attached SOP and the analytical method.
- Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. The completeness objective for this project will be not less than 90%.
- Method accuracy will be assessed by laboratory analysis of calibration and control standards with known concentrations of the analyte of interest.

Method accuracy performance will be considered acceptable if daily quality control sample results fall within the normal range of acceptable values as indicated by the laboratory quality assurance plan (Appendix B). Sample specific and batch QA/QC will be reported in the data package received from the contract laboratory.

Field precision will be assessed by collection of collocated samples (two samplers located together). Field precision performance will be considered acceptable if sample results fall within +/- 70 Relative Percent Difference (RPD).

A8. Special Training Requirements/Certification

Experienced EPA air sampling personnel will be deployed to set up sampling equipment and retrieve samples for this project. Field personnel must be experienced in the operation of low volume particulate air samplers.

A9. Documentation and Records

The Program Lead is responsible for ensuring that the QAPP currently represents the sample collection activities in the field and that the most current version of the QAPP has been distributed to the list in Section A.3. For field documentation see section B3.

The records retention schedule for this project is as follows:

Function Code	Schedule	Disposition	Description
304-104-06	185a	Disposable 10 years after file closure	Collection of approved Quality Assurance Plans, QAPP
108-25-01-01-02	484a	Disposable 10 years after file closure	Data Records
305-109-01	258a(1)	Disposable 20 years after file closures	Final Deliverable and Reports

B. Measurement/Data Acquisition

B1. Sampling Process Design

To collect representative data great care must be taken during the field sampling to ensure proper purging, leak testing, and vacuum of the sample collection systems. Note that it is well reported in the literature that outdoor air samples have a high degree of variability. Factors that can influence air quality include distance from the source, source characteristics such as building dimensions and stack heights, topographic elevation of the source and receptors, and seasonal weather variations such as outdoor air temperature, wind speed and direction, and relative percent humidity.

As stated above, samples will be collected from two, collocated air samplers at a frequency of one per every three days, for a duration of a minimum of six months. The first phase of sampling will result in approximately 56 outdoor air samples (28 samples from each sampler). Initially, a minimum of 20 field blanks will be collected. Depending on the results of the initial 20 field blanks, as discussed above, the number of field blanks collected may be reduced. For the purposes of this QAPP, it is estimated that field blanks will be collected biweekly, for a total number of 24. The project team will evaluate the data after six months and decide whether to continue, reduce or expand the study.

The Technical Lead will be responsible for identifying and implementing any corrective action in the field, and as a part of sample handling and shipment. All corrective actions taken must be documented in the field logbook. Issues and corrective action taken that affect the quality and usability of the data must be reported to the Program Lead to ensure that data are validated appropriately and usability is considered as a part of decision making.

B2. Sampling Methods Requirements

Samples will initially be collected from two collocated low volume particulate air samplers in accordance with Appendix E, "Measurement of Hexavalent Chromium Using the BGI PQ167R Low Volume Sampler (U. S. EPA, 2011), which is based on Appendix C, "Standard Operating Procedure for Measurement of Hexavalent Chromium using the BGI PQ167R Low Volume Sampler, School Air Toxics Study," (U. S. EPA 2009). Per the study conducted by ERG (Appendix D), the following sample preservation procedures need to be employed:

- Teflon filters must be used to collect the samples;
- Filter media must be pre-washed with acid and rinsed before coating with sodium bisulfate to prevent Cr(VI) background interference;
- Samples must be retrieved within 24-hours after collection to prevent sample loss; and
- All samples must be delivered to the laboratory frozen to reduce sample loss.

The Technical Lead is responsible for ensuring that these field procedures are strictly adhered to, and documenting and reporting any deviations from these procedures that may affect data quality and usability.

B3. Sample Handling and Custody Requirements

Sample containers, preservation, and holding times will be those found in the EPA SOP (Appendix C) and the procedures listed in B.2 above that are from the "Collection and Analysis of Hexavalent Chromium in Ambient Air," transmitted from ERG to Mike Jones, EPA OAQPS, in a letter dated January 9, 2007 (Appendix D).

Chain-of-Custody documentation will be recorded on the form provided by ERG similar to the example provided on page 19 of the SOP found in Appendix C. This form also records the date and time of collection, location, total sampling time, meteorological conditions, and air sample volume. The field team will record this information and other site-specific observations in a field logbook using indelible ink.

B4. Analytical Methods Requirements

Air sample analysis for Cr(VI) will be conducted by ERG in accordance with a modified CARB SOP 039 in accordance with ERG's quality assurance plan. This analytical method employs the use of both Ion Chromatography (IC) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Results from this study will be compared to the cancer and non-cancer risk screening values as provided in Tables 1 and 2 above. As noted above, the SOP for the method is proprietary; however, it will be made available to EPA personnel upon request.

Correction action for analytical quality control issues is the responsibility of the laboratory to conduct in accordance with its Quality Assurance Plan (Appendix B). However, it is the responsibility of the Laboratory Program Manager/Chemist to inform the Program Lead of issues requiring corrective action, actions taken and the affect, if any, on the analytical data reported.

The turnaround time for sample analysis is 30 days from sample receipt, per the laboratory's contract.

B5. Quality Control Requirements

Collocated samples and trip blanks will be collected during the project. Two collocated samples will be collected on each day of sampling. The collection of two collocated samples will provide measurement of sampling precision and environmental variability.

Field blanks (sample media handled, exposed to outdoor air briefly, and shipped to the contract laboratory for analysis along with the collocated field samples) will be prepared and analyzed initially at a frequency with every shipment of field samples to the laboratory. The field blanks will be used to assess sampling accuracy and the potential for cross-contamination to occur during sample handling and shipment. As the study progresses, the frequency of field blank preparation and analysis may be reduced to biweekly if the following conditions are met: 20 trip blank samples have been submitted for analysis and the results are less than field sample results; the collocated field sample data do not indicate the potential for cross-contamination of samples; and the laboratory blank sample results analyzed as a part of the batch including the field samples indicate no significant laboratory contamination issues.

Laboratory quality control elements, including spikes and blanks will be performed in accordance with the ERG quality assurance plan (Appendix B).

B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The field equipment instrumentation testing, inspection, and maintenance will be performed in accordance with the field SOPs (Appendix C). Analytical instrumentation testing, inspection, and maintenance will be performed in accordance with the ERG quality assurance plan (Appendix B).

B7. Instrument Calibration and Frequency

Field equipment and analytical instrument calibrations will be performed in accordance with the appropriate referenced analytical or sample collection SOP and manufacturer's recommendations. Analytical instrumentation calibration will be performed in accordance with the ERG quality assurance plan (Appendix B).

B8. Inspection/Acceptance Requirements for Supplies and Consumables

The Technical Lead will be responsible for receipt and inspection of sample media and containers for return shipment to the laboratory. As described in B.2 above, the sample media need to be shipped to the field coated with sodium bisulfate. Rejection of sampling media and supplies needs to be reported to Mike Jones, OAQPS, with a copy to the Program Lead, because these are contract requirements that must be resolved by the EPA Contracting Officer for the analytical contract with ERG.

B9. Data Acquisition Requirements

Acquired data for this project include modeling results that were generated using an EPA-approved model, AERMOD, using protocols that are established in 40 CFR Part 58, Appendix W. Thus, the quality and reliability of the modeling is assured by using an approved model and following a prescriptive process.

B10. Data Management

Analytical data management will be in accordance with EPA's national contract for air sample analysis with ERG. Data will be reported both to Mike Jones, the EPA Contract Officer Representative, and Region 7's Program Lead. The Program Lead will review and validate the data, and transmit it to the project team for further review and analysis.

C. Assessment/Oversight

C1. Assessments and Response Actions

The EPA Region 7 QA Manager (RQAM) or designee may conduct an audit of the field activities for this project if requested by the EPA Program Lead or Technical Lead. The EPA RQAM will have the authority to issue a stop work order upon finding a significant condition that would adversely affect the quality and usability of the data. The EPA Technical Lead will have the responsibility for initiating and implementing response actions associated with findings identified during the on-site audit. Once the response actions have been implemented, the EPA RQAM will perform a follow-up audit to verify and document that the response actions were implemented effectively.

C2. Reports to Management

A six-month technical report will be prepared by the Program Lead and Technical Lead with support from the Regional Risk Assessor. The report shall incorporate the results from EPA air sampling and shall be distributed in accordance with section A3. The six-month report will contain environmental sampling results and will compare the results with the respective human health risk-based levels. The six-month report will also recommend whether additional sampling is needed.

D. Data Validation and Usability

D1. Data Review, Validation, and Verification Requirements

The data will be reviewed and reported by the contract laboratory in accordance with its procedures documented in the quality assurance plan (Appendix B). The EPA Program Lead and Technical Lead will be responsible for overall validation and final approval of the data in accordance with project purpose and use of the data.

D2. Validation and Verification Methods

ERG, the contract laboratory performing the analysis will input the data to EPA's Air Quality System (AQS). AQS contains outdoor air data collected by EPA, state, local, and tribal air pollution control agencies from thousands of monitoring stations. AQS also contains meteorological data, descriptive information about each monitoring station (including its geographic location and its operator), and data quality assurance/quality control information. OAQPS staff review and validate AQS using air program guidelines before release on the publically available portion of the AQS website.

The EPA Program Lead and Technical Lead will perform the final review and approval of the data prior to it being reported to the project team for decision making. The final review will consist of verifying that the sample collection and analyses were performed in accordance with the approved QAPP, and the SOPs provided in Appendices C and E. Final review and validation will include a review of the results of the collocated samples and trip blanks to ensure they are acceptable and have met precision and accuracy goals set forth in this QAPP. The final review will also compare the sample descriptions with the chain-of-custody/field sheets for consistency and will ensure that any anomalies in the data are appropriately documented.

D3. Reconciliation with User Requirements

Once the results are compiled, the EPA Program Lead and Technical Lead will review the results from collocated samples and trip blanks to determine if they fall within the acceptance limits as defined in this QAPP. Completeness will also be evaluated to determine if the completeness goal for this project has been met (> 90%). If data quality indicators do not meet the project's requirements as outlined in this QAPP (including the accuracy for lab spikes), the data may be discarded and re-sampling may occur. The EPA Program Lead and Technical Lead will evaluate the cause of the failure (if possible) and make the decision to discard the data and re-sample. If the failure is tied to the analysis, calibration and maintenance techniques will be reassessed as identified by the appropriate lab personnel. If the failure is associated with the sample collection and re-sampling is needed, sampling personnel will be retrained or the sampling method modified accordingly to correct the problem.

Data will be compared with meteorological data from the Kansas City Downtown Airport, looking particularly at the data when the predominant wind direction is from the source and toward the samplers. Results for dates when the wind direction is toward the monitors will be compared with the model predicted results. At a minimum, the average, maximum and minimum results will be reported by month and for the duration of the sampling program.

The data from dates when the predominant wind direction is not toward the samplers will be examined to determine whether the CertainTeed facility is the only source of Cr(VI) emissions in the area, or if there are other possible sources unknown to EPA at this time. Should the data indicate other potential sources of Cr(VI), EPA may adjust the number and location of samplers deployed as a part of this study, and/or, in consultation with KDHE, will conduct a more rigorous review of emissions inventory data and industrial classifications for facilities that may be contributing to measured levels of Cr(VI) in outdoor air.

