EMISSIONS OF METALS, CHROMIUM AND NICKEL SPECIES, AND ORGANICS FROM MUNICIPAL WASTEWATER SLUDGE INCINERATORS

VOLUME II: SITE 5 EMISSION TEST REPORT
HEXAVALENT CHROMIUM METHOD EVALUATION

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DISCLAIMER

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the research and the user community.

The problem of disposing of primary and secondary sludge generated at municipal wastewater treatment facilities is one of growing concern. Sludge of this type may contain toxics such as heavy metals and various organic species. Viable sludge disposal options include methods of land disposal or incineration. In determining the environmental hazards associated with incineration, the Risk Reduction Engineering Laboratory and the Office of Water sponsored a program to monitor the emissions of metals and organics from a series of municipal wastewater sludge incinerators. The following document presents the final results from the Site 5 emissions test program.

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) Office of Water (OW) has drafted risk-based sewage sludge regulations under Section 405d of the Clean Water Act and EPA's Risk Reduction Engineering Laboratory (RREL) has been assisting OW in the collection of supporting data for the proposed regulations. Because of the associated cancer risk, there is particular concern regarding chromium and nickel species in the emissions from sludge incineration.

An RREL/OW research program was implemented to determine the ratios of hexavalent to total chromium and nickel subsulfide to total nickel in sewage sludge incinerator emissions under varied incinerator operating conditions. This report presents the test results from the first of a series of five incinerator test sites. Four incinerators tested under a previous project conducted by Radian Corporation are included in the Site numbering convention used. Thus, the first site in the series tested under the present project, covered by this report, is referred to as Site 5.

Three candidate sampling methods and two candidate analytical methods for hexavalent chromium were assessed at this site. The conversion of hexavalent chromium (Cr^{+6}) to other valence states of chromium during sampling and sample storage was of primary concern. All Method 5-type train samples and impinger train samples were collected by PEI Associates, Inc. (PEI). Dilution train samples were collected by Southern Research Institute.

Method 5-type train samples were analyzed by Technology Applications, Inc.'s (TAI) staff under contract to EPA's Environmental Monitoring Systems Laboratory (EMSL) in Cincinnati, Ohio. Dilution train samples, Method 5-type samples, and impinger train samples were analyzed by Entropy Environmentalists, Inc. under contract to RREL. TAI used an ion chromatograph with post column reaction (IC/PCR) and inductively coupled argon plasmography/mass spectrometry (ICP/MS) to analyze the Method 5-type samples. A stable chromium isotope ($^{53}Cr^{+6}$) spiked onto the Method 5 filter prior to sample collection was used to assess conversion of Cr^{+6} conversion during sampling/sample recovery.

The samples analyzed by Entropy were collected using a dilution train on an 8.5 in X 11 in glass fiber filter, a Method 5-type sampling train on an 82 mm quartz fiber filter, and an impinger sampling train with an alkaline impinger reagent. Since PEI did not have a recirculating impinger train, the system that was evaluated in this test was an impinger train without the recirculating system. The glass fiber filters and impinger solutions were spiked with native hexavalent chromium ($^{52}Cr^{+6}$) and a radioactively-labeled chromium isotope ($^{51}Cr^{+6}$). The samples were analyzed for hexavalent chromium by IC/PCR and for the radioactive isotopes by scintillation (gamma) counting.

Site 5 was a typical multiple hearth incinerator controlled by a venturi/impingement tray scrubber system. Process samples were not collected for analysis since the purpose of the test program was the evaluation of conversion of hexavalent chromium during flue gas sampling.

Hexavalent chromium test data for the Method 5-type train samples analyzed by TAI have not been released by EMSL, and are therefore not presented or discussed.

The preliminary method evaluation testing demonstrated that all sampling methods had problems with conversion of hexavalent chromium during sample and storage prior to analysis. EPA decided that the Method 5-type train and the recirculating reagent impinger train would be further evaluated during testing at Site 6.

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ACKNOWLEDGEMENTS

1.0 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) Office of Water (OW) has been developing new regulations for sewage sludge incinerators and EPA's Risk Reduction Engineering Laboratory (RREL) has been assisting OW in the collection of supporting data. There is particular concern regarding chromium and nickel species in the emissions from incineration of municipal wastewater sludge because of the associated cancer risk. OW has drafted risk-based sludge regulations under Section 405d of the Clean Water Act which have been published for comment in the Federal Register, Volume 54, No. 23, February 6, 1989. Final regulations are scheduled for promulgation in January 1992.

The draft regulations are based on the risk incurred by the "most exposed individual" (MEI). The MEI approach involves calculating the risk associated with an individual residing for seventy years at the point of maximum ground level concentration of the emissions just outside the incinerator facility property line. EPA's proposal for regulating sewage sludge incinerators is based on ensuring that the increased ambient air concentrations of metal pollutants emitted from sludge incinerators are below the ambient air human health criteria. The increase in ambient air concentrations for four carcinogenic metals, arsenic, chromium, cadmium, and nickel, are expressed as annual averages. The concentrations are identified in the proposed regulations as Risk Specific Concentrations (RSC). Both nickel and chromium emissions from sludge incinerators presented a specific problem in establishing RSCs, because unknown portions of the emissions of these metals are in forms which are harmful to human health. In performing the risk calculations, EPA assumed that 1% of the emissions of chromium from the sludge incinerators is in the most toxic form, hexavalent chromium. For nickel,

EPA assumed that 100% of the nickel emissions are in the most toxic form, nickel subsulfide.

Chromium is likely to be emitted in either the highly carcinogenic hexavalent state (Cr^{+6}) or in the noncarcinogenic trivalent state (Cr^{+3}). Trivalent chromium has not been shown to be carcinogenic and is toxic only at levels higher than those normally found in sewage sludge incinerator emissions. Although hexavalent chromium (as the most oxidized form) could be reasonably expected to result from combustion processes, investigators speculate that most of the chromium is likely to be emitted in the trivalent state.[1] This is because hexavalent chromium is highly reactive, and thus likely to react with reducing agents to form trivalent chromium.

Studies have been conducted to determine the potential for chromium in sewage sludge to be converted to the hexavalent form. Analysis of laboratory combusted sludges dosed with various levels of lime and ferric chloride revealed that the hexavalent to total chromium ratio increased with lime dosage.[1] One-hundred percent conversion of trivalent chromium to hexavalent chromium was observed in several of the tests.[1] These tests indicate that when lime and ferric chloride are used as sludge conditioners, high ratios of hexavalent to total chromium may be formed under certain incinerator operating conditions.

EPA has previously sponsored emission testing studies for measurement of hexavalent chromium at two sludge incinerators.[2,3] For one site, the hexavalent chromium concentrations were below the analytical detection limit; for the other site, a hexavalent-to-total chromium ratio of 13% was calculated. The 1% value chosen for the draft regulations may seem low. This is the result, however, of weighting various values to give the most credible ones more influence. With this approach, lower values were assigned a stronger contribution. The lack of a substantial data base on hexavalent chromium emissions prompted the following statement in the EPA's Technical Support Document for the Incineration of Sewage Sludge: "EPA plans to perform additional tests of sewage sludge incinerator emissions for hexavalent chromium before this proposed rule is finalized. The additional data should allow the Agency to better understand how hexavalent chromium is generated in sewage sludge incinerators." There were no

published EPA emission measurement test methods for the sampling and analysis of hexavalent chromium. In addition, very little data exist on the conditions that may cause its formation. The primary objectives of the RREL/OW research described in this report were to conduct preliminary evaluations of available hexavalent chromium sampling and analytical methodologies. The conversion of hexavalent chromium to other valence states during sampling and sample storage was the primary concern. Three sampling techniques were evaluated: 1) a Method 5-type sampling system that collects the chromium species in a heated sampling probe and on a heated glass fiber filter, 2) an impinger sampling train that collects the chromium species in an alkaline impinger reagent, and 3) a dilution train that dilutes the sample gas 15-fold with ambient air and collects the chromium species on an unheated glass fiber filter. The Method 5-type samples and the impinger train samples were collected by PEI Associates, Inc. (PEI). The dilution train samples were collected by Southern Research Institute (SRI). Half of the Method 5-type train samples were analyzed by Technology Applications, Inc.'s (TAI) staff under an EPA Contract with the Environmental Monitoring Systems Laboratory (EMSL) in Cincinnati, Ohio. The remainder of the Method 5-type samples, and all of the dilution train and the impinger train samples were analyzed by Entropy Environmentalists, Inc. under contract to RREL.

TAI used an ion chromatograph with post column reaction (IC/PCR) and inductively coupled argon plasmography/ mass spectrometry (ICP/MS) for analysis. A stable chromium isotope ($^{53}Cr^{+6}$) spike was used to assess hexavalent chromium conversion. However, the analytical data were never released by EMSL, and are therefore, not discussed in this report.

The samples analyzed by Entropy were collected using the dilution train, the Method 5-type train, and the impinger sampling train. Since PEI did not have a recirculating impinger train, the system evaluated in this test was an impinger train without the recirculating system. A radioactively-labeled chromium spike ($^{51}Cr^{+6}$) was used to assess hexavalent chromium conversion. The samples were analyzed by IC/PCR for the hexavalent chromium and scintillation (gamma) counting for the radioactively-

labeled spike. No process or control equipment operating data were collected during this test program.

This report presents the method evaluation results for the hexavalent chromium samples analyzed by Entropy. This test program was the first in a series of five test sites (Sites 5, 6, 7, 8, and 9). Four incinerators tested under a previous project conducted by Radian Corporation are included in the Site numbering convention used. Thus, the first site in the series tested under the present project, covered by this report, is referred to as Site 5.

The following sections present detailed descriptions of the testing and results from the Site 5 program. Section 2.0 present a summary of the test results. Section 3.0 presents a short process description and process operating conditions. Section 4.0 provides a more detailed discussion of the sampling and analytical results. Section 5.0 describes the sampling procedures, Section 6.0 describes the analytical procedures, and Section 7.0 describes the quality assurance/quality control (QA/QC) program.

2.0 SITE 5 TEST SUMMARY

2.1 TESTING PROGRAM DESIGN

The primary objectives of the RREL/OW research described in this report were to conduct preliminary evaluations of available hexavalent chromium sampling and analytical methodologies. The conversion of hexavalent chromium to other valence states during sampling and sample storage was of primary concern. Three sampling techniques were evaluated: 1) a Method 5-type sampling system that collects the sample in a heated sampling probe and on a heated filter, 2) an impinger sampling train that collects the sample in an alkaline impinger reagent, and 3) a dilution train that dilutes the sample gas 15-fold with ambient air and collects the sample on an unheated glass fiber filter.

The emission testing at Site 5 was conducted on June 9 (first method evaluation test day) and August 3, 1989 (second method evaluation test day). The test program sampling matrix is shown in Table 2-1. Sampling was conducted at the outlet of the venturi/impingement tray scrubber used to control the multiple hearth incinerator emissions. The sampling and analytical methods used are described in detail in Sections 5.0 and 6.0, respectively.

2.2 TEST PROGRAM RESULTS

The emission results are summarized in this section; the run-by-run data are presented in Section 4.0.