APPENDIX A

FIGURES

FIGURE 1 - LOCATION MAP & PROPOSED SAMPLER LOCATION

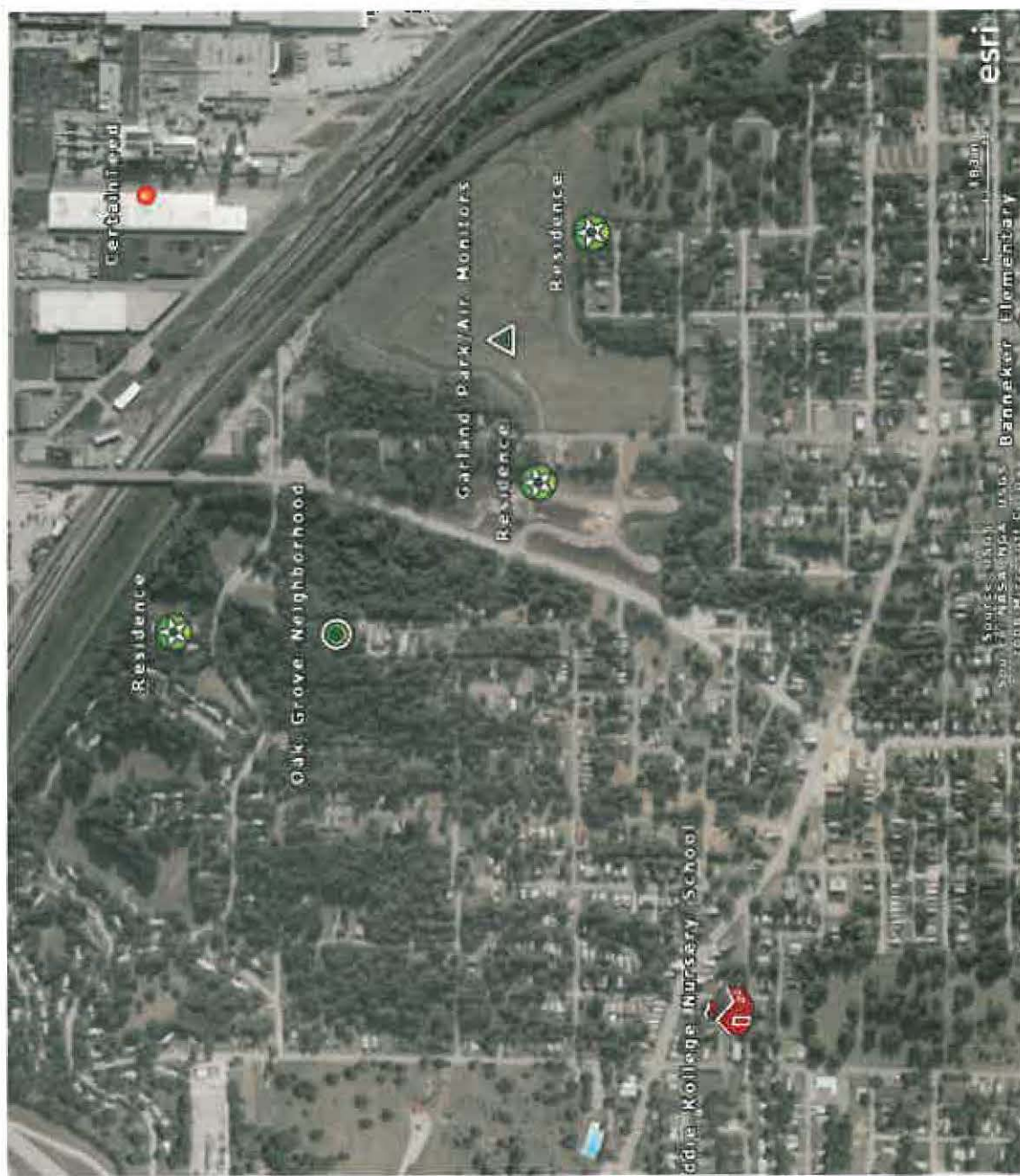
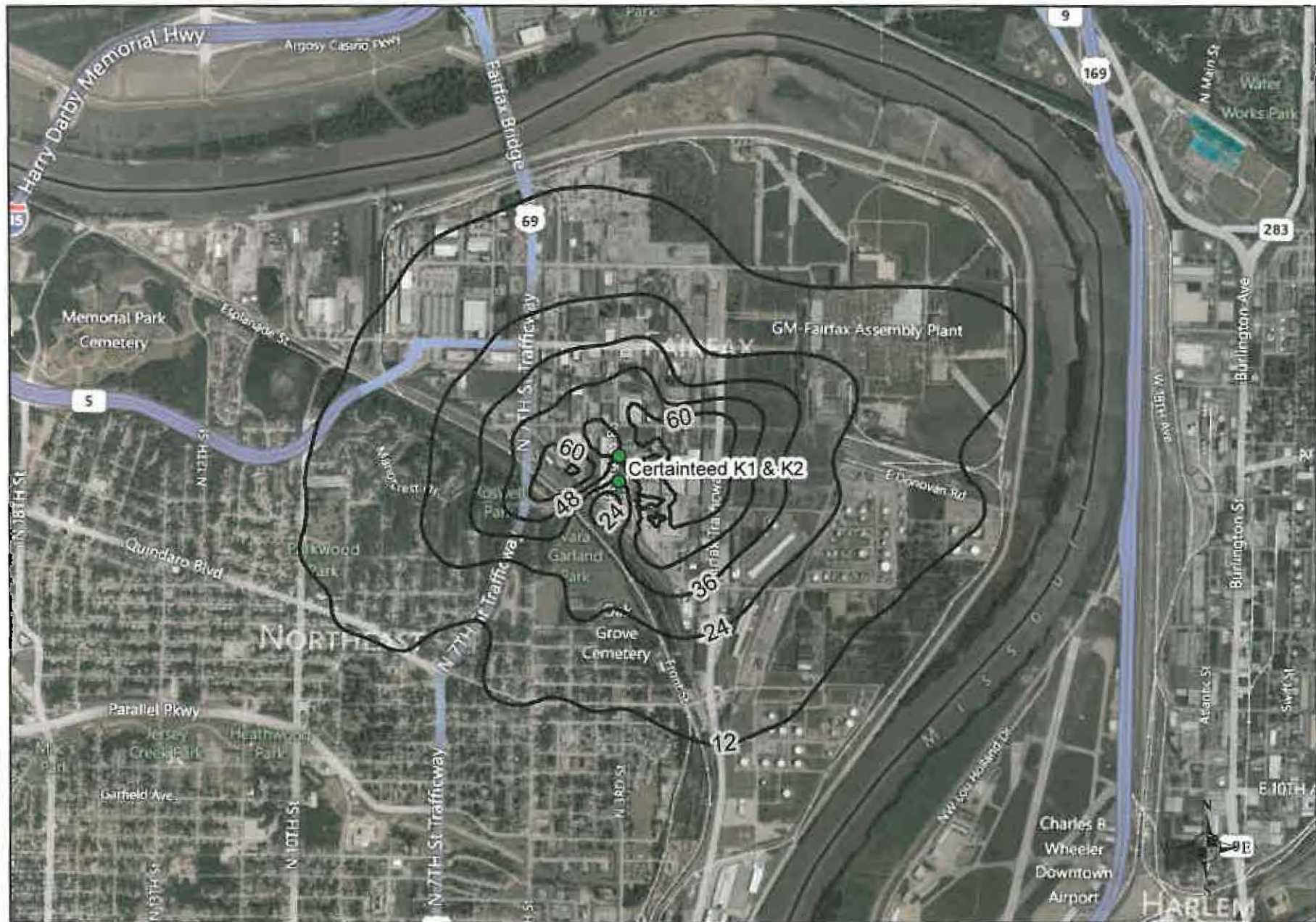


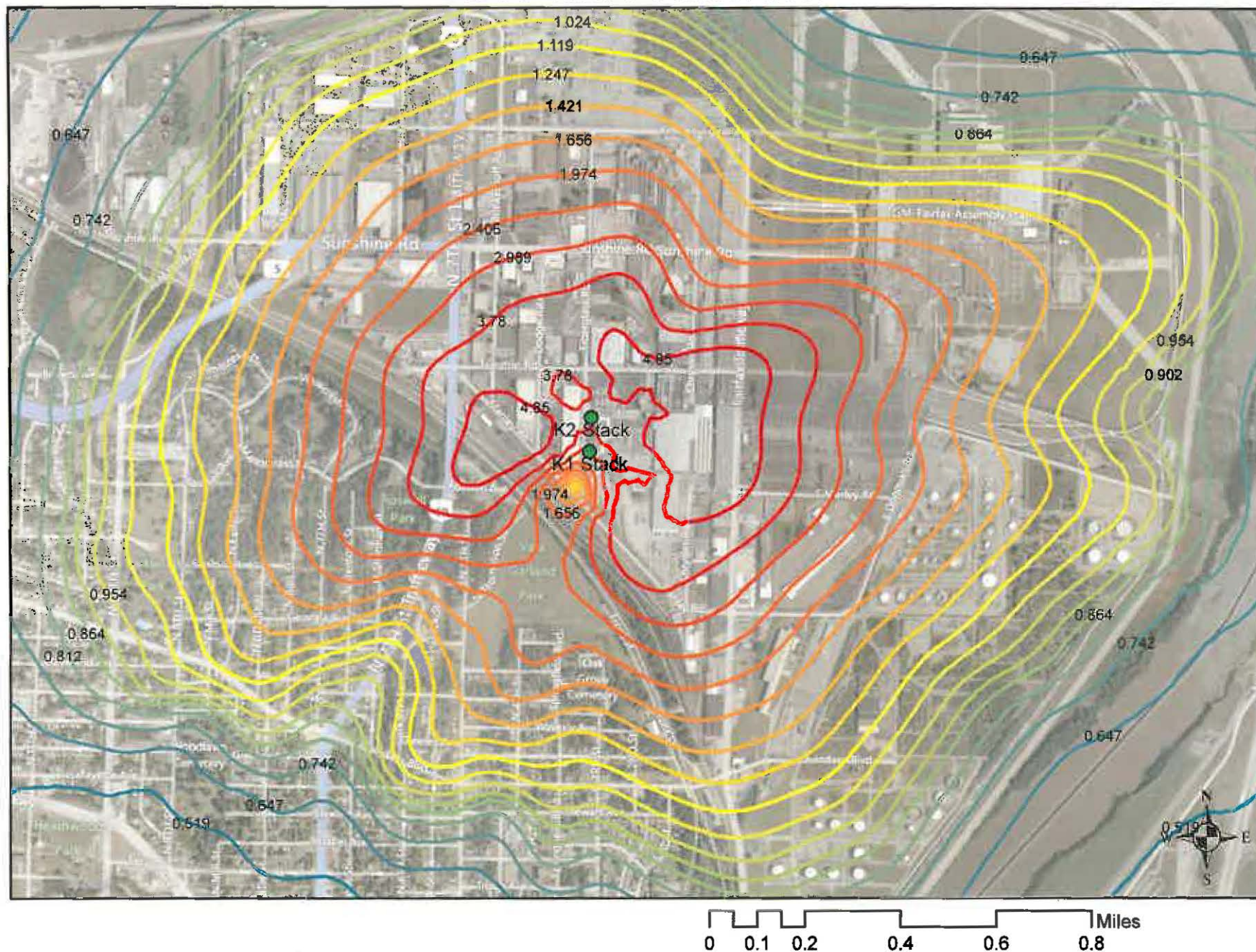
Figure 2 Maximum Individual Cancer Risk (MIR)
Chromium (VI) Air Study
October 2011