TABLE 2-1. TEST PROGRAM SAMPLING MATRIX

Testing Date	Sampling Technique	Analytical Techniques	No. of Samples Collected	Length of Run (min.)	Cr^{+6} Spike Timing
First Test Day (June 9, 1989)					
6/9/89	Dilution Train	IC/PCR Scintillation	1	15	Before
"	"	"	1	30	Before
"	"	"	1	60	Before
"	"	"	1	120	Before
"	"	"	1	60	Before
6/9/89	Method 5-type Train	IC/PCR Scintillation	4	60	Before
6/9/89	Impinger Train	IC/PCR Scintillation	8	60	Before
Second Test Day (August 3, 1989)					
8/3/89	Method 5-type Train	IC/PCR Scintillation	4	120	2-Unspiked 2-After
"	"	"	4	120	Before
8/3/89	Impinger Train	IC/PCR Scintillation	8	120	Before

2.2.1 Dilution Train Sampling Approach

Five dilution train sample runs were conducted on the first test day. As shown in Table 2-2, the recoveries seen for both the native and radioactively-labeled hexavalent chromium spikes were similar, with averages of 76.6% and 77.4%, respectively. Thus, approximately 25% of the native and labeled hexavalent chromium were converted to trivalent chromium. The recoveries were fairly consistent from run-to-run and did not appear to be related to the length of the sample run.

2.2.2 Method 5-Type Sampling Approach

Method 5-type sampling runs were conducted on both test days. Some of the Method 5-type samples collected were analyzed by TAI under contract to EMSL. The data from these trains have not been released by EMSL and will not be presented in this report.

Four samples from a Method 5-type quadruplicate "quad" train collected on June 9 were analyzed by Entropy. The filters were spiked with native and labeled hexavalent chromium prior to sampling. As shown in Table 2-3, the average recoveries for these chromium species were 29.5% and 54.8%, respectively, indicating that approximately 70% of the native hexavalent chromium and 45% of the labeled hexavalent chromium were converted to trivalent chromium during sampling and/or sample recovery.

Because there were problems in recovering the native and labeled chromium from the control samples (see Section 4) for the first Method 5-type sample run, the second second set of Method 5-type test runs (August 3, 1989) included posttest spiking as well as pretest spiking of the filters. Two quad-train runs were conducted. The analytical procedures for measuring the labeled hexavalent chromium were also improved under a different contract with EPA's Quality Assurance Division in the two months between the first and second test dates. The results are presented in Table 2-4. For the flue-gas exposed, spiked filters, the recoveries were 66.1% and 67.3% for the native Cr^{+6}; and 91% of the recovered ^{51}Cr was Cr^{+6}. The recoveries for three exposed filter samples,

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TABLE 2-2. HEXAVALENT CHROMIUM RECOVERY USING DILUTION TRAIN FROM JUNE 9,1989

Sample ID	Sample Time (min)	% native Cr^{+6} Recovered from Filter
	Native Hexavalent Chromium Analytical Data	
F-1	15	73.7
F-2	30	67.0
F-3	60 (interrupted)	64.5
F-4	120	99.2
F-5	60	76.8
Average		76.6

Sample ID	Sample Time (min)	% $^{51}Cr^{+6}$ Recovered from Filter
	Radioactively-Labeled Chromium Analytical Data	
F-1	15	67.1
F-2	30	76.5
F-3	60 (interrupted)	75.3
F-4	120	87.3
F-5	60	80.8
Average		77.4

TABLE 2-3. HEXAVALENT CHROMIUM RECOVERY USING METHOD 5-TYPE TRAIN FROM JUNE 9, 1989

Sample ID	Sample Time (min)	% native Cr^{+6} Recovered from Filter
Native Hexavalent Chromium Analytical Data		
F-A	60	19.1
F-B	60	34.3
F-C	60	38.5
F-D	60	25.9
Average		29.5

Sample ID	Sample Time (min)	% $^{51}Cr^{+6}$ Recovered from Filter
Radioactively-Labeled Chromium Analytical Data		
F-A	60	43.0
F-B	60	57.8
F-C	60	63.2
F-D	60	55.0
Average		54.8

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TABLE 2-4. HEXAVALENT CHROMIUM RECOVERY USING METHOD 5-TYPE TRAIN FROM AUGUST 3, 1989

Native Hexavalent Chromium

Sample Identity	Expected (μg)	Found (μg)	% of Expected
Posttest Spiked Method 5-Type Filters (2 hr run)			
Spiked Control	10.8	9.4	87.0
Spiked Control	10.8	8.9	82.4
Posttest Spike (B-2)	13.7	9.0	66.1
Posttest Spike (B-4)	13.7	9.2	67.3
Exposed Filter (B-1)	0	2.9	NA
Exposed Filter (B-3)	0	2.8	NA
Pretest Spiked Method 5-Type Filters (2 hr run)			
Spiked Filter (I-1)	13.7	6.4	47.0
Spiked Filter (I-2)	13.7	6.4	47.0
Spiked Filter (I-4)	13.7	6.6	48.3
Spiked Filter FB	10.8	0.6	5.3

Radioactively-Labeled Hexavalent Chromium

Sample Identity	Percent of Total	
	$^{51}Cr^{+3}$	$^{51}Cr^{+6}$
Posttest Spiked Method 5-Type Filters		
Spiked Control	2.3	97.7
Spiked Control	1.5	98.5
Posttest Spike (B-2)	11.5	88.5
Posttest Spike (B-4)	9.0	91.0
Exposed Filter (B-1)	NA	NA
Exposed Filter (B-3)	NA	NA
Pretest Spiked Method 5-Type Filters		
Spiked Filter (I-1)	38.5	61.5
Spiked Filter (I-2)	37.4	62.6
Spiked Filter (I-4)	26.7	73.3
Spiked Filter FB	68.6	31.4

relative to the expected value of 13.7 μg, averaged 47.4%. Relative to the spiked control filter samples, the recoveries averaged 70.9%. Of the recovered ^{51}Cr, about 65% was apparently in the hexavalent state. The results of the tests conducted on August 3 using the improved technique indicated that, for the pretest and posttest spike respectively, 87% and 92% of the soluble radioactively-labeled chromium extracted from the filters were in the hexavalent state.

The experimental results for the Method 5-type trains indicate that chromium conversion does occur during sampling and/or sample recovery by extraction, and can be measured, semi-quantitatively, using ^{51}Cr^{+6} and/or native Cr^{+6} spikes.

2.2.3 Impinger Train Approach

Since PEI Associates, Inc. did not have a recirculating reagent impinger train, the evaluation testing was conducted using only the impinger portion of the recirculating reagent sampling train. On June 9, 1989, two quad-train runs were conducted. The impinger reagent used was 80% isopropyl alcohol and 20% 2 N NaOH (IPA/NaOH). As shown in Table 2-5, the average recoveries of the native and labeled hexavalent chromium were 65.4% and 99.7%, respectively.

The results for the spiked impinger train sampling conducted on August 3 are summarized in Table 2-6. The improved analytical technique, described in Section 4.0, was used for the analysis of the labeled hexavalent chromium. Recoveries of spiked native chromium (10.8 μg) from two IPA/NaOH samples with a 2-hr sampling period averaged 78.3%. These recoveries constituted an average of 94.8% of a spiked IPA/NaOH control sample where 8.9 μg of the native chromium was recovered. The average recovery of spiked ^{51}Cr^{+6} in the two samples at 78.4% was in agreement with the average native Cr recovery; recovery in the control sample was higher at 89.8%.

A 0.5 M phosphate buffer used in the impinger train yield very low chromium recoveries, about 25% for the native Cr^{+6} and about 15% for ^{51}Cr^{+6} (see Table 2-6). Both control and field blank samples yielded good recoveries of both native Cr^{+6} and ^{51}Cr^{+6}. While the phosphate buffer did not prevent conversion during sampling, the

TABLE 2-5. HEXAVALENT CHROMIUM RECOVERY USING IMPINGER TRAIN FROM THE FIRST DEVELOPMENT TEST

Sample ID	Sample Time (min)	% native Cr^{+6} Recovered from Solution
Native Hexavalent Chromium Analytical Data		
I-1 (A-1)	60	87.0
I-2 (A-2)	60	59.0
I-3 (B-1)	60	24.5
I-4 (B-2)	60	73.7
I-5 (C-1)	60	69.2
I-6 (C-2)	60	74.4
I-7 (D-1)	60	74.0
I-8 (D-2)*	60	(21.1)
Average		65.4

Sample ID	Sample Time (min)	% $^{51}Cr^{+6}$ Recovered from Solution
Radioactively Labeled Chromium Analytical Data		
I-1 (A-1)	60	99.8
I-2 (A-2)	60	99.8
I-3 (B-1)	60	99.9
I-4 (B-2)	60	99.8
I-5 (C-1)	60	99.6
I-6 (C-2)	60	99.6
I-7 (D-1)	60	99.9
I-8 (D-2)*	60	(13.7)
Average		99.7

* The sample from run I-8 had silica gel in the impinger solution; results not included in average.

TABLE 2-6. HEXAVALENT CHROMIUM RECOVERY USING IMPINGER TRAIN FROM AUGUST 3, 1989

Native Hexavalent Chromium

Sample Identity	Expected (μg)	Found (μg)	% of Expected	% of Control
Spiked 80% IPA/20% 1.0 N NaOH Impinger Reagent (2 hr run)				
IPA/NaOH Control	10.8	8.9	82.5	NA
IPA/NaOH Sample (I-2)	10.8	8.8	81.7	99.0
IPA/NaOH Sample (I-3)	10.8	8.1	74.8	90.6
IPA/NaOH Field Blank	10.8	4.9	45.4	55.0
Spiked 0.5 M Phosphate Buffer Impinger Reagent (2 hr run)				
0.5 M PO_4 Control	10.8	11.2	103.5	NA
PO_4 Sample (P-1)	10.8	2.8	26.2	25.3
PO_4 Sample (P-2)	10.8	3.1	28.5	27.5
PO_4 Field Blank	10.8	9.2	84.7	81.8

Radioactively-Labeled Chromium

Sample Identity	Percent of Total	
	$^{51}Cr^{+3}$	$^{51}Cr^{+6}$
Spiked 80% IPA/20% 2 N NaOH Reagent (2 hr run)		
IPA/NaOH Control	10.2	89.8
IPA/NaOH Sample (I-2)	24.3	75.7
IPA/NaOH Sample (I-3)	18.9	81.1
·IPA/NaOH Field Blank	20.9	79.1
Spiked 0.5 M Phosphate Reagent (2 hr run)		
0.5 M PO_4 Control	6.8	93.2
PO_4 Sample (P-1)	87.4	12.6
PO_4 Sample (P-2)	85.0	15.0
PO_4 Field Blank	9.7	90.3

presence of both $^{51}Cr^{+6}$ and $^{51}Cr^{+3}$ in the filtrate demonstrated the ability of the improved analytical technique (see Section 4.0, Figure 4-2)) to separate soluble ^{51}Cr species.

In summary, the IPA/NaOH proved to be the best collection media, with the native and radioactively-labeled chromium results agreeing quite well. The precision of the impinger train measurements was also good. However, the IPA did cause long-term problems with the analytical column on the IC/PCR.