Presumptive Limit on Maximum Individual Risk = 100 in a million
Risk assumes continuous 70 year exposure

0 0.2 0.4 0.8 1.2 1.6 Miles

Figure 3 Ambient Cr (VI) Concentrations (ng/m³)
Chromium (VI) Air Study
QAPP Rev. 0 October 2011



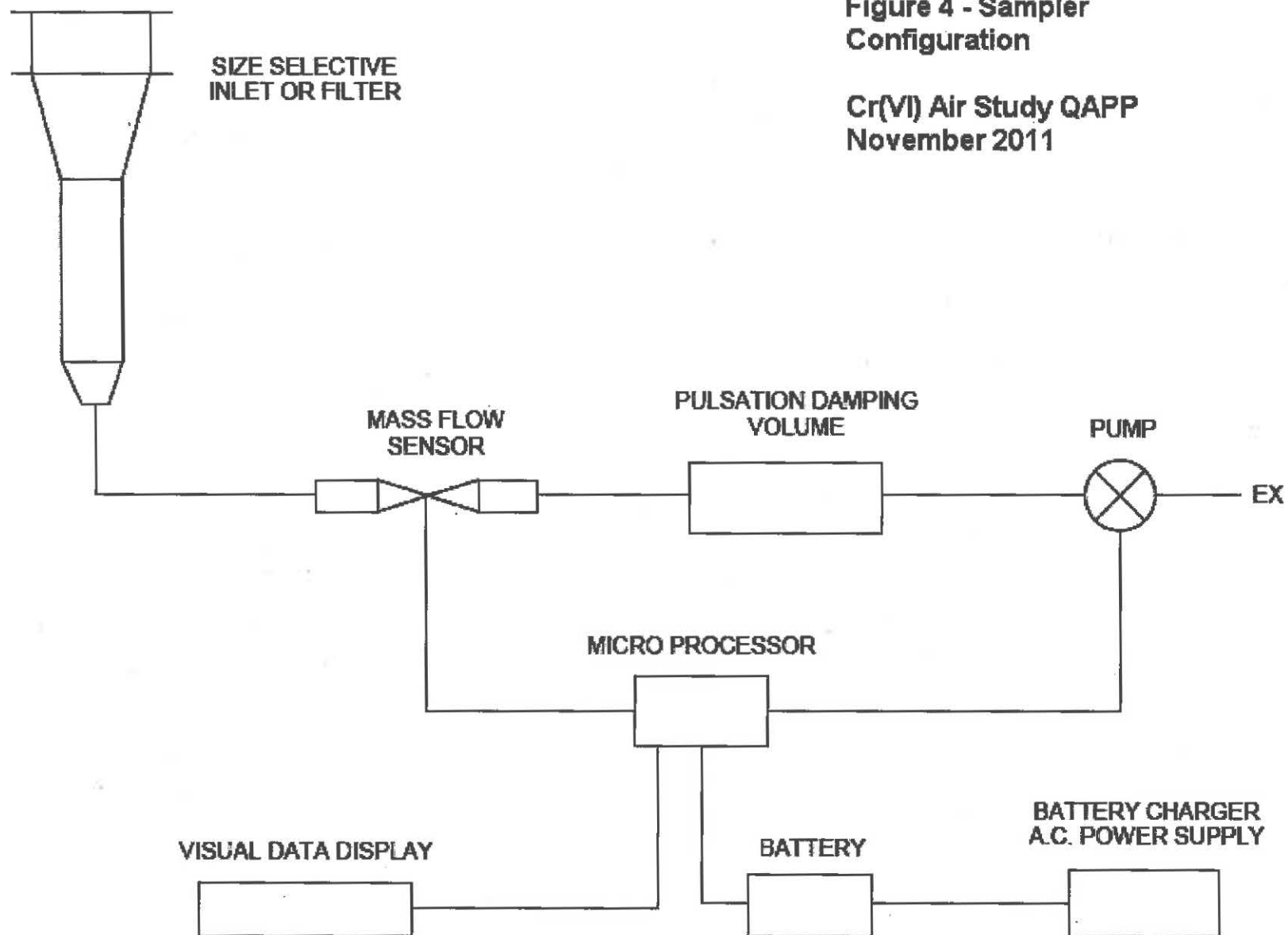


Figure 4 - Sampler Configuration

**Cr(VI) Air Study QAPP
November 2011**

APPENDIX B

2011 ERG LABORATORY QUALITY ASSURANCE PLAN

APPENDIX C

**STANDARD OPERATING PROCEDURE
FOR
MEASUREMENT OF HEXAVALENT CHROMIUM
USING THE
BGI PQ167R LOW VOLUME SAMPLER
(U. S. EPA, 2009)**

**STANDARD OPERATING PROCEDURE
FOR
MEASUREMENT OF HEXAVALENT CHROMIUM
USING THE
BGI PQ167R LOW VOLUME SAMPLER**



**U.S. Environmental Protection Agency
Region 4, Science and Ecosystem Support Division
Athens, Georgia, 30605**

Acknowledgement

This Standard Operating Procedure (SOP) was developed by EPA Region 4, Science and Ecosystem Support Division. This SOP is based on the Commonwealth of Kentucky's ambient monitoring SOP template. Special thanks to BGI Inc. and ERG for operational content and illustrations.

For questions or comments please contact:

Greg Noah, EPA, Region 4, SEDS at noah.greg@epa.gov or 706-355-8635
Mike Jones, EPA-OAQPS-AQAD at jones.mike@epa.gov or 919-541-0528

Table of Contents

I. Introduction.....	4
II. Installation.....	7
A. Sampler Siting.....	7
B. Sampler Installation.....	7
Cr+6 Retrofit Instructions.....	7
III. Operating Procedure.....	9
A. Equipment and Supplies.....	9
B. Sampler and Sample Media Receipt Activities.....	9
C. Verification.....	10
D. Calibration.....	11
E. Conducting the Sampling Event.....	12
Site Arrival Daily Activities.....	12
Preparing Sampler for a Sampling Event.....	13
Installing the ERG Cr+6 Filter Holder Module.....	16
Sample Recovery and Data Collection.....	16
Sample Shipping.....	17
IV. Quality Assurance.....	18
A. Flow Calibration.....	18
B. Flow Verifications.....	18
C. Independent Audits.....	18
V. Data Forms.....	18
ERG Ambient Hexavalent Chromium Data Sheet.....	19

I. **INTRODUCTION**

This procedure is designed to provide instruction on collecting hexavalent chromium (Cr+6) in air using the BGI PQ167R air sampler for metals analysis.

The BGI PQ100 is an "Intelligent Air Pump" that can monitor its own airflow rate and thereby adjust the pump speed to compensate for changes in load pressure and/or other forces which would otherwise hamper the flow of air through a filter (or sample collector). The PQ100 unit can be programmed to begin its sampling job at a specific date, time, and stop sampling after the user defined run time is depleted. However, the sampling time should always be 24 hours for Cr+6 sampling the Toxics in Schools Study.

The PQ100 was designed to operate from 1 standard liter per minute (1000 cc per minute) to 25.0 standard liters per minute and is unaffected by changes in ambient temperature and barometric pressure. The flow rate precision is guaranteed to 2% of the calibration set point.

This SOP is designed to be a step by step method for operating the sampler to be used in conjunction with the manufacturer's operators manual. Laboratory Analysis Methodology may be referenced by contacting the Eastern Research Group (ERG) directly at 919-468-7800 or by email Julie.Swift@erg.com. Maintenance and troubleshooting should be conducted using the BGI167R operator's manual.

FIGURE 1. Schematic of PQ167 Sampling System
(Cr+6 filter holder apparatus replaces PM10 inlet head)

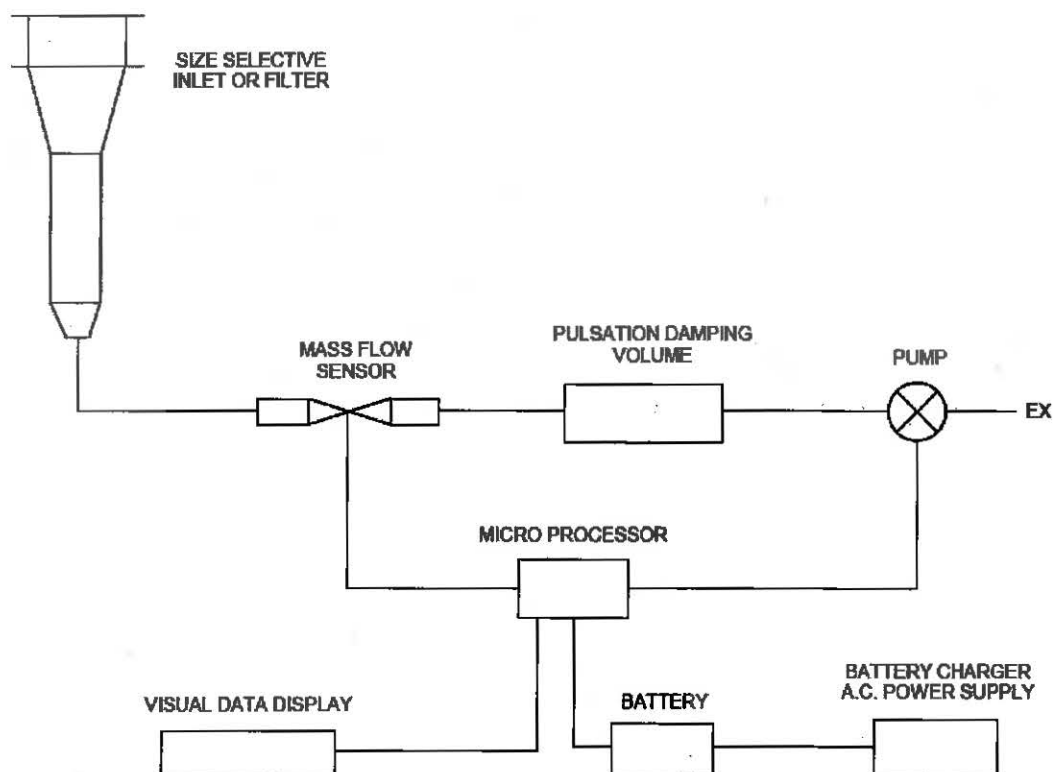
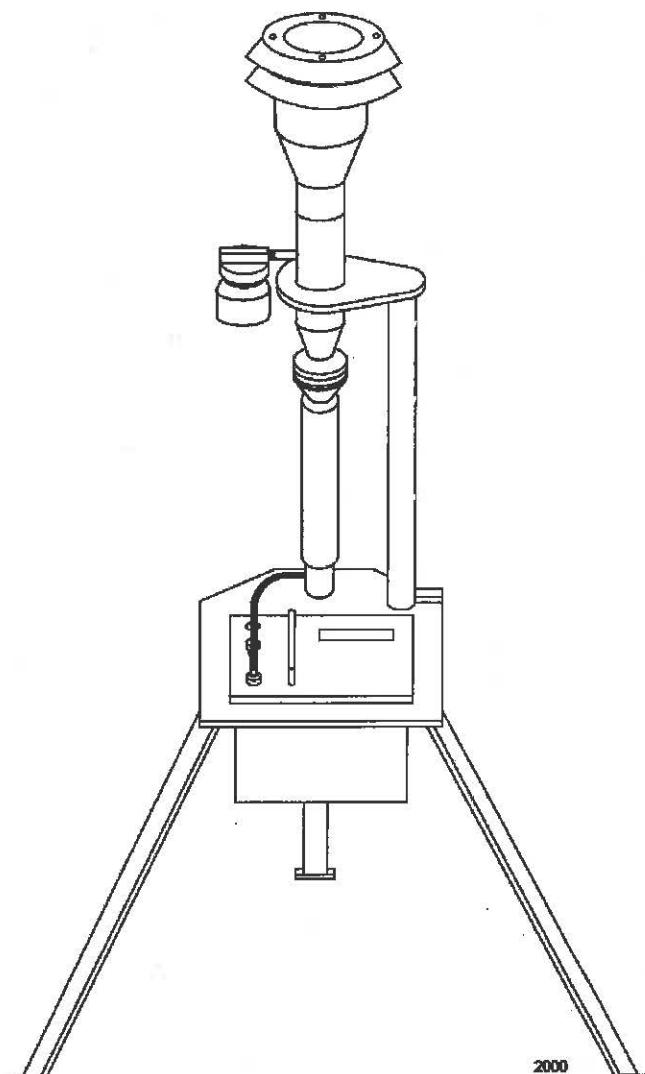