2.2.4 Conclusions

The goal of this preliminary testing was to develop a sampling and analytical method for hexavalent chromium that could attain approximately 100% recovery for both native and labeled chromium. The test results demonstrated that all the candidate methods showed some conversion of the hexavalent chromium during sampling and sample storage prior to analysis. Consequently, it was decided that the Method 5-type sampling train and the "recirculating reagent" impinger train would undergo further evaluation testing at Site 6. Although the recirculating reagent impinger train was not used at Site 5 because PEI did not have the equipment, studies previously conducted by Entropy indicated that the conversion of hexavalent chromium during sampling was significantly reduced by continuously recirculating the impinger reagent to the inlet of the sampling probe. The dilution train was eliminated from further evaluations because of the cost, operating difficulties, potential for filter contamination, and the conversion of 25% of the native and labeled hexavalent chromium during sampling and sample storage.

The data collected in this field evaluation was not emissions data and was not intended to support the OW regulations. The study was conducted to evaluate the conversion of internal spiked standards of hexavalent chromium. Therefore, none of the data should be used for any standard setting purposes.

The cause of the conversion of the hexavalent chromium during sample collection and/or recovery could not be determined from the method evaluation test. Additional

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work was conducted on the hexavalent chromium method by Entropy under a contract to EPA's Quality Assurance Division (QAD) in the Research Triangle Park, North Carolina. QAD plans to publish a report on the hexavalent chromium method development at the conclusion of their work on the method. Therefore, a description of the additional method development work is not discussed in this report.

3.0 PROCESS DESCRIPTION AND OPERATION

Site 5 was a typical small multiple hearth incinerator with emissions controlled by a venturi scrubber/impinger tray scrubber. The site was selected based on its close proximity to PEI Associates, Inc. (one of the testing contractors). Sampling was conducted in the discharge stack of the venturi scrubber/impingement tray scrubber. Since the primary purpose of the testing was to assess the recovery of native and labeled hexavalent chromium from the sampling trains, no process samples were taken for analyses.

The first series of test runs was conducted on June 9, 1989, and the second series of test runs was conducted on August 3, 1989. The average incinerator operating conditions for these two days are shown in Table 3-1. These values are typical of operating conditions for a small multiple hearth incinerator.

TABLE 3-1. SITE 5 INCINERATOR OPERATING CONDITIONS

Date (1989)	Sludge Feed Rate (tons/hr, wet basis)	Average Hearth Temperature (°F)				
		No. 1	No. 2	No. 3	No. 4	No. 5
6/9	1.5	1000	1350	1500	1600	700
8/3	1.4	790	1240	1100	1410	490

4.0 TEST RESULTS

The detailed results of the hexavalent chromium methods development tests performed at Site 5 on June 9 and August 3, 1989 are presented in this section. Since sampling train flow rates and sample volumes were not used to assess conversion of hexavalent chromium, they are presented in Section 5 with the detailed description of the sampling procedures.

The primary objectives of the testing were to conduct preliminary evaluations of several available hexavalent chromium sampling and analytical methodologies. The conversion of hexavalent chromium to other valence states during sampling and sample storage was of primary concern. Conversion was assessed by determining the recovery of known spikes of native hexavalent chromium (Cr^{+6}) and radioactively-labeled hexavalent chromium ($^{51}Cr^{+6}$).

In addition to the test results, variability and outliers in the data are discussed. The relationship of the process parameters to the results are not discussed.

Results are presented in terms of percent recovery of the native and labeled hexavalent chromium spikes. Flue gas emission results are presented as measured. Supporting data for the results presented in this section are included in the appendices.

4.1 TESTING PROGRAM DESIGN

Three sampling techniques were evaluated: 1) a Method 5-type sampling system that collects the sample in a heated sampling probe and on a heated filter, 2) a reagent impinger sampling train that collects the sample in an alkaline impinger reagent, and 3) a dilution train that dilutes the sample gas 15-fold with ambient air and collects the sample on an unheated glass fiber filter. The Method 5-type samples and the impinger

train samples were collected by PEI Associates, Inc. The dilution train samples were collected by Southern Research Institute. The sampling and analytical methods are described in detail in Sections 5.0 and 6.0, respectively.

4.2 TEST PROGRAM RESULTS

The samples collected during the two methods development tests were analyzed by two laboratories. EPA has not released the hexavalent chromium data from the TAI analysis. This section presents only the detailed method evaluation results for the hexavalent chromium samples analyzed by Entropy Environmentalists Inc..

4.2.1 Flue Gas Conditions

The flue gas conditions measured on the two test days are presented in Table 4-1. These results are typical for a small multiple hearth incinerator operation. An emission gas sample was collected in a bag on August 2 and analyzed for carbon monoxide (CO) by a nondispersive infrared analyzer. The recorded value was 430 ppm CO on a dry basis.

TABLE 4-1. SUMMARY OF FLUE GAS CONDITIONS FOR SITE 5

Date (1989)	Volumetric Flow Rate*		Moisture content (%)	Flue gas temperature (°F)	Composition (%)	
	acfm	dscfm			O_2	CO_2
6/9	3224	2800	5.5	103	12	6
8/3	3691	3116	6.9	105	16	5

* - acfm (actual cubic feet per min), dscfm (dry standard cubic feet per min)

4.2.2 Dilution Train Sampling Approach

Five dilution train sample runs were conducted during the first day of testing. The sample run times (see Table 4-2) were 15, 30, 60, 120, and 60 minutes. The recoveries seen for both the native and labeled hexavalent chromium spikes were similar with averages of 76.6% and 77.4%, respectively. Thus, approximately 25% of the native hexavalent chromium and labeled hexavalent chromium were converted to trivalent chromium. The recoveries were fairly consistent from run-to-run and did not appear to be related to the length of the sample run.

However, the dilution train is expensive to purchase, difficult to operate including the move from sampling point to point, and requires an extremely large filter for sample collection. This large filter greatly increases the background contamination levels of total chromium and requires a large volume of extraction reagent.

The dilution train was eliminated from further evaluations because of the cost, operating difficulties, potential for filter contamination, and the conversion of 25% of the native and labeled hexavalent chromium during sampling and sample storage.

4.2.3 Method 5-Type Sampling Approach

The Method 5-type sampling runs were conducted on both June 9 and August 3, 1989. Portions of the Method 5-type samples collected on June 9 and August 3 were analyzed by TAI under contract to EPA's EMSL in Cincinnati, Ohio. The data from these trains have not been released for publication and are not reported.

On June 3, one Method 5-type quad-train run was conducted for 60 minutes and the samples analyzed by Entropy. The filters used in all four trains were spiked with native and radioactively-labeled chromium prior to testing. Four control samples were included in the test program. The control samples were digested after the test as follows: 2-with water, 1-with 0.2 M phosphate buffer, and 1-with 0.1 N NaOH. As shown in Table 4-3, the best recovery of 83% of the native chromium was obtained using the 0.1 N NaOH. Each sample filter was then digested with 250 mL of 0.1 N NaOH.

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TABLE 4-2. HEXAVALENT CHROMIUM RECOVERY USING DILUTION TRAIN FROM JUNE 9, 1989

Sample ID	Sample Time (min)	% Native $^{52}Cr^{+6}$ Recovered from Filter
	Native Hexavalent Chromium Analytical Data	
F-1	15	73.7
F-2	30	67.0
F-3	60 (interrupted)	64.5
F-4	120	99.2
F-5	60	76.8
Average		76.6

Sample ID	Sample Time (min)	% $^{51}Cr^{+6}$ Recovered from Filter
	Radioactively-Labeled Chromium Analytical Data	
F-1	15	67.1
F-2	30	76.5
F-3	60 (interrupted)	75.3
F-4	120	87.3
F-5	60	80.8
Average		77.4

TABLE 4-3. HEXAVALENT CHROMIUM RECOVERY USING METHOD 5-TYPE TRAIN FROM JUNE 9, 1989

Sample ID	Extraction Reagent	Sample Time (min)	% native Cr^{+6} Recovered from Filter
Native Hexavalent Chromium Analytical Data			
Control 6	Water		55.1
Control 7	Phosphate		ND(0)
Control 8	Water		79.3
Control 9	NaOH		83.0
F-A	NaOH	60	19.1
F-B	"	60	34.3
F-C	"	60	38.5
F-D	"	60	25.9
Average			29.5

Sample ID	Sample Time (min)	% $^{51}Cr^{+6}$ Recovered from Filter
Radioactively-Labeled Chromium Analytical Data		
F-A	60	43.0
F-B	60	57.8
F-C	60	63.2
F-D	60	55.0
Average		54.8

As shown in Table 4-3, the recoveries of the native and labeled hexavalent chromium spikes averaged 29.5% and 54.8%, respectively. This demonstrates that approximately 70% of the native hexavalent chromium and 45% of the labeled hexavalent chromium were converted to trivalent chromium during sampling and/or sample recovery.

Entropy encountered similar conversion results for hexavalent chromium in previous laboratory research using a Method 5-type train to sample emissions containing organics, acid gases, and sulfur dioxide. Because there were problems in recovering the native and labeled chromium from the control samples from the first Method 5-type sample run (June 9), the second set of Method 5-type test runs (August 3) included posttest as well as pretest spiking of the filters. In addition, the analytical procedures for separating and measuring labeled hexavalent chromium were improved between the first and second test dates as described in Section 4.2.4.

On August 3, two quad-train runs were conducted, each over a 2-hr sampling period. The results for the Method 5-type filter samples are presented in Table 4-4. For the first quad-train run, four unspiked filters were used to sample the flue gas for 2 hr to obtain a representative particulate loading. Two of the exposed filters were then extracted and analyzed for Cr^{+6} yielding catches of 2.8 and 2.9 μg of hexavalent chromium in the emissions. The other two filters plus two control filters were spiked with a mixture of $^{51}Cr^{+6}$ and native Cr^{+6}, and extracted. Spike recoveries of the native Cr^{+6} were 87.0% and 82.4% for the control filters; based on ion chromatographic separation of the hexavalent and trivalent chromium about 98% of this recovered ^{51}Cr was in the hexavalent state. For the flue-gas exposed, posttest spiked filters, the recoveries were 66.1% and 67.3% for the native Cr^{+6} with 89.9% to 91% of the recovered ^{51}Cr in the hexavalent state. The expected amount of native Cr (13.7 μg) used to calculate the spike recoveries was the sum of the native chromium spike (10.8 μg) and the native chromium in the emissions (2.87 μg) based on the values measured for the unspiked exposed filters.

The results for the filters spiked with native Cr^{+6} and $^{51}Cr^{+6}$ prior to sampling are also presented in Table 4-4. The recoveries for three pretest spiked filter samples, based on an expected value of 13.7 μg, ranged from 47.0% to 48.3%. These recoveries

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TABLE 4.4. RECOVERY OF HEXAVALENT CHROMIUM FOR METHOD 5-TYPE TRAIN FOR AUGUST 3, 1989

Sample Identity	Native Hexavalent Chromium				Spiked Hexavalent ^{51}Chromium (total counts)			IC Separation		Percent of Total	
	Expected (ug)	Found (ug)	% of Expected	% of Control	Total	Residue	Soluble	$^{51}Cr^{+3}$	$^{51}Cr^{+6}$	$^{51}Cr^{+3}$	$^{51}Cr^{+6}$
Post Test Spiked Quartz Method 5-Type Filters Exposed to 2 Hours of Flue Gas											
Spiked Control	10.8	9.4	87.0	NA	867869	1619	866250	18261	847989	2.3	97.7
Spiked Control	10.8	8.9	82.4	NA	858487	3962	854525	8804	845721	1.5	98.5
Post Test Spike (B 2)	13.7	9.0	66.1	98.8	866047	17997	848050	81345	766705	11.5	88.5
Post Test Spike (B-4)	13.7	9.2	67.3	100.5	872866	21841	851025	56920	794105	9.0	91.0
Exposed Filter (B-1)	0	2.9	NA	NA	394	9	385	NA	NA	NA	NA
Exposed Filter (B-3)	0	2.8	NA	NA	292	12	280	NA	NA	NA	NA
Pretest Spiked Quartz Method 5-Type Filters Exposed to 2 Hours of Flue Gas											
Spiked Filt. (I-1)	13.7	6.4	47.0	70.3	458210	113495	344715	63106	281609	38.5	61.5
Spiked Filt. (I-2)	13.7	6.4	47.0	70.2	441934	126759	315175	38554	276621	37.4	62.6
Spiked Filt. (I-4)	13.7	6.6	48.3	72.1	444449	91019	353430	27489	325941	26.7	73.3
Spiked Filt. FB	10.8	0.6	5.3	6.2	430161	176761	253400	118253	135147	68.6	31.4

constituted 70% to 72% of the spiked control filter recoveries from the previous quad-train run. Of the recovered ^{51}Cr, 61.5% to 73.3% was found to be in the hexavalent state using the IC/PCR separation.

An improved analytical technique for separation and measurement of hexavalent chromium including radioactively-labeled species was developed between the first and second test days (see Section 6.1.3 for details). This technique required that the sample discharge from the IC/PCR which had been separated by the analytical column be collected at 30 sec intervals. The radioactively-labeled chromium content of each aliquot was then measured by scintillation counting. Figure 4-1 contains two radio-chromatograms of the radioactive content versus the aliquot time in min. Trivalent chromium is separated by the IC column in the range of 2 to 4 min. The hexavalent chromium is separated by the IC column in the 5 to 6.5 min range. The radio-chromatograms show that the soluble radioactively-labeled chromium extracted from both the pretest spiked and posttest spiked filters was principally in the hexavalent state 87% and 92%, respectively.

Overall, the Method 5-type filter experiments indicated that conversion during sampling and/or matrix effects on recovery by extraction do occur, and can be measured, semi-quantitatively, with $^{51}Cr^{+6}$ and/or native Cr^{+6} spikes.

4.2.4 Impinger Train Approach

Entropy had determined in previous studies that the recirculating reagent impinger train, which continuously recirculates the impinger reagents to the inlet of the sampling probe, reduces the conversion of hexavalent chromium especially in the sampling probe. Since, PEI Associates, Inc. did not have a "recirculating reagent" impinger train, the preliminary evaluation testing was conducted using the only impinger portion of the recirculating reagent train.

On June 9, two quad-train runs were conducted over a 60-min sampling period. The impinger reagent used was isopropyl alcohol and NaOH (IPA/NaOH). As shown in Table 4-5, the recovery of the native and labeled hexavalent chromium was 65.4% and
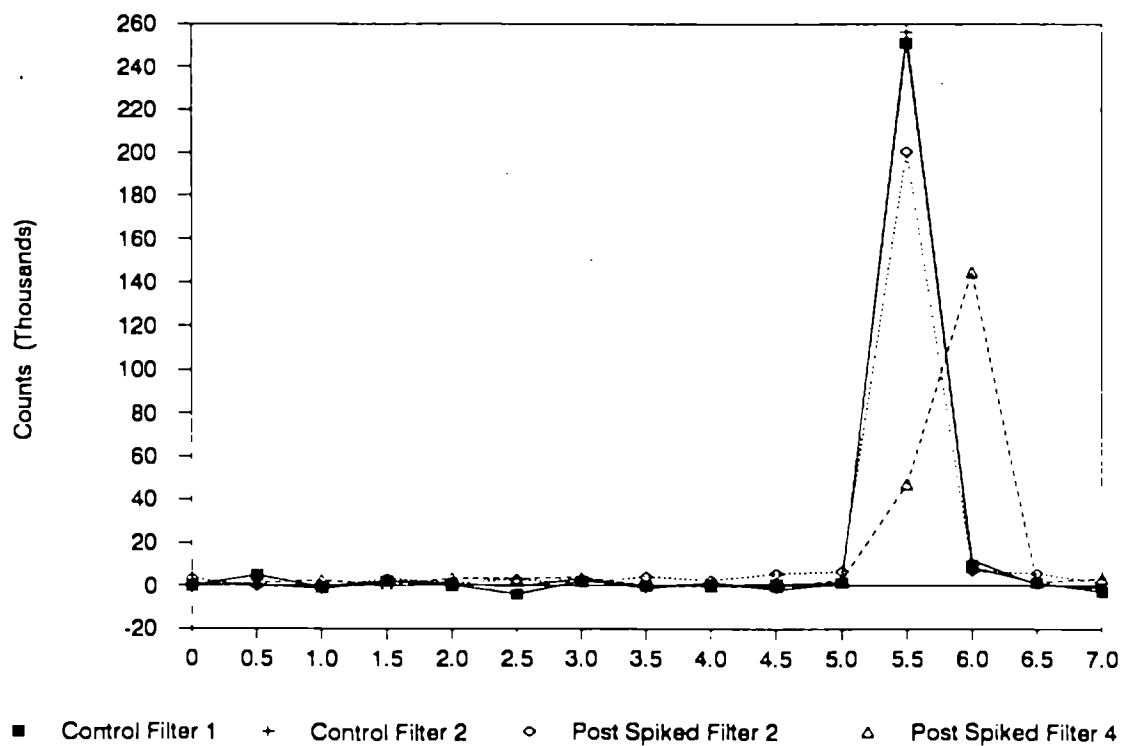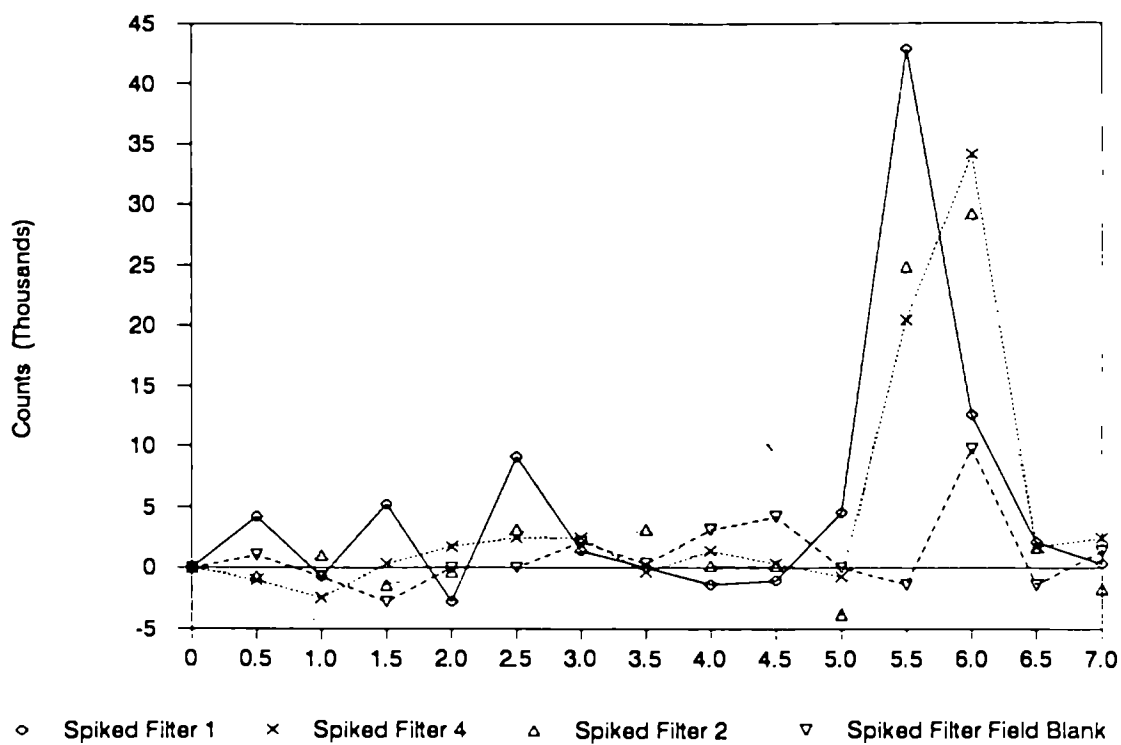
Figure 4-1. Radiochromatograms for the pretest and posttest spiked Method 5-type samples.

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TABLE 4-5. HEXAVALENT CHROMIUM RECOVERY USING IMPINGER TRAIN FROM THE FIRST DEVELOPMENT TEST

Sample ID	Sample Time (min)	% $^{52}Cr^{+6}$ Recovered from Solution
Native Hexavalent Chromium Analytical Data		
Control sample	NA	95.5
I-1 (A-1)	60	87.0
I-2 (A-2)	60	59.0
I-3 (B-1)	60	24.5
I-4 (B-2)	60	73.7
I-5 (C-1)	60	69.2
I-6 (C-2)	60	74.4
I-7 (D-1)	60	74.0
I-8 (D-2)*	60	21.1
Average		65.4

Sample ID	Sample Time (min)	% $^{51}Cr^{+6}$ Recovered from Solution
Radioactively-Labeled Chromium Analytical Data		
I-1 (A-1)	60	99.8
I-2 (A-2)	60	99.8
I-3 (B-1)	60	99.9
I-4 (B-2)	60	99.8
I-5 (C-1)	60	99.6
I-6 (C-2)	60	99.6
I-7 (D-1)	60	99.9
I-8 (D-2)*	60	(13.7)
Average		99.7

* The sample from Run I-8 had silica gel collected in the impinger solution; results not included in average.

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99.7%, respectively. These recovery averages imply that approximately 35% of the native hexavalent chromium and none of the labeled hexavalent chromium were converted to trivalent chromium. The radioactively-labeled chromium was measured using a scintillation counter assuming that all labeled chromium in the sample filtrate must be in the hexavalent state. The poor agreement between the recoveries for native and labeled chromium clearly demonstrated that this assumption was wrong and additional laboratory studies were conducted. These studies revealed that there was soluble labeled trivalent chromium in the filtrate. It was determined that improved separation of the labeled hexavalent and trivalent chromium could be accomplished through the use of the analytical column on the IC/PCR. However, by the time the modified procedure was developed, the radioactivity of the labeled chromium in the samples collected on June 9 was too low to conduct an additional analysis. In addition, the organic content of the IPA/NaOH reagent was creating problems with the analytical column.

The results for the spiked impinger sampling conducted on August 3, 1989 are summarized in Table 4-6. The improved analytical technique for separation of the hexavalent and trivalent chromium prior to scintillation counting was used by Entropy in the analysis of these samples. Recoveries of a native chromium spike (10.8 μg) from two IPA/NaOH impinger reagent samples exposed to the flue gas for 2 hr were 81.7% and 74.8%. Relative to a spiked IPA/NaOH control sample where 8.9 μg was recovered, the recoveries were 99.0% and 90.6% of the control value. The recoveries of spiked $^{51}Cr^{+6}$ in the two samples were in agreement with the native Cr recoveries, at 75.7% and 81.1%; the recovery of $^{51}Cr^{+6}$ in the control sample was 89.8%.