FIGURE 2. PQ167R with Mounting Stand
(Cr+6 filter holder apparatus replaces PM10 inlet head and filter cassette module
and downtube assembly brace are not used)



II. INSTALLATION

A. Sampler Siting

Check the areas for safety. Ensure there will be enough room for the operator to move freely while working, and ensure physical conditions of the location will allow the operator to work safely.

The sampler should be set in a location unobstructed from any side. No tree limbs or other hanging obstructions should be above the sampler. It is suggested that the horizontal distance from the sampler to the closest vertical obstruction higher than the sampler be at least twice the height of the vertical obstruction. There should be no sources located nearby that may bias sampling measurements.

Locate the sampler on a reasonably level structure at a height between two (2) and fifteen (15) meters above the ground.

B. Sampler Installation

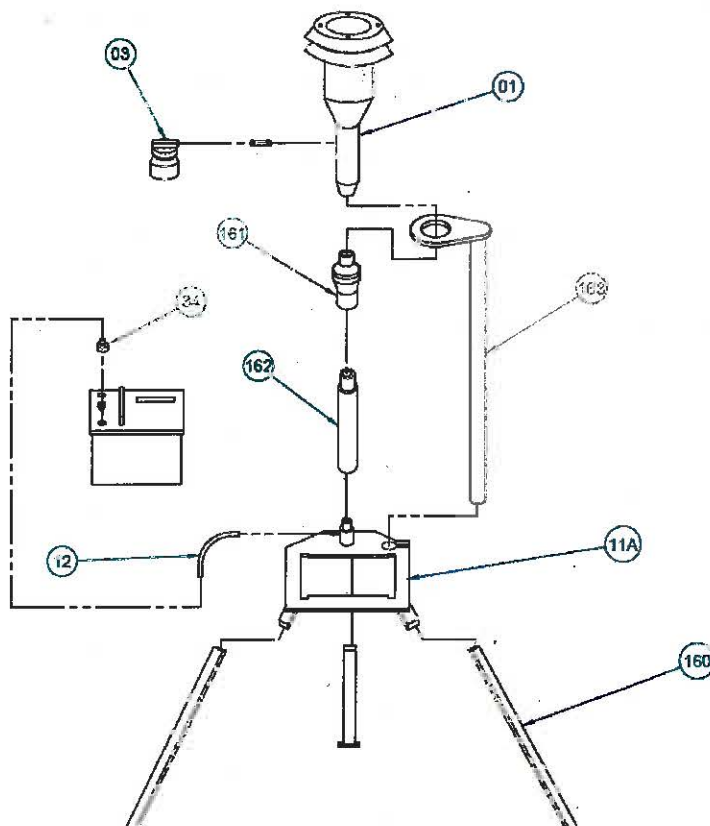
Assemble the sampler according to Figure 3 below omitting the installation of the PM10 inlet head, filter cassette holder assembly, and downtube assembly brace. For detail and illustration, refer to the BGI PQ167 Quick Start document, pages 2 through 8.

Cr+6 Retrofit Instructions

1. The sampling unit, at this point, should have legs mounted on the stand, and the pump and power components should be secured in the stand according to the PQ167 Quick Start document. The downtube, PM10 inlet head, and filter cassette holder assembly should NOT be installed.
2. Install the downtube on the top of the cylindrical mount on the stand. The mount should have tubing leading from the port on its side to the inlet on the pump module.
3. The total ERG Cr+6 filter holder apparatus consists of a BGI flow adapter with shut-off valve, stainless steel connector fitting, a length of "U" shaped stainless steel ¼ inch tubing, ERG filter assembly, and a glass funnel. **The ERG filter assembly and glass funnel will be provided for each sampling run and should not be installed until a sampling run is setup.** Place this apparatus (without ERG filter assembly) on the top of the downtube, and ensure that the shut-off valve is in the open position.

4. The open end of the stainless steel tubing should be capped when sampling is not in progress to prevent contamination.

Figure 3. Sampler Assembly Diagram
(Cr+6 filter holder apparatus replaces PM10 inlet head and filter cassette module and downtube assembly brace are not used)



- 01 PM10 Inlet head
- 03 Water collection bottle
- 11A Tripod frame
- 12 Rubber hose
- 34 Hose adapter
- 160 Sampler leg
- 161 Filter cassette holder assembly
- 162 Downtube
- 163 Downtube assembly brace

Place and level the sampler on site. To secure the sampler and protect membrane roofs, 2 x 4 wooden studs may be cut into one foot sections and fastened to the feet of the legs using lag bolts. Place sand bags on these skids to prevent tipping of the sampler.

Connect the sampler to a grounded electrical outlet with 115 volts, and at least 5 amp service. Protect the connector from precipitation by fastening beneath the sampler or wrapping it with plastic tape.

If operating using a deep cycle marine battery for power, install the external power cord by screwing the round harness into the "utility adapter" port on top of the sampler. Attach the positive and negative contacts to the deep cycle marine battery and secure. A fully charged battery should provide power for at least 2 sampling runs. Depending on the battery available, more consecutive runs may be possible. Store the battery in a plastic container near the sampler to conceal and protect it from the weather.

If collocated samplers will be located at the site, the two samplers must be within four (4) meters of each other, but outside of two (2) meters. The inlet heights must be within one (1) meter vertically.

III. OPERATING PROCEDURE

A. Equipment and Supplies

BGI PQ167R
ERG Cr+6 filter holder apparatus
Flow calibrator
Logbook
ERG filter assembly with glass funnel
Cooler with ice substitute
Powderfree gloves
ERG sample paperwork

B. Sampler and Sample Media Receipt Activities

1. Plug sampler into AC power and charge the internal battery for at least 24 hours.
2. Check parts and components against the packing list.
3. After charging, ensure sampler will power up and that the main screen is operational.
4. The sampler may arrive with a default flow rate of 16.7 Lpm. If

during the initial verification, the sampler's target flow rate is displayed as 16.7 Lpm, it must be changed to 15 Lpm. Proceed directly to the calibration section of the SOP for direction in making the change.

5. The ERG Cr+6 Filter Holder Modules will arrive to the field office in a cooler with frozen ice substitutes. The modules will have paperwork designating them for a specific site and run day. **The modules must be kept in a freezer prior to sampling and kept cold during transport to the monitoring site for run preparation.**
6. It is highly recommended that there be as little time as reasonably possible between preparing the sampler for the next run (i.e. loading the sample media); the day prior is optimal.
7. **Samples must be retrieved the day following sampling, preferably NLT NOON LST, and returned to ERG cold using the ice substitutes provided.**

C. Verification

NOTE: THE PQ100 DOES NOT REQUIRE A LEAK TEST. CUTTING OFF THE FLOW OF AIR BY COVERING OR RESTRICTING THE AIR FLOW TO THE INLET WILL CAUSE DAMAGE TO THE INTERNAL PUMP AND WILL VOID THE WARRANTY.

To VERIFY flow:

1. Install a test ERG Cr+6 filter holder module if available. If a test module is not available, the module to be used for the next sample day is acceptable; however, the module must be used immediately following the verification/calibration.
2. Attach a NIST traceable flow standard to the inlet of the filter module. Ensure the flow standard is on and has equilibrated to ambient conditions.
3. Turn on the PQ167R by pushing the "ON/OFF" button. If a message is blinking on the display, press "ENTER" to proceed to the "MAIN IDLE DISPLAY".

The screen display should read:

ET0000Min TS00.00M (Date)
Q(Flow)Lpm T(Time) Bty(Capacity)%

(Date) – today's date in military notation; e.g., 01JAN= January 1st

(Flow) - the current flow rate selected to be regulated.

(Time) - military time; e.g., 13:08= 13 Hours 8 Minutes or 1:08 PM

(Capacity) - remaining charge in the internal battery.

4. Press SETUP three times until the Set START DATE and TIME screen appears: The screen should appear as below:

Set START DATE and TIME
(Date) (Time) Off

5. The word, "Off", should be displayed in the lower right corner of the screen. The bottom line of the display should be flashing. If "On" is displayed, press the "ENTER" button until "On" stops flashing. Then toggle to "Off" by pressing the + or - buttons.
6. Press the "SETUP" button twice to get to the "MAIN IDLE DISPLAY"
7. Press the "RUN/STOP" button to activate the pump.
8. Allow the pump to stabilize for at least 2 minutes.
9. If the measured flow and the flow indicated on the flow standard are within 4%, the sampler's calibration is acceptable. If the flow is outside 4%, the unit must be recalibrated.
10. Press the "RUN/STOP" button to turn off the pump.

D. Calibration

NOTE: THE PQ100 DOES NOT REQUIRE A LEAK TEST. CUTTING OFF THE FLOW OF AIR BY COVERING OR RESTRICTING THE AIR FLOW TO THE INLET WILL CAUSE DAMAGE TO THE INTERNAL PUMP AND WILL VOID THE WARRANTY.

To CALIBRATE flow:

1. Install a test ERG Cr+6 filter holder module if available. If a test module is not available, the module to be used for the next sample day is acceptable; however, the module must be used immediately following the verification/calibration.
2. Press "SETUP". The screen will read; "Select FLOW RATE"
3. From the "MAIN IDLE DISPLAY" press the "Setup" key once until the message below appears;

Select FLOW RATE

The Target Q should read 15.0 Lpm. If it does not read 15.0 Lpm, set TARGET FLOW RATE to 15.0 Lpm by pressing ENTER. The whole number value will remain on constant while the tenths still blink); use "+" or "-" to increase or decrease until 15 is displayed. Press ENTER (Tenths value will now remain constant while whole number blinks); use "+" or "-" to increase or decrease until .0 is displayed.