The analysis for $^{51}Cr^{+6}$ involves filtering the entire impinger sample followed by IC separation of the resulting filtrate. In using this protocol, it is assumed that soluble radioactive species in the filtrate that coelute with the native hexavalent chromium will be hexavalent ^{51}Cr. The radiochromatogram for the IPA/NaOH samples is shown at the top of Figure 4-2. Note that the majority of the radioactivity eluted from the IC between 4.5 and 6 min, which is the same time period in which the native hexavalent chromium

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TABLE 4.6. RECOVERY OF HEXAVALENT CHROMIUM FOR IMPINGER TRAIN FOR AUGUST 3, 1989

| Sample Identity | Native Hexavalent Chromium | | | | Spiked Hexavalent ^{51}Chromium (total counts) | | | IC Separation | | Percent of Total | |
	Expected (ug)	Found (ug)	% of Expected	% of Control	Total	Residue	Soluble	^{51}Cr^{+3}	^{51}Cr^{+6}	^{51}Cr^{+3}	^{51}Cr^{+6}
Spiked 80% IPA/20% 1.0 N NaOH Impinger Reagent Exposed to 2 Hours of Flue Gas											
IPA/NaOH Control	10.8	8.9	82.5	NA	536845	450	536395	54571	481824	10.2	89.8
IPA/NaOH Sample (I-2)	10.8	8.8	81.7	99.0	414468	26458	388010	74057	313953	24.3	75.7
IPA/NaOH Sample (I-3)	10.8	8.1	74.8	90.6	398358	15750	382608	59632	322976	18.9	81.1
IPA/NaOH Field Blank	10.8	4.9	45.4	55.0	230848	284	230564	47979	182585	20.9	79.1
Spiked 0.5 M Phosphate Buffer Impinger Reagent Exposed to 2 Hours of Flue Gas											
0.5 M PO$_4$ Control	10.8	11.2	103.5	NA	NC	NC	NC	11100	151300	6.8	93.2
PO$_4$ Sample (P-1)	10.8	2.8	26.2	25.3	563977	5579	558398	487509	70889	87.4	12.6
PO$_4$ Sample (P-2)	10.8	3.1	28.5	27.5	541406	6654	534752	453351	81401	85.0	15.0
PO$_4$ Field Blank	10.8	9.2	84.7	81.8	435957	908	435049	41561	393488	9.7	90.3

Figure 4-2. Radiochromatograms for the impinger train samples.

elutes. Of the soluble radioactive chromium, 83% coeluted from the IC/PCR with native hexavalent chromium.

A field blank sample was also collected with the IPA/NaOH set. Inexplicably, the recovery of the spike native chromium was only about 50%, and the recovery of the radioactively-labeled chromium was low also.

Use of a 0.5 M phosphate buffer in the impinger reagent resulted in very low recoveries, about 25% for the native Cr^{+6} and about 15% for the $^{51}Cr^{+6}$. Both a control sample and field blank sample showed good recoveries for the native Cr^{+6} and $^{51}Cr^{+6}$. While the phosphate buffer did not prevent conversion during sampling, the radiochromatogram (see the bottom of Figure 4-2) for the control sample and the field samples (P-1 and P-2) graphically demonstrates the ability of the improved IC technique to separate the soluble $^{51}Cr^{+6}$ and $^{51}Cr^{+3}$. Of the soluble ^{51}Cr, only 14% coeluted from the IC/PCR with the native hexavalent chromium.

In summary, the IPA/NaOH proved to be the best collection media, with the native and radioactively labeled chromium results agreeing quite well. The precision of the impinger train measurements was also good. However, the IPA did cause long-term problems with the analytical columns on the IC/PCR.

4.3 CONCLUSIONS

This preliminary method evaluation testing demonstrated that all three candidate methods showed some conversion of hexavalent chromium during sampling and/or sample storage prior to analysis. Consequently, it was decided that the Method 5-type sampling train and the "recirculating reagent" impinger train would undergo further evaluation testing at Site 6. Although the recirculating reagent impinger train was not used at Site 5 because PEI did not have the equipment, studies previously conducted by Entropy indicated that the conversion of hexavalent chromium during sampling was significantly reduced by continuously recirculating the impinger reagent to the inlet of the sampling probe. The dilution train was eliminated from further evaluations because of the cost, operating difficulties, potential for filter contamination, and the conversion of

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25% of the native and labeled hexavalent chromium during sampling and sample storage.

The data collected in this field evaluation was not emissions data and was not intended to support the OW regulations. The study was conducted to evaluate the conversion of internal spiked standards of hexavalent chromium. Therefore, none of the data should be used for any standard setting purposes.

The cause of the conversion of the hexavalent chromium during sample collection and/or recovery could not be determined from the method evaluation test. Additional work was conducted on the hexavalent chromium method by Entropy under a contract to EPA's Quality Assurance Division (QAD) in the Research Triangle Park, North Carolina. QAD plans to publish a report on the hexavalent chromium method development at the conclusion of their work on the method. Therefore, a description of the additional method development work is not discussed in this report.

5.0 SAMPLING PROCEDURES

Sampling procedures used during the Site 5 program are briefly described in this section. Standard EPA methods or draft EPA procedures were used when available.

5.1 DILUTION TRAIN

The stack gas dilution sampling system (dilution train) developed by SRI was evaluated only on the first test day (June 9, 1989). It was thought that the 15-fold dilution of the emissions using ambient air provided by this train might reduce the effects of the emissions matrix species in converting the hexavalent chromium to other valence states. As previously mentioned, prior to this method evaluation testing, no sampling system yet evaluated had demonstrated the ability to prevent the conversion of hexavalent chromium during the sampling. The gases contributing to the conversion were thought to include organics, acid gases, and sulfur dioxide.

The dilution train system used (see Figure 5-1) withdraws the emissions from the stack through a sampling nozzle and probe. The emission gases then enter a dilution chamber where they are diluted about 15-fold with ambient air. This approximates collecting the emissions as they would exist in ambient air.

The dilution train sampling rate from the stack is approximately 17 L/min. The total diluted flow rate of 425 L/min is monitored by using an orifice in the exhaust line. Gas flow rates are adjusted using the two blowers shown in Figure 5-1. These blowers are controlled by variable transformers.

The dilution air is forced through an ice bath condenser, reheated to the desired temperature, filtered, and introduced tangentially in the inlet assembly at the bottom of the dilution chamber. Dilution air flow is directed upward in the annulus border on the
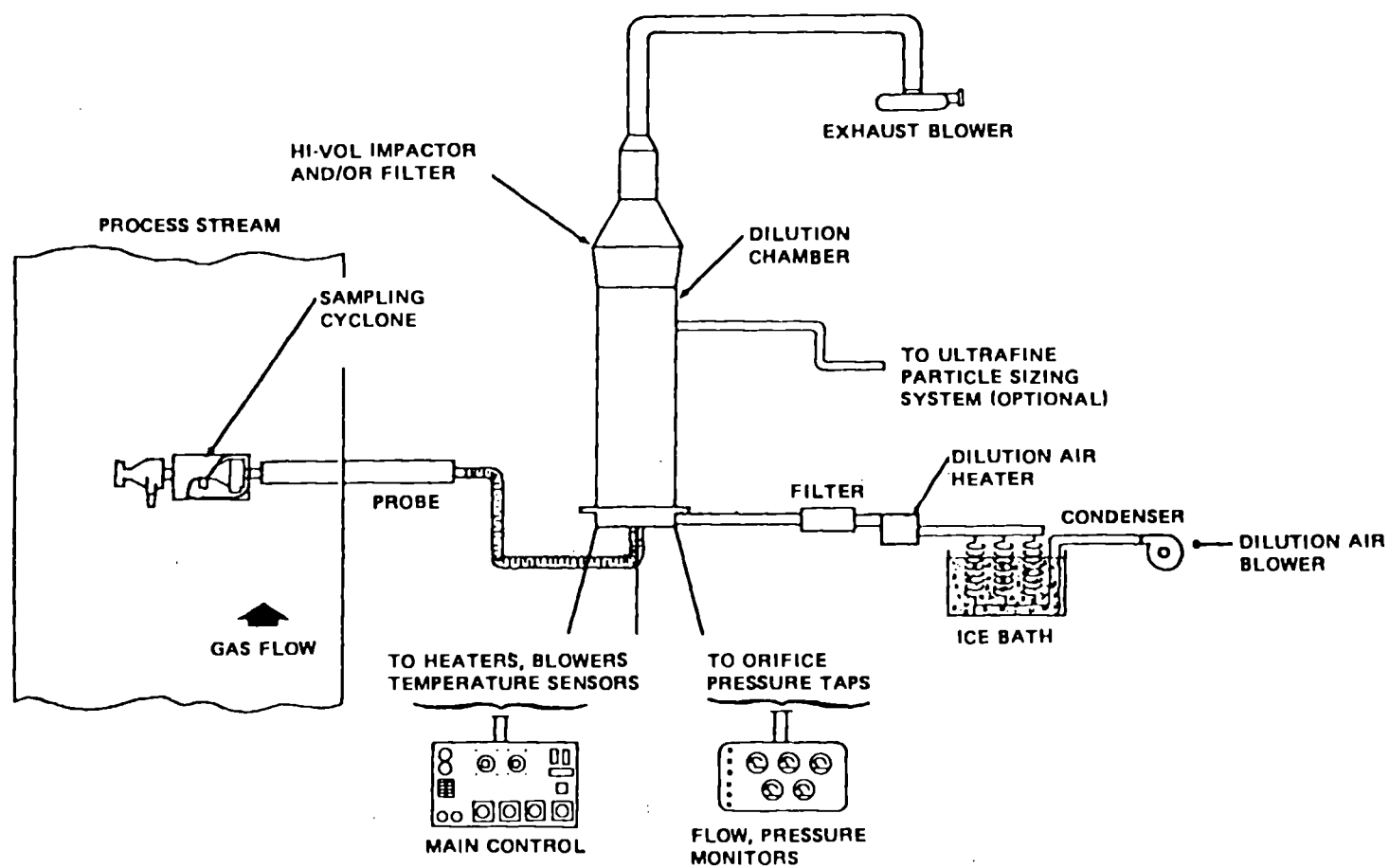
Figure 5-1. Dilution train sampling system.

outside of the dilution chamber and collected on a glass fiber filter.

The dilution train uses 8.5 in by 11 in glass fiber filters for sample collection. Prior to sampling, these filters were spiked by Entropy with 10.8 μg of native hexavalent chromium (Cr^{+6}) and less than 0.1 millicurie of radioactively-labeled hexavalent chromium ($^{51}Cr^{+6}$). The sampling train conditions including flow rates for the five test runs conducted by SRI using the dilution train are shown in Table 5-1.