4. From the "Select FLOW RATE" message screen, press both the "Reset" key and the "Run/Stop" key simultaneously to enter the calibration mode and the message below will appear;

CALIBRATE Target=15.0 Lpm

5. Press the "RUN/STOP" button to activate the pump and the message below will appear:

CALIBRATE Target = 15.0 Lpm
Reference Q.. XX.X

The Reference Q is an approximate flow rate used only as a visual aid in finding the corrected flow on the calibration device. This value may indicate 5 to 15% error. This is for reference only!

6. Use the "+/-" keys to move the pump speed up or down until the calibration device indicates the desired flow rate.
7. When a stable reading has been achieved, press the "ENTER" key to store the flow rate.
8. Exit the Setup menu and return to the "MAIN IDLE DISPLAY". CALIBRATIONS ARE NOT AFFECTED UNTIL THE ENTER KEY IS PRESSED AND THE PUMP IS RUNNING.
9. Record pre- and post- flow measurements and adjustments in the logbook.

E. Conducting the Sampling Event**Site Arrival Daily Activities**

1. Visually inspect and ensure all O-rings are in place and secure. Replace if necessary.

2. Always ensure that samples and unused ERG Cr+6 Filter Holder Modules are transported to and from the site cold.
3. Confirm all cables (electrical connections) are secure, and that exterior connections are protected from the elements.
4. Record activities, site observations, and maintenance activities in logbook.

Preparing Sampler for a Sampling Event

1. Prepare sample paperwork. On the ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET, complete the "Lab Pre-Samp." and "Field Setup" sections. Record any pertinent observations in the notes section at the bottom of the form.
2. Turn on the PQ167R by pushing the "ON/OFF" button. If a message is blinking on the display, press "ENTER" to proceed to the "MAIN IDLE DISPLAY". Then press "RESET" to clear prior run data.
3. Conduct an initial flow check (verification) by following the instructions in section **C. Verification**. Record the measurement from the flow standard on the ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET under the "Field Setup" section on the "Initial Rotameter Setting".
4. Following the flow check, the screen display should read:

ET0000Min TS00.00M (Date)
Q(Flow)Lpm T(Time) Bty(Capacity)%

(Date) - today's date in military notation; e.g., 01JAN= January 1st
(Flow) - the current flow rate selected to be regulated.
(Time) - military time; e.g., 13:08= 13 Hours 8 Minutes or 1:08 PM
(Capacity) - remaining charge in the internal battery.
5. Press "SETUP". The screen will read; "Select FLOW RATE"
The flow rate value will be blinking.
6. The flow rate should read 15.0 Lpm. If it does not read 15.0 Lpm, the unit must be calibrated to 15.0 Lpm. See calibration section for adjusting target flow rate and calibration.
7. Press "SETUP". This is the date and time screen.

The screen should read;

Set DATE and TIME
(dd) (mmm) (yyyy) (time)

To change the Date and Time;

TIP: Only the field not blinking can be adjusted. Push enter to move to the next field.

- a. DAY: Press ENTER and change by pressing the + or - key. When the day is correct, press ENTER.
 - b. MONTH: To change, press + or - key. When correct, press ENTER.
 - c. YEAR: To change, press + or - key. When correct, press ENTER.
 - d. TIME (hrs): To change, press + or - key. When correct, press ENTER.
 - e. TIME (min): To change, press + or - key. When correct, press ENTER.
8. When date and time are correct press "SETUP"
 9. This is the sample start screen which reads;

Set START DATE and TIME
(dd) (mmm) 00:00 Off

This screen allows you to set a start date and time for a sampling run. The default is set to midnight the next day. To designate your own start date and time:

- a. DAY: Press ENTER and change by pressing the + or - key. When the day is correct, press ENTER.
- b. MONTH: To change, press + or - key. When correct, press ENTER.
- c. YEAR: To change, press + or - key. When correct, press ENTER.
- d. TIME (hrs): To change, press + or - key. When correct, press ENTER.

- e. TIME (min): To change, press + or - key. When correct, press ENTER.
- f. Enable the run by setting the "On/Off" function on the screen to "On".

WARNING: The sampler will not automatically activate if this option is set to "Off".

10. Press "SETUP"

The screen will read;

Set RUN TIME
Hours: 24 Min: 00 On

Set to 24 hours 0 minutes. The default is always 24 hrs 0 min, the required sample duration. If the sample time needs to be modified, adjust as instructed in step 6 and 8.

11. Press "SETUP". The screen will return to the "MAIN IDLE DISPLAY"

WARNING: DO NOT PRESS THE RESET BUTTON AT THIS TIME AS THE START TIME AND RUN TIME WILL DEFAULT.

12. Press "RUN/STOP"

If the START TIME ENABLE is set to "On" then the message "Alarm Triggered Run..." followed by "PQ100 Powering Down.." will appear briefly. The PQ100 is now waiting for the internal real time clock to achieve the designated start time and will then power itself on and begin the sampling run. If the START TIME ENABLE is set to "Off" then the pump will begin to run immediately. If this occurs, press RUN/STOP and begin back at step 2 ensuring START TIME ENABLE is set to "On".

Installing the ERG Cr+6 Filter Holder Module

NOTE: Gloves must be changed for each sample, i.e. between retrieving a sample and preparing a new run gloves MUST be changed to prevent cross contamination.

1. Remove the sample inlet cover on the stainless steel probe and make sure there is no contamination on the probe.

2. Put on a clean pair of powderfree gloves
3. Take the ERG Cr+6 Filter Holder Module storage container from the cooler and carefully remove the module. The module may be in a plastic bag. Return the bag to the container for use in the collection procedure.
4. Make sure the glass funnel is securely attached to the filter holder. Loosen the small top nut on the filter container. Arrows will be present on the filter holder showing air flow direction and they should always point to the end of the sample probe line.
5. Holding the module with the glass funnel facing down, slide the probe into the top fitting of the filter module and tighten the nut. Tighten the nut until the ERG Cr+6 Filter Holder Module is securely fastened to the probe. Do not overtighten the plastic nut.

NOTE: If running a field blank, repeat steps 1 through 5, count to 10, and then remove the field blank filter holder module and place it back into the antistatic bag. Label the bag to designate the filter module as a field blank. Log the filter ID as field blank in the comments section of the ERG Hexavalent Chromium Sample Data Sheet. The field blank must be run before the sample filter module is fastened to the probe.

Sample Recovery and Data Collection

NOTES:

- I. **Samples must be retrieved the day following sampling, preferably NLT NOON LST, and returned to ERG cold using the ice substitutes provided.**
 - II. **Gloves must be changed for each sample, i.e. between retrieving a sample and preparing a new run, to prevent cross contamination.**
1. On the ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET, fill in the "Field Recovery" section. Be sure to fill in the "Recovery Date", "Recovery Time", "Elapsed Time" (ETXXXXMin from sampler), and circle a "Status" selection. This information will be on the "MAIN STATUS SCREEN".
 2. Conduct a final flow check (verification) by following the instructions in section C. **Verification.** Record the measurement from the flow standard on the ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET under the "Field Setup" section, "Final Rotameter Reading".

3. Put on a clean pair of powderfree gloves
4. Take the module storage container from the cooler, open, and set aside.
5. While holding the ERG Cr+6 Filter Holder Module, loosen the top nut holding the module to the sample inlet and slide the module off the stainless steel probe.
6. Place the ERG Cr+6 Filter Holder Module including glass funnel in the plastic bag and place back into the storage container. Place the storage container into a cooler with ice substitutes.
7. Place cover back on end of probe line.
8. Data may be downloaded to a laptop using the PQ100/200 DOWNLOAD SOFTWARE. ERG does not require this data, but direction can be found in the BGI PQ167 Quick Start document, pages 16 and 17.

Sample Shipping

The ERG Cr+6 Filter Holder Module container must be packed in a cooler with ice substitutes and shipped overnight cold to ERG. The sample paperwork must be included in the shipment. Use the pre-filled out FedEx label provided by ERG, and fill out the "Sender" section with the sampling agency's address and phone number. Send priority overnight to ERG.

If the shipping form is lost, use the address below for shipping to ERG, and contact them directly for the FedEx accounting.

Address: ERG
601 Keystone Park Drive
Suite 700
Morrisville, NC 27560
919-468-7924

IV. QUALITY ASSURANCE

To ensure that quality data is being collected the following checks should be considered:

A. Flow Calibration

A flow verification must be completed at the beginning of the study period. If the verification does not compare within 4%, the flow must be calibrated. Document all quality assurance activities in the logbook.

B. Flow Verifications

The flow must be verified or checked at the beginning and end of the sampling event to determine an average sample flow. Document all quality assurance activities and observations in the logbook.


C. Independent Audits

If possible, it is recommended that an independent flow check of the sampler be conducted at some point during the study. This check may be conducted by a state or local agency's quality assurance team or independent audit program.

V. DATA FORMS

All sample related run data forms will be supplied by ERG. Check the data sheets for completion after every setup or retrieval event. The operator is expected to keep a logbook to document all site activities, quality assurance activities, and sampling activities. The ERG AMBIENT HEXAVALENT CHROMIUM DATA SHEET is attached below.

ERG Ambient Hexavalent Chromium Sample Data Sheet

		ERG Lab ID # _____	
AMBIENT HEXAVALENT CHROMIUM DATA SHEET			
Lab Pre-Sampling	Site Code: _____		Collection Date: _____
	City/State: _____		Primary Event (Y/N): _____
	AQS Code: _____		Collocated Event (Y/N): _____
Field Setup	Site Operator: _____		System #: _____
	Set-Up Date: _____		Elapsed Timer Reset (Y/N): _____
	Collection Date: _____		
	Batch I.D. No.: _____		
	Initial Rotameter Setting (C.O. B.): _____ (After 5 minutes warm-up)		
	Programmed Start Time: _____		Programmed End Time: _____
Field Recovery	Recovery Date: _____		Recovery Time: _____
	Final Rotameter Reading (C.O.B.): _____ (After 5 minutes warm-up)		
	Elapsed Time: _____		Status: Valid Void (Circle one)
Lab Recovery	Received by: _____		Date: _____
	Status: Valid Void (Circle one)		Refrigerator No: _____
	Temperature: _____		
	If void, why: _____		
	Collection Time (Minutes): _____		
Flowrate (L/min): _____			
Total Volume of Air Sampled (m ³): _____			

Comments: _____

White: Sample Traveler

Canary: Lab Copy

Pink: Field Copy

APPENDIX D
COLLECTION AND ANALYSIS
OF
HEXAVALENT CHROMIUM IN AMBIENT AIR



www.erg.com

January 9, 2007

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

Prepared by J. Swift, M. Howell, D. Tedder

Eastern Research Group, 601 Keystone Park Drive, Suite 700, Morrisville, NC 27560

ABSTRACT

Hexavalent chromium (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 Cr^{6+} monitoring. Attempts to sample and analyze 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 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 Cr^{6+} stability with less than 30 Relative Percent Difference (RPD). The stability of Cr^{6+} was also evaluated using collocated samplers with spiked and blank filters. Data, using improvements to the Cr^{6+} sampling and analysis procedure for the NATTS, will be presented to show the recent history of 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 (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 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[®]; and
- Polyvinyl Chloride (PVC).

The results of this study show that the best media is the cellulose filters. The Teflon[®] 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 [®]
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 Cr⁶⁺ in the background contamination study. To determine if the preferred filter preparation method would interfere with recovery of Cr⁶⁺ samples, 32 bicarbonate coated cellulose and 32 Teflon filters were prepared and spiked. All filters were spiked with 2.5 total ng Cr⁶⁺ 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: Cr⁶⁺ Filter Stability Study

Spiked Samples	Cellulose Filters		Teflon Filters	
	Average Concentration (total ng)	Percent Recovery	Average Concentration (total ng)	Percent Recovery
Stored at Room Temperature				
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	77 ± 10%	2.53	110 ± 3%
Stored at -18°C				
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 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 Cr^{6+} . All filters were spiked with 10 total ng of Cr^{6+} . Four separate sets of filters were spiked with 10 total ng of 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 Cr^{6+} .

Method Validation

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

Cr^{6+} 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 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^{6+} 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: Cr⁶⁺ 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)
Spiked and placed in Freezer after Days presented and analyzed after sample pickup.				
33 Hours	1.76	70%	30% ± 6%	8%
57 Hours	1.27	51%	49% ± 6%	13%
81 Hours	1.19	48%	53% ± 4%	9%
105 Hours	1.05	42%	58% ± 5%	11%

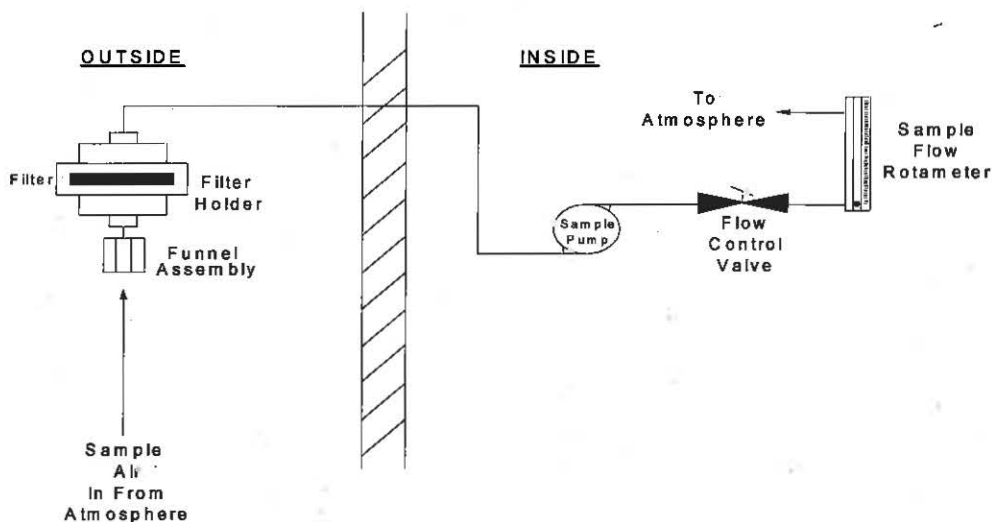
NOTE: Results listed in **bold** are outside the required relative percent difference (RPD) of 25%.

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 Cr⁶⁺ can be considered stable and can be left on the cellulose filters for up to 11 days (as presented in Table 2).

Cr⁶⁺ 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 Cr⁶⁺ sampling layout.

Figure 1. Cr⁶⁺ Sampler Layout



Cr⁶⁺ 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 m³ sample is 0.12 ng/m³. 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 ³)	Humidity	Temperature	Comments		
1	21.57	88%	48.8°F	Rain	28	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	73	27%
MS – 3		(37% - 100%)	(34°F - 42.1°F)		9.1	109%
4	21.7	42%	35.3°F	Cloudy to Clear	58	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%.

Cr⁶⁺ Sampling Study – Teflon® 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	24	76%
Teflon Set 2		64	36%
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		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%.

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 Cr^{6+} collection.

Cr^{6+} 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 m³,
- Particulate Check - the particulate reacted with the Cr^{6+} to reduce it to 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 Cr^{6+} to Cr^{3+} .

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

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

Sample	Spiked in total ng	Results in total ng	Percent Recovery
Volume Check – collected at 11.5 m ³ (instead of standard 21.6 m ³)			
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^{6+} in their samples. The results are presented in Table 7 below.

Table 7: Comparison of Cr^{6+} Recovery on Cellulose and Teflon Filters

Site	Total # of Samples	Cellulose Concentration Higher (>30% RPD)	Similar Results on Cellulose and Teflon ($\pm 30\%$ RPD)	Teflon Concentration Higher (>30% RPD)
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^{6+} 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^{6+} 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^{6+} to Cr^{3+} . 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^{6+} 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^{6+} more efficiently for real-world ambient samples.

FIELD SAMPLE RESULTS FOR HEXAVALENT CHROMIUM

Twenty-two National Monitoring Program (NMP) sites collected Cr^{6+} 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.

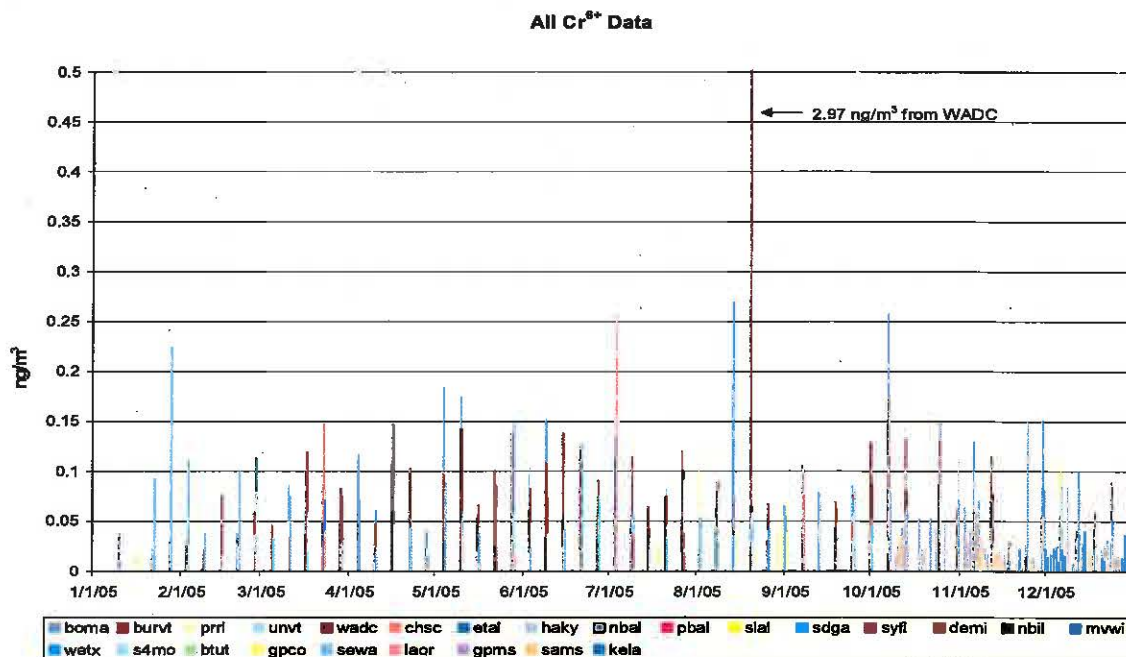
Sites	% Frequency	Maximum Value (ng/m ³)	Minimum Value (ng/m ³)	Median (ng/m ³)	Average (ng/m ³)
Roxbury, MA	78%	0.269	0.017	0.048	0.071
Burlington, VA	80%	0.147	0.003	0.054	0.065
Providence, RI	100%	0.119	0.006	0.023	0.028
Underhill, VT	32%	0.101	0.005	0.027	0.034
Washington, DC	54%	2.970	0.010	0.026	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 Cr⁶⁺ 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 Cr⁶⁺ measurements, 67% of these results were detects and 9% of these concentrations were below the MDL. The average Cr⁶⁺ concentration was 0.044 ng/m³.

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

Washington, DC, at 2.97 ng/m³. 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 Cr⁶⁺ 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%	35%	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	41%	41%	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	33%	33%	0%
St. Louis, MO	4	4%	8%	11%
Grand Junction, CO	5	0%	10%	22%
Seattle, WA	6	10%	32%	55%
Gulf Port, MS	7	27%	27%	25%
Stennis Airport, MS	1	19%	19%	0%
Kenner, LA	4	17%	35%	43%
Average	4	8%	17%	16%

CONCLUSIONS

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

ERG laboratory's detection limit for acrolein is 0.012 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 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 Cr^{6+} negative bias (loss) (up to 20% on the first day).
- All samples must be frozen after collection to reduce the risk of Cr^{6+} loss.

Analysis of sodium bicarbonate coated cellulose filters containing known concentrations of 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 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

The authors would like to express their appreciation for the hard work and dedication shown by the U.S. EPA, OAQPS staff and Eastern Research Group's laboratory.

REFERENCES

1. California Air Resources Board, Standard Operating Procedure for the Analysis of Hexavalent Chromium at Ambient Atmospheric Levels by Ion Chromatography, MLD039, Revision 3. March 2002.
2. Swift, J.; Merrill, R.; Tedder, D. Hexavalent Chromium Method Development. J. Homolya, Work Assignment Manager, U.S. Environmental Protection Agency, Research Triangle Park, NC.

3. Swift, J.; Merrill, R. Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air Analyzed By Ion Chromatography (IC). J. Homolya, Work Assignment Manager, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Appendix E

**Region 7 Standard Operating Procedure No. 2314.06A,
"Measurement of Hexavalent Chromium Using the BGI PQ167R
Low Volume Sampler,"
(U. S. EPA, 2011)**

STANDARD OPERATING PROCEDURE

NO. 2314.06A

Measurement of Hexavalent Chromium Using the BGI PQ167R Low Volume Sampler

November 7, 2011

Leland P. Grooms
ENSV/CARB/ASRS

Approved

Peer Reviewer

Date

Chemical Analysis and Response Brach Manager

Date

Independent Quality Assurance Reviewer

Date

Table of Contents

A.	Purpose.....	3
B.	Applicability.....	3
C.	Summary of Procedure.....	3
D.	Definitions and Acronyms	4
E.	Personnel Qualifications	4
F.	Health and Safety.....	4
G.	Cautions	4
H.	Interferences.....	5
I.	Equipment and Supplies	5
J.	Procedures.....	5
1.	Siting the Monitor.....	5
2.	Set-up	5
3.	Operation	7
4.	Verification	7
5.	Calibration Procedures.....	9
6.	Conducting the Sampling	10
7.	Installing the ERG Cr+6 Filter Holder.....	12
8.	Sample Recovery and Data Collection.....	13
9.	Sample Shipping.....	14
K.	Records Management.....	14
L.	Quality Assurance / Quality Control.....	14
M.	References.....	14