5.2. METHOD 5-TYPE TRAIN

The Method 5-type train was evaluated on both test days. Sampling followed the procedures of the draft EPA method, "Determination of Hexavalent Chromium from Stationary Sources," dated December 13, 1984. A diagram of the sampling train is shown in Figure 5-2; the draft method is not reproduced in this report since the $^{53}Cr^{+6}$ data were not released by EPA. Briefly, the procedure involves the use of the EPA Method 5 sampling train with the following modifications:

- A glass nozzle and probe liner are used, and
- the glassware is cleaned according to the procedure in Table 5-2.

The sampling train nozzle, probe liner, and filter holder were made of borosilicate glass. Both the probe and filter holder were heated to 248°F $\pm$ 25°F to prevent moisture condensation. High purity quartz fiber filters without organic binder and with a 99.95% collection efficiency for 0.3 μm dioctyl phthalate (DOP) smoke particles were used.

The filters spiked with a stable hexavalent chromium isotope ($^{53}Cr^{+6}$) were analyzed by TAI under contract to EPA's EMSL in Cincinnati, Ohio. The results of the Method 5-type train testing have not been released by EPA and are not presented in this report.

On June 9, 1989, a single quad-train run was conducted yielding four filters. These filters were spiked by Entropy prior to testing with 13.18 μg of native chromium

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TABLE 5-1.   DILUTION TRAIN SAMPLING CONDITIONS

Sample ID	Start Time 24 hr	Run Time min.	Sample Flow Rate (scfm)	Dilution Flow Rate (scfm)	Total Sample Vol. (dscf)	Total Dil. Vol. (dscf)	Stack Temp. (°F)	Filter Temp. (°F)
F1	1050	15	0.89	13.8	12.6	207	91	82
F2	1118	30	0.90	13.8	25.5	414	93	82
F3*	1156	60†	0.90	13.8	51	1450	95	88
F4	1557	120	0.90	14.0	102	1680	95	86
F5	1813	60	0.90	14.0	51	840	93	84

* Run interrupted by plant operation problems. Sample flow was discontinued and dilution air flow was reduced during upset period.
† Does not include upset period.
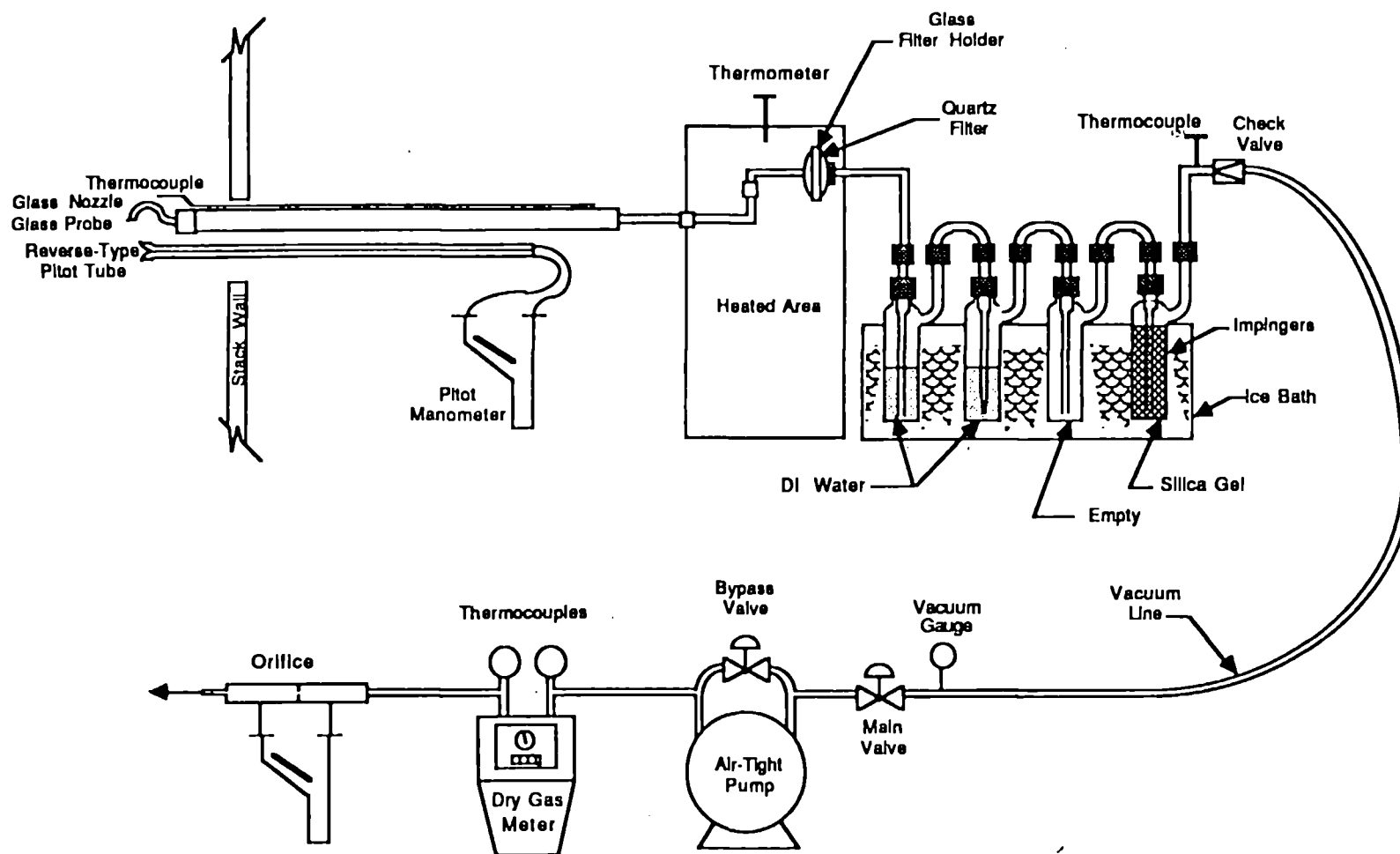
Figure 5-2. Method 5-type sampling train.

TABLE 5-2. Cr/Cr^{+6} GLASSWARE CLEANING PROCEDURES

NOTE: Use disposable gloves and adequate ventilation.

1. Soak all glassware in hot, soapy water (Alconox).

2. Rinse with tap water, three times.

3. Rinse with deionized water, three times.

4. Soak in 10% HNO$_3$ for 10 hours.

5. Rinse with deionized water, three times.

6. Cap glassware with Teflon tape.

7. Leave cleaned glassware remained capped until field assembly.

Cr^{+6} and less than 0.1 millicurie of radioactive labeled hexavalent chromium (^{51}Cr^{+6}). Four control filter samples were set aside for digestion with water, 0.2 M phosphate buffer, and 0.1 N NaOH.

On August 3, 1989, two quad-train runs were conducted yielding eight filters for Entropy analysis. One of the quad-train runs utilized four filters spiked prior to sampling (referred to as a pretest spike); and the other run utilized four unspiked filters. One of the spiked filters was lost during testing. Two of the four unspiked filters used for the second quad-train run were spiked following sampling just prior to digestion (posttest spike).

The spiking was done by Entropy using 10.8 μg of native chromium and less than 0.1 millicurie of radioactive labeled hexavalent chromium (^{51}Cr). Two posttest spiked control filter samples and one pretest spiked control filter sample were set aside for analysis with the field samples.

The sampling train conditions for both test days are presented in Table 5-3.

TABLE 5-3. METHOD 5-TYPE TRAIN SAMPLE CONDITIONS

Sample ID.	Start Time (24 hr)	Run Time (min)	Sample Volume (dscf)
First Test Day - June 9, 1989			
F-A		60	
F-B		60	
F-C		60	
F-D		60	
Second Test Day - August 3, 1989			
7-A	0828	120	85.5
7-B	0828	120	84.7
7-C	0828	120	92.1
7-D	0828	120	89.1
8-A	1050	120	86.8
8-B	1050	120	85.5
8-C	1050	120	90.6
8-D	1050	120	89.3

5.3 IMPINGER TRAIN

The impinger train was evaluated on both test days. It was originally anticipated that the method evaluation would be conducted using the recirculating reagent impinger developed for hexavalent chromium testing. However, since PEI Associates, Inc. did not own a recirculating impinger reagent train, an impinger train configured by removing the front filter from a Method 5 train was used (see Figure 5-3). Because the analysis only examined the recovery of native and labeled hexavalent chromium spiked into the impinger reagents, the material collected in the nozzle and probe was not recovered with the sample. Previous research had shown that glass components in the sampling train could contribute to the background levels of trivalent chromium in the acid rinse, but,

Thermocouple
Glass Nozzle
Glass Probe

Reverse-Type
Pilot Tube

Stack Wall

Pilot
Manometer

Thermocouple   Check
Valve

Impingers

Ice Bath

80% IPA / 20% 2N NaOH
or
0.5 M Phosphate Buffer

Silica Gel

Empty

Orifice

Thermocouples

Bypass
Valve

Vacuum
Gauge

Vacuum
Line

Main
Valve

Dry Gas
Meter

Air-Tight
Pump
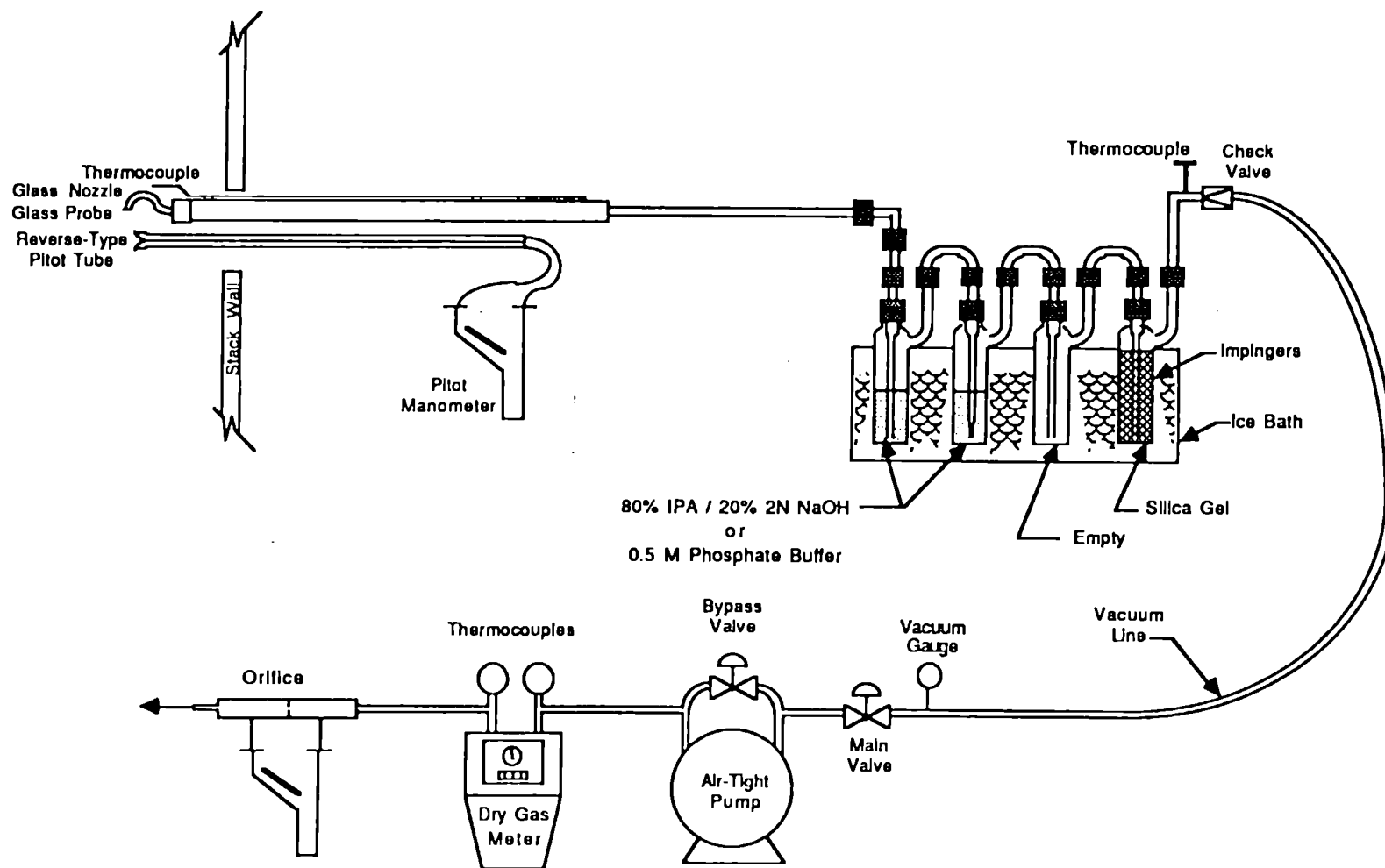
Figure 5-3. Impinger sampling train

since the evaluation did not include a nitric rinse of the sampling train, the use of glass components was not considered a problem.