Attachments

None

A. Purpose

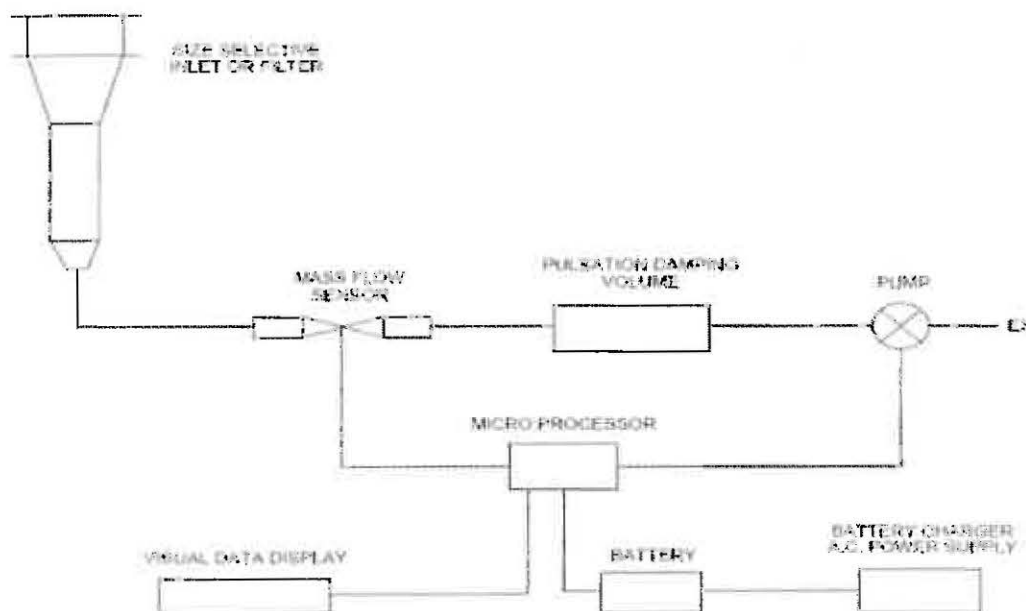
This procedure is designed to provide instruction on collecting hexavalent chromium (Cr+6) in air using the BGI PQ167R ambient air sampler for metals analysis. These procedures are not intended to replace the manufacturer's operations or technical manuals. This SOP is designed to be a step by step method for operating the sampler to be used in conjunction with the manufacturer's operator's manual. Maintenance and troubleshooting should be conducted using the BGI167R operator's manual.

B. Applicability

This SOP is intended to be used during the 2011-2012 CertainTeed ambient air sampling project.

C. Summary of Procedure

The operating principle of the BGI PQ167R can be appreciated by referring to the block diagram in Figure 1 below. The BGI PQ167R is an "Intelligent Air Pump" that can monitor its own airflow rate and thereby adjust the pump speed to compensate for changes in load pressure and/or other forces which would otherwise hamper the flow of air through a filter (or sample collector). The PQ100 unit can be programmed to begin its sampling job at a specific date, time, and stop sampling after the user defined run time is depleted. Air is drawn by the pump through a size selective inlet device and/or filter. It then passes inside the instrument housing to a Mass Flow Sensor. The signal generated by the sensor is then routed to a microprocessor which determines if the flow is at the set value and adjusts the pump speed to maintain the correct flow rate. Because the flow sensor is extremely sensitive and all pumps produce pulsation to some degree, a pulsation damping volume has been introduced to control this effect. The microprocessor not only controls the flow rate accurately and precisely to the set point but also performs several other functions. These include turning the instrument on at a preselected time and running it for a selected interval. The flow is maintained by the processor to a designated pressure and temperature value. A pulse width modulated signal is configured and sent to the pump motor in a constantly updated manner based on signal information received from the Mass Flow Sensor. The microprocessor also stores all parametric information generated during the run period and configures it for presentation on the visual display and downloading to the software provided with the instrument. The system is completed by its 12 volt battery and external battery charger/A.C. power supply. The power supply function permits operation if desired with no battery whatsoever.



(Figure 1)

D. Definitions/Acronyms

1. ERG: Eastern Research Group
2. SOP: Standard Operating Procedure

E. Personnel Qualifications

Only persons familiar with procedures described in the SOP should use the BGI PQ167R.

F. Health and Safety Warnings

1. The BGI PQ167R instrument is not intrinsically safe and should not be used in explosive environments.
2. Whenever the BGI PQ167R is to be installed at a height greater than 3 meters it must be securely bolted in place or anchored in some way.

G. Cautions

Siting instructions should be followed carefully in order to obtain useful data. When determining appropriate sites to place this instrument, both project objectives (how will the data be used and what information is needed?) and site conditions (where are obstructions relative to the monitor?) need to be considered.

H. Interference

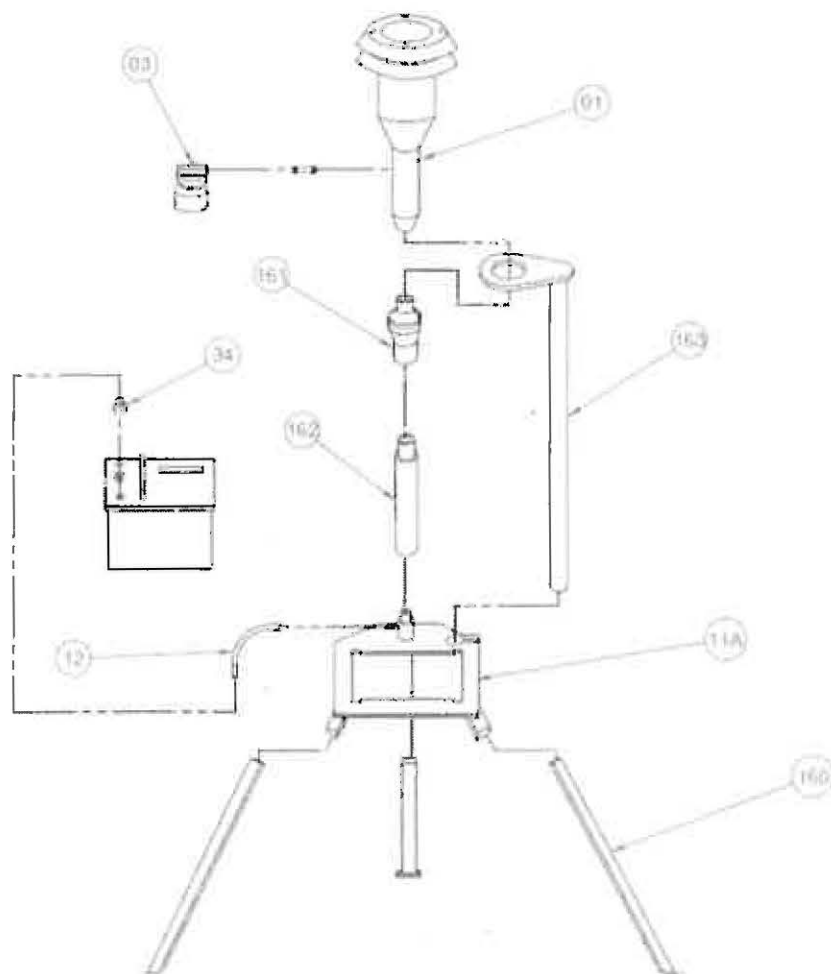
The instrument's electronic and mechanical parts should be protected against heavy rain, snow and inclement weather.

I. Equipment and Supplies

1. BGI PQ167R
2. ERG Cr+6 filter holder apparatus
3. Flow calibrator
4. Logbook
5. ERG filter assembly with glass funnel
6. Cooler with ice substitute
7. Powder-free gloves
8. Sample processing paperwork

J. Procedures

1. Siting the Monitor – The optimal site for ambient air monitoring is in a location where the BGI PQ167R instrument is near the breathing zone. If the BGI PQ167R is placed on a roof or other structure there must be a minimum of 2 meters of separation from walls, parapets, penthouses, etc. If the BGI PQ167R is placed near trees it should be placed at least 20 meters from the drip line of the tree. In general, the BGI PQ167R must be located in an area free from obstructions. The distance between obstructions and the sampler must be at least twice the height of the obstruction. If possible, the BGI PQ167R should not be placed near busy roads (more than 3,000 vehicles per day), if placing the BGI PQ167R near a lower traffic road is unavoidable then it should be placed at least 5 meters from the edge of the nearest traffic lane.
2. Setup
 - a. Assemble the sampler according to Figure 2 below omitting the installation of the PM10 inlet head, filter cassette holder assembly, and downtube assembly brace. For detail and illustration, refer to the BGI PQ167 Quick Start document, pages 2 through 8.
 - b. Place and level the sampler on site. To secure the sampler and protect membrane roofs, 2 x 4 wooden studs may be cut into one foot sections and fastened to the feet of the legs using lag bolts. Place sand bags on these skids to prevent tipping of the sampler.
 - c. Connect the sampler to a grounded electrical outlet with 115 volts, and at least 5 amp service. Protect the connector from precipitation by fastening beneath the sampler or wrapping it with plastic tape.



(Figure 2)

- d. If operating using a deep cycle marine battery for power, install the external power cord by screwing the round harness into the “utility adapter” port on top of the sampler. Attach the positive and negative contacts to the deep cycle marine battery and secure. A fully charged battery should provide power for at least 2 sampling runs. Depending on the battery available, more consecutive runs may be possible. Store the battery in a plastic container near the sampler to conceal and protect it from the weather.
- e. If collocated samplers will be located at the site, the two samplers must be within four (4) meters of each other, but outside of two (2) meters. The inlet heights must be within one (1) meter vertically.
- f. The sampling unit, at this point, should have legs mounted on the stand, and the pump and power components should be secured in the stand

according to the PQ167 Quick Start document. The downtube, PM10 inlet head, and filter cassette holder assembly should NOT be installed.

- g. Install the downtube on the top of the cylindrical mount on the stand. The mount should have tubing leading from the port on its side to the inlet on the pump module.
- h. The total ERG Cr+6 filter holder apparatus consists of a BGI flow adapter with shut-off valve, stainless steel connector fitting, a length of "U" shaped stainless steel ¼ inch tubing, ERG filter assembly, and a glass funnel. The filter assembly and glass funnel will be provided for each sampling run and should not be installed until a sampling run is setup. Place this apparatus (without ERG filter assembly) on the top of the downtube, and ensure that the shut-off valve is in the open position.
- i. The open end of the stainless steel tubing should be capped when sampling is not in progress to prevent contamination.

3. Operation

- a. Plug sampler into AC power and charge the internal battery for at least 24 hours.
- b. Check parts and components against the packing list.
- c. After charging, ensure sampler will power up and that the main screen is operational
- d. The sampler may arrive with a default flow rate of 16.7 Lpm. If during the initial verification, the sampler's target flow rate is displayed as 16.7 Lpm, it must be changed to 15 Lpm. Proceed directly to the calibration section of the SOP for direction in making the change.
- e. The ERG Cr+6 Filter Holder Modules will arrive to the field office in a cooler with frozen ice substitutes. The modules will have paperwork designating them for a specific site and run day. The modules must be kept in a freezer prior to sampling. During transport to the monitoring site for run preparation, the filters must be kept cold as well. Samples must be returned to ERG cold using ice substitutes.

4. Verification (Note: The PQ167 does not require a leak test. Cutting off the flow of air by covering or restricting the air flow to the inlet will cause damage to the internal pump and will void the warranty).