Sampling and analysis followed the procedures in the draft EPA method, "Determination of Hexavalent Chromium from Stationary Sources," except as noted above. A diagram of the full recirculating reagent sampling train is shown in Figure 5-4; the draft method is reproduced in Appendix B. This procedure is based on EPA Method 5 with the following modifications:

- 80% IPA/20% 2 N NaOH replaces water in the impingers (0.5 M phosphate buffer was used in the impingers for one quad-train run on the second test day);
- the entire surface exposed to sample is constructed of Teflon and/or glass;
- the Teflon and/or glass components are cleaned according to the procedure in Table 5-4;
- the train does not have a filter section; and
- the reagents are continuously recirculated from the first impinger back to the nozzle to provide a flow of reagents through the probe, and thus preventing hexavalent chromium in the probe drying out and possibly converting to another valence state (not done for this testing).

TABLE 5-4. Cr^{+6}/Cr TEFLON/GLASS COMPONENTS CLEANING PROCEDURES

1. Soak all components in hot, soapy water (Alconox).
2. Rinse with tap water, three times.
3. Rinse with deionized water, three times.
4. Soak in 10% HNO_3 for 10 hours.
5. Rinse with deionized water, three times.
6. Cap Teflon/glassware with Teflon tape.
7. Leave cleaned Teflon/glassware capped until field assembly.
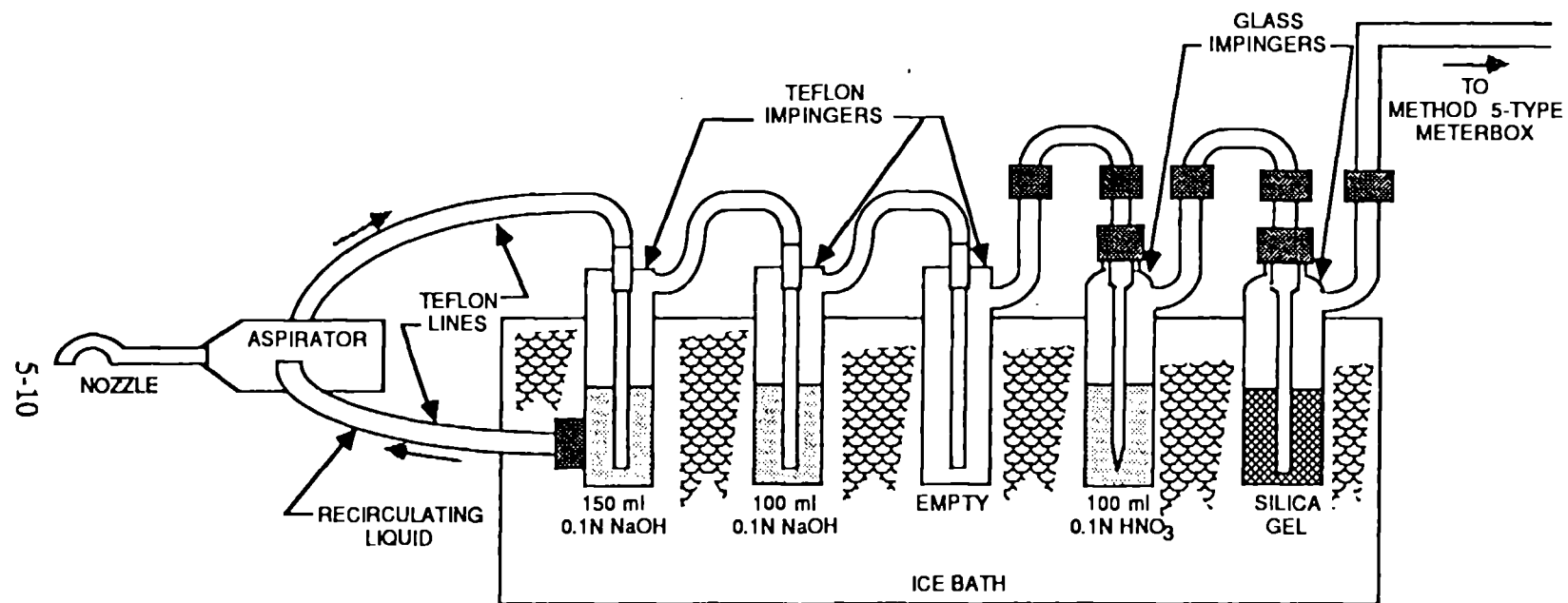
Figure 5-4. Recirculating reagent sampling train.

On June 9, two quad-train runs were conducted yielding eight impinger samples. A 2-L volume of the impinger reagent (80% IPA/20% 2 N NaOH) was spiked by Entropy prior to testing with 18.83 μg per 200 mL of native hexavalent chromium and less than 1 millicurie per 200 mL of radioactively-labeled hexavalent chromium ($^{51}Cr^{+6}$). Each sampling train was charged with a 200 mL of the spiked impinger reagent. To verify the spike concentration and as a check for contamination, control samples of the spiked impinger reagent were set aside and analyzed with the field samples.

On August 3, two quad-train runs were conducted yielding eight samples. For the first run, a 2-L volume of impinger reagent (80% IPA/20% 2 N NaOH) was spiked by Entropy prior to testing with 10.8 μg per 200 mL of native hexavalent chromium and less than 1 millicurie per 200 mL of radioactively-labeled hexavalent chromium ($^{51}Cr^{+6}$). Each train was charged with a 200 mL spiked impinger reagent. For the second run, a 2-L volume of a phosphate buffer impinger reagent (0.5 M) was spiked by Entropy prior to testing with 10.8 μg per 200 mL of native hexavalent chromium and less than 1 millicurie per 200 mL of $^{51}Cr^{+6}$. Each train was charged with a 200 mL spiked impinger reagent. One control sample and the concentrated spiking solution were analyzed for each impinger reagent. The impinger train run conditions for both quad-train runs are shown in Table 5-5.

5.4 EPA METHODS 1, 2, 3, AND 4

EPA Methods 1, 2, 3, and 4 were used to determine the volumetric flow rate, the molecular weight, and the flue gas moisture content.

The volumetric gas flow rate was determined during this program using procedures described in EPA Methods 1 and 2. Based on these methods, the volumetric gas flow rate is determined by measuring the cross-sectional area of the stack and the average velocity of the flue gas. The average flue gas velocity is calculated from the average pitot tube pressure (ΔP), the average flue gas temperature, the wet molecular weight, and the absolute static pressure measured at a single point in the stack.

TABLE 5-5. IMPINGER TRAIN SAMPLING CONDITIONS

Sample ID.	Start Time (24 hr)	Run Time (min)	Sample Volume (dscf)
		First Test Day - June 9, 1989	
I-1		60	
I-2		60	
I-3		60	
I-4		60	
I-1		60	
I-2		60	
I-3		60	
I-4		60	
		Second Test Day - August 3, 1989	
9-A	1318	120	88.6
9-B	1318	120	88.1
9-C	1318	120	92.8
9-D	1318	120	90.6

The integrated sampling technique described in EPA Method 3 was used to obtain composite flue gas samples for fixed gas (O_2, CO_2) analysis. A small diaphragm pump and a stainless steel probe were used to extract a single-point flue gas sample which was collected in a Tedlar bag. Moisture was removed from the gas sample by a water-cooled condenser so that the fixed gas analysis is on a dry basis. The composition of the gas sample was determined using an Orsat analyzer.

The moisture content of the flue gas was determined using the methodology described in EPA Method 4. Based on this method, a known volume of particulate-free gas was pulled through a chilled impinger train. The quantity of condensed water was determined gravimetrically and then related to the volume of gas sampled to determine the moisture content.

6.0 ANALYTICAL PROCEDURES

Three analytical procedures were employed to speciate chromium compounds in the samples to determine the recovery of native and labeled hexavalent chromium: IC/PCR, ICP/MS, and gamma or scintillation counting. The dilution train, Method 5-type train, and impinger samples collected for Entropy were analyzed using ion chromatography with a Cr^{+6}-specific post column reaction (IC/PCR). Entropy also performed gamma counting measurements of labeled hexavalent chromium ($^{51}Cr^{+6}$) spiked into samples to determine the recovery and, consequently, conversion of native and labeled hexavalent chromium that may occur during sampling, sample handling, and sample preparation. Since the results for the hexavalent chromium filter train analyses conducted by TAI using IC/PCR and ICP/MS were not released, their analytical techniques will not be discussed.

The IC/PCR system was calibrated daily with a series of three freshly prepared Cr^{+6} standard solutions at concentrations ranging from 23-to-108 ng/ml.

6.1 FIRST TEST DAY - JUNE 9, 1989

6.1.1 Dilution Train

The dilution train uses an 8.5 in. by 11 in. glass fiber filter to collect the sample. Prior to testing, filters were spiked by Entropy with 10.8 μg of native hexavalent chromium and less than 0.1 millicurie of radioactively-labeled hexavalent chromium ($^{51}Cr^{+6}$). The mass of radioactively-labeled hexavalent chromium was well below the detection limit of the IC/PCR, and therefore, there was no interference of the labeled chromium in the native chromium analysis. If the mass of the radioactively-labeled

hexavalent chromium was above the detection limit of the IC/PCR, it would measured as native hexavalent chromium. The radioactive chromium used ($^{51}Cr^{+6}$) has a half life of 28 days. Native chromium does not contain any radioactive hexavalent chromium and would therefore not interfere with the gamma counting analysis.

Each of the five dilution train filter samples was extracted using 500 mL of 0.1 N NaOH. The extraction included sonication for 50 min followed by vacuum filtering through a 0.45 μm Teflon filter. The filtrate was then analyzed for native hexavalent chromium by IC/PCR and radioactive content with a scintillation (gamma) counter. The glass fiber filter and 0.45 μm Teflon filter were also analyzed for radioactivity with the scintillation counter. It was assumed that all the radioactive chromium in the filtrate was in the hexavalent state.