- a. Install a test ERG Cr+6 filter holder module if available. If a test module is not available, the module to be used for the next sample day is acceptable; however, the module must be used immediately following the verification/calibration.
- b. Attach a NIST traceable flow standard to the inlet of the filter module. Ensure the flow standard is on and has equilibrated to ambient conditions.
- c. Turn on the PQ167R by pushing the "ON/OFF" button. If a message is blinking on the display, press "ENTER" to proceed to the "MAIN IDLE DISPLAY".

The screen display should read:

ET0000Min TS00.00M (Date)

Q(Flow)Lpm T(Time) Bty(Capacity)%

(Date) – today's date in military notation; e.g., 01JAN= January 1st

(Flow) - the current flow rate selected to be regulated.

(Time) - military time; e.g., 13:08= 13 Hours 8 Minutes or 1:08 PM

(Capacity) - remaining charge in the internal battery.

- d. Press SETUP three times until the Set START DATE and TIME screen appears: The screen should appear as below:

Set START DATE and TIME

(Date) (Time) Off

- e. The word, "Off", should be displayed in the lower right corner of the screen. The bottom line of the display should be flashing. If "On" is displayed, press the "ENTER" button until "On" stops flashing. Then toggle to "Off" by pressing the + or – buttons.
- f. Press the "SETUP" button twice to get to the "MAIN IDLE DISPLAY"
- g. Press the "RUN/STOP" button to activate the pump.
- h. Allow the pump to stabilize for at least 2 minutes.
- i. If the measured flow and the flow indicated on the flow standard are within 4%, the sampler's calibration is acceptable. If the flow is outside 4%, the unit must be recalibrated.

j. Press the "RUN/STOP" button to turn off the pump.

5. Calibration (Note: The PQ167 does not require a leak test. Cutting off the flow of air by covering or restricting the air flow to the inlet will cause damage to the internal pump and will void the warranty).

a. Install a test ERG Cr+6 filter holder module if available. If a test module is not available, the module to be used for the next sample day is acceptable; however, the module must be used immediately following the verification/calibration.

b. Press "SETUP". The screen will read; "Select FLOW RATE"

c. From the "MAIN IDLE DISPLAY" press the "Setup" key once until the message below appears;

Select FLOW RATE

The Target Q should read 15.0 Lpm. If it does not read 15.0 Lpm, set TARGET FLOW RATE to 15.0 Lpm by pressing ENTER.

The whole number value will remain on constant while the tenths still blink); use "+" or "-" to increase or decrease until 15 is displayed.

Press ENTER (Tenths value will now remain constant while whole number blinks); use "+" or "-" to increase or decrease until .0 is displayed.

d. From the "Select FLOW RATE" message screen, press both the "Reset" key and the "Run/Stop" key simultaneously to enter the calibration mode and the message below will appear;

CALIBRATE Target=15.0 Lpm

e. Press the "RUN/STOP" button to activate the pump and the message below will appear:

CALIBRATE Target = 15.0 Lpm

Reference Q.. XX.X

The Reference Q is an approximate flow rate used only as a visual aid in finding the corrected flow on the calibration device. This value may indicate 5 to 15% error. This is for reference only!

f. Use the "+/-" keys to move the pump speed up or down until the calibration device indicates the desired flow rate.

- g. When a stable reading has been achieved, press the "ENTER" key to store the flow rate.
- h. Exit the Setup menu and return to the "MAIN IDLE DISPLAY".

CALIBRATIONS ARE NOT AFFECTED UNTIL THE ENTER KEY IS PRESSED AND THE PUMP IS RUNNING.

- i. Record pre- and post- flow measurements and adjustments in the logbook.

6. Conducting the Sampling Event

- a. Visually inspect and ensure all O-rings are in place and secure. Replace if necessary.
- b. Always ensure that samples and unused ERG Cr+6 Filter Holder Modules are transported to and from the site cold.
- c. Confirm all cables (electrical connections) are secure, and that exterior connections are protected from the elements.
- d. Record activities, site observations, and maintenance activities in logbook.
- e. Turn on the PQ167R by pushing the "ON/OFF" button. If a message is blinking on the display, press "ENTER" to proceed to the "MAIN IDLE DISPLAY". Then press "RESET" to clear prior run data.
- f. Conduct an initial flow check (verification) by following the instructions in Section 4. Verification. Record the measurement from the flow standard on the *Ambient Hexavalent Chromium Data Sheet* under the "Field Setup" section on the "Initial Rotameter Setting".
- g. Following the flow check, the screen display should read:

ET0000Min TS00.00M (Date)

Q(Flow)Lpm T(Time) Bty(Capacity)%

(Date) – today's date in military notation; e.g., 01JAN= January 1st

(Flow) - the current flow rate selected to be regulated.

(Time) - military time; e.g., 13:08= 13 Hours 8 Minutes or 1:08 PM

(Capacity) - remaining charge in the internal battery.

- h. Press "SETUP". The screen will read; "Select FLOW RATE"

The flow rate value will be blinking.

- i. The flow rate should read 15.0 Lpm. If it does not read 15.0 Lpm, the unit must be calibrated to 15.0 Lpm. See calibration section for adjusting target flow rate and calibration.
- j. Press "SETUP". This is the date and time screen.

The screen should read;

Set DATE and TIME

(dd) (mmm) (yyyy) (time)

- k. DAY: Press ENTER and change by pressing the + or - key. When the day is correct, press ENTER.

MONTH: To change, press + or - key. When correct, press ENTER.

YEAR: To change, press + or - key. When correct, press ENTER.

TIME (hrs): To change, press + or - key. When correct, press ENTER.

TIME (min): To change, press + or - key. When correct, press ENTER.

When date and time are correct press "SETUP"

- l. This is the sample start screen which reads;

Set START DATE and TIME

(dd) (mmm) 00:00 Off

This screen allows you to set a start date and time for a sampling run. The default is set to midnight the next day. To designate your own start date and time:

DAY: Press ENTER and change by pressing the + or - key. When the day is correct, press ENTER.

MONTH: To change, press + or - key. When correct, press ENTER.

YEAR: To change, press + or - key. When correct, press ENTER.

TIME (hrs): To change, press + or - key. When correct, press ENTER.

TIME (min): To change, press + or - key. When correct, press ENTER

- m. Enable the run by setting the "On/Off" function on the screen to "On".
WARNING: The sampler will not automatically activate if this option is set to "Off".
 - n. Press "SETUP"

The screen will read;

Set RUN TIME

Hours: 24 Min: 00 On

Set to 24 hours 0 minutes. The default is always 24 hrs 0 min, the required sample duration. If the sample time needs to be modified, adjust as instructed in step 6 and 8.
 - o. Press "SETUP". The screen will return to the "MAIN IDLE DISPLAY".
WARNING: DO NOT PRESS THE RESET BUTTON AT THIS TIME AS THE START TIME AND RUN TIME WILL DEFAULT.
 - p. Press "RUN/STOP"

If the START TIME ENABLE is set to "On" then the message "Alarm Triggered Run..." followed by "PQ100 Powering Down" will appear briefly. The PQ100 is now waiting for the internal real time clock to achieve the designated start time and will then power itself on and begin the sampling run. If the START TIME ENABLE is set to "Off" then the pump will begin to run immediately. If this occurs, press RUN/STOP and begin back at step 2 ensuring START TIME ENABLE is set to "On".
7. Installing the ERG Cr+6 Filter Holder Module (NOTE: Gloves must be changed for each sample, i.e. between retrieving a sample and preparing a new run gloves MUST be changed to prevent cross contamination).
- a. Remove the sample inlet cover on the stainless steel probe and make sure there is no contamination on the probe.
 - b. Put on a clean pair of powder-free gloves.
 - c. Take the ERG Cr+6 Filter Holder Module storage container from the cooler and carefully remove the module. The module may be in a plastic bag. Return the bag to the container for use in the collection procedure.
 - d. Make sure the glass funnel is securely attached to the filter holder. Loosen the small top nut on the filter container. Arrows will be present on the

filter holder showing air flow direction and they should always point to the end of the sample probe line.

- e. Holding the module with the glass funnel facing down, slide the probe into the top fitting of the filter module and tighten the nut. Tighten the nut until the ERG Cr+6 Filter Holder Module is securely fastened to the probe. Do not overtighten the plastic nut.

(Note: If running a field blank, repeat steps 1 through 5, count to 10, and then remove the field blank filter holder module and place it back into the antistatic bag. Label the bag to designate the filter module as a field blank. Log the filter ID as field blank in the comments section of the ERG Hexavalent Chromium Sample Data Sheet. The field blank must be run before the sample filter module is fastened to the probe).

8. Sample Recovery and Data Collection-NOTE: Gloves must be changed for each sample, i.e. between retrieving a sample and preparing a new run, gloves MUST be changed to prevent cross contamination.
 - a. Record pertinent data on sample sheets. This information will be on the "MAIN STATUS SCREEN".
 - b. Conduct a final flow check (verification) by following the instructions in section 4-Verification. Record the measurement from the flow standard on the *Ambient Hexavalent Chromium Data Sheet* under the "Field Setup" section, "Final Rotameter Reading".
 - c. Put on a clean pair of powder free gloves
 - d. Take the module storage container from the cooler, open, and set aside
 - e. While holding the ERG Cr+6 Filter Holder Module, loosen the top nut holding the module to the sample inlet and slide the module off the stainless steel probe.
 - f. Place the ERG Cr+6 Filter Holder Module including glass funnel in the plastic bag and place back into the storage container. Place the storage container into a cooler with ice substitutes.
 - g. Place cover back on end of probe line.
 - h. Data may be downloaded to a laptop using the PQ100/200 DOWNLOAD SOFTWARE. ERG does not require this data, but direction can be found in the BGI PQ167 Quick Start document, pages 16 and 17.

9. Sample Shipping - The Cr+6 Filter Holder Module container must be packed in a cooler with ice substitutes and shipped overnight cold to ERG. The sample paperwork must be included in the shipment. Use the pre-filled out FedEx label provided by ERG, and fill out the "Sender" section with the sampling agency's address and phone number. Send priority overnight to ERG.

K. **Records Management**

The BGI PQ167R instrument may be used as a part of a broad range of project types, and the management of records and data from the operation of the PQ100 instrument are dependent upon the type of project for which it is used. Therefore, operation records and data from the PQ167R will be supplied to the Project Manager for inclusion in the project file. In this way Cr+6 information and data will be managed in accordance with other records and data from the same project.

L. **Quality Assurance/Quality Control**

1. Flow Calibration - A flow verification must be completed at the beginning of the study period. If the verification does not compare within 4%, the flow must be calibrated. Document all quality assurance activities in the logbook.
2. Flow Verifications - The flow must be verified or checked at the beginning and end of the sampling event to determine an average sample flow, document all quality assurance activities and observations in the logbook.
3. Independent Audits - If possible, it is recommended that an independent flow check of the sampler be conducted at some point during the study. This check may be conducted by a state or local agency's quality assurance team or independent audit program.

M. **References**

1. BGI Inc. PQ167 Quick Start Guide (Using the PQ100 Immediately) Revision "G"
2. BGI Inc. PQ100 Air Sampler Instruction Manual PM10 Reference Sampler