The recovery of native hexavalent chromium was calculated by comparing the amount of hexavalent chromium spiked onto the glass fiber filter with the amount of hexavalent chromium recovered in the filtrate.

At the end of the first test day, there were no spiked filters remaining to serve as a control sample and, therefore, a control sample could not be analyzed.

6.1.2 Method 5-Type Train

A single Method 5-type quad-train run on the first test day was conducted and four 82 mm glass fiber filter samples were collected. The filters were spiked by Entropy prior to sampling with 13.18 μg of native Cr^{+6} and less than 0.1 millicurie of ($^{51}Cr^{+6}$). Four control filter samples were spiked and extracted as described for the dilution train filters. Two with water, 1-with 0.2 M phosphate buffer, and 1-with 0.1 N NaOH. The best recovery of 83% was obtained using the 0.1 N NaOH to extract the filter. Each field sample filter was then digested with 250 mL of 0.1 N NaOH using the same procedure. The filtrate was analyzed for native hexavalent chromium by IC/PCR and radioactivity with a scintillation counter. The glass fiber filter and 0.45 μm Teflon filter were analyzed for radioactivity with a scintillation counter. It was assumed that all the radioactive chromium in the filtrate was in the hexavalent state.

6.1.3 Impinger Train

Two quad-train runs yielded eight impinger samples for analysis. Each impinger train was charged with 200 mL of spiked impinger reagent (80% IPA/20% 2 N NaOH). Two liters of impinger reagent were spiked by Entropy prior to testing with 18.83 μg per 200 mL of native Cr^{+6} and less than 1 millicurie per 200 mL of $^{51}Cr^{+6}$. One control reagent sample and three dilutions of the concentrated spiking solution were also analyzed. Each impinger sample was vacuum filtered through a 0.45 μm Teflon filter. The filtrate was boiled to reduce the concentration of IPA, and then analyzed for native hexavalent chromium by IC/PCR and radioactivity with a scintillation counter. The Teflon filter was also analyzed for radioactivity with the scintillation counter. It was assumed that all the radioactive chromium in the filtrate was in the hexavalent state.

As mentioned in Section 4.0, the poor agreement between the recovery of native chromium and labeled chromium indicated that all the soluble chromium in the filtrate must not be in the hexavalent state. Laboratory experiments were then conducted under a separate work assignment with EPA's Quality Assurance Division, Research Triangle Park, NC. A new analytical procedure was developed to separate the hexavalent and trivalent chromium prior to scintillation counting. In this procedure, the discharge from the IC/PCR (sample separated by analytical column) is collected every 30 sec over the typical analytical run time of 8 min. These individual aliquots are analyzed using the scintillation counter. By the time the new analytical technique had been developed, the radioactivity levels from the first test day samples were too low to detect.

6.2 SECOND TEST DAY - AUGUST 3, 1989

The new analytical technique developed following the first field test was used to analyze the labeled hexavalent chromium in the samples from the second test. Because of poor recoveries seen for the control samples for the first test, it was decided to use a pretest spike and a posttest spike in the second test.

6.2.1 Dilution Train

No dilution train samples were collected during the second test day.

6.2.2 Method 5-Type Train

Two quad-train runs conducted on August 3 resulted in eight glass fiber filters samples. The filters for one of the quad-train runs were spiked prior to testing; the filters for the other quad-train run were unspiked prior testing and two of these were spiked prior to extraction. One of the spiked filters was lost during sampling. The filters were spiked by Entropy prior to sampling (pretest spike) or just prior to extraction (posttest spike) with 10.8 μg of native Cr^{+6} and less than 0.1 millicurie of $^{51}Cr^{+6}$. Two posttest spiked control samples and one pretest spiked control sample were prepared and analyzed. Each filter was extracted with 250 mL of 0.1 N NaOH including sonication and vacuum filtering through a 0.45 μm Teflon filter. The filtrate was then analyzed for native hexavalent chromium by IC/PCR. The IC/PCR sample discharge was collected at 30-sec intervals and these aliquots were analyzed for radioactivity with a scintillation counter. The filters were analyzed for radioactivity by scintillation counting.

6.2.3 Impinger Train

Two quad-train runs generated eight impinger samples for analysis. Each impinger train was charged with 200 mL of spiked impinger reagent. For the first quad train run, 2 L of impinger reagent (80% IPA/20% 2 N NaOH) were spiked by Entropy prior to testing with 10.8 μg per 200 mL of native Cr^{+6} and less than 1 millicurie per 200 mL of $^{51}Cr^{+6}$. For the second quad-train run, 2 L of impinger reagent (0.5 M phosphate buffer) were spiked by Entropy in a similar manner. One control sample of spiked impinger reagent and one sample of concentrated spiking solution were analyzed for each impinger solution. Each impinger sample was vacuum filtered through a 0.45 μm Teflon filter. The filtrate was boiled to reduce the concentration of IPA, and then

analyzed for native hexavalent chromium by IC/PCR and radioactivity with a scintillation counter. The Teflon filter used to remove the solids for each sample was analyzed for radioactivity with a scintillation counter.

The resulting filtrates were analyzed by the new IC/PCR analytical technique. To determine the ratio of the soluble $^{51}Cr^{+3}$ and $^{51}Cr^{+6}$ species where there was a spike, 30-sec aliquots was collected during the IC/PCR analysis, and the gamma counts measured for each fraction.

7.0 QUALITY ASSURANCE AND QUALITY CONTROL

This section discusses the quality assurance and quality control (QA/QC) program and the QA/QC results for the sewage sludge incineration test program at Site 5. For this site, the test program was designed for methods development and evaluation purposes only and, therefore, no emissions data was collected. This eliminated the need to perform isokinetic sampling, since primarily quadruplicate sampling trains were employed and only the relative differences between the trains was of interest. The objectives of and basic activities for the QA/QC program are briefly discussed in the section below.

7.1 QA/QC PROGRAM OBJECTIVES

For any environmental measurement, a degree of uncertainty exists in the data generated due inherent limitations of the measurement systems employed. To assess the quality of the data and to establish limitations on the ultimate use of the data, a limited QA/QC program was implemented for this test effort. The objective of the QA/QC program was to produce complete, representative, and comparable data of known quality. All elements of the QA/QC program were implemented during the sampling and analytical phases of the sewage sludge incinerator test program for Site 5.

7.2 FLUE GAS SAMPLING AND ANALYSIS QC RESULTS

Quality control activities for flue gas sampling include: (1) equipment calibrations, (2) glassware and equipment cleaning, (3) procedural checks during sampling and sample recovery, (4) sample custody procedures, (5) procedural checks during sample analysis,

and (6) the use of labeled surrogates, field blanks, laboratory blanks, QC check samples, matrix spikes, and duplicate analyses. The QC results for these activities are discussed in this section for each of the three sampling procedures evaluated at Site 5 and for the analytical procedures employed.

7.2.1 Dilution Train Sampling

During sampling, the dilution rates were kept constant for each of the five test runs. The dilution ratio of total sample volume to gas sample volume ranged from 15.3 to 15.6. The temperature of the filters where the diluted sample mass was collected ranged from 82 to 88 °F during the five sample runs. The relatively consistent dilution train sampling conditions established for the five runs allowed for meaningful comparison of the main variable, the sample collection time.

Each of the dilution train filters were spiked with 10.8 μg of native hexavalent chromium and less than 0.1 millicurie of radioactively-labeled hexavalent chromium ($^{51}Cr^{+6}$) to assess conversion and recovery of hexavalent chromium using the dilution sampling train. Due to process problems, additional sampling runs were required, and the filters sent to the field designated as controls had to be used. Therefore, no control samples were available for analysis.

There was good agreement between the recovery of the spiked native hexavalent chromium and the spiked $^{51}Cr^{+6}$ that averaged 76.6% and 77.4%, respectively.

Even though the dilution train sampling approach provided comparable recoveries of hexavalent chromium as the impinger method, the dilution train was eliminated from further consideration due to practical and technical considerations.

7.2.2 Method 5-Type Sampling

All sampling train glassware and Teflon components and sample containers were precleaned initially with soap and water followed by a DI water rinse, an 0.1 N nitric

7-2

acid rinse, and a final DI water rinse. During on-site testing, all sampling train glassware was capped with Parafilm or Teflon tape prior to and immediately after each test run. A clean, dust-free environment was maintained on-site for sampling train assembly and sample recovery.

Method 5-type 82 mm quartz fiber filters were used to evaluate this sampling procedure. The filters were spiked with 13.18 μg of native hexavalent chromium and less than 0.1 millicurie of $^{51}Cr^{+6}$ to assess conversion and recovery of hexavalent chromium. For the first test series, four filters were spiked and then extracted with different reagents to determine which reagent gave the best recovery. It was determined that 0.1 N NaOH was superior to water and phosphate buffer. The remaining filters were exposed to flue gas for 60 minutes at the nominal Method 5 sampling rate. The filters were extracted with 0.1 N NaOH and the native and $^{51}Cr^{+6}$ recoveries determined. The radiochromatography procedure (discussed in Section 7.2.4) was not employed on these samples.

Of the extraction reagents evaluated on the control filters, 0.1 N NaOH gave the highest recovery (83.0%) of native hexavalent chromium. There was not good agreement between the recoveries of the spiked hexavalent chromium and the spiked $^{51}Cr^{+6}$ that averaged 29.5% and 54.8%, respectively. This difference may have been due to the assumption that, after 0.45 μm filtration of the extraction solution, all of the soluble radioactivity was $^{51}Cr^{+6}$ (see Section 7.2.4).

For the second test series, filters were spiked with 10.8 μg of native hexavalent chromium and less than 0.1 millicurie of $^{51}Cr^{+6}$. A set of filters were spiked prior to exposure to flue gas (pretest spike) and a second set were spiked after flue gas exposure but prior to extraction (posttest spike). The pretest spikes were used to assess native and $^{51}Cr^{+6}$ recovery after exposure to flue gas. The posttest spikes were used to assess matrix effects on the recovery of native and $^{51}Cr^{+6}$ from the filter and particulate matter on the filter. Posttest spiked controls were prepared and analyzed to determine native and $^{51}Cr^{+6}$ from the filter matrix. Unspiked filters were exposed to flue gas to provide a measure of native hexavalent chromium collected from the source during sampling to

allow for correction of the spiked native hexavalent chromium recovery. A pretest spiked filter not exposed to flue gas was used as a field blank.

All recoveries of $^{51}Cr^{+6}$ for the second test series were determined by radiochromatography (see Section 7.2.4).

Posttest spiked controls had 82.4 to 87.0% recovery of native hexavalent chromium and 97.7 to 98.5% recovery of $^{51}Cr^{+6}$. The posttest spikes of exposed filters had 98.8 to 100.5% and 88.5 to 91.0% recovery of the native and $^{51}Cr^{+6}$, respectively, relative to the posttest spiked controls. The pretest spiked field blank had only 6.5% and 31.4% recovery of the native and $^{51}Cr^{+6}$, respectively, relative to the posttest spiked controls. The field blank had lower recoveries than the recoveries determined for the pretest spiked filters exposed to flue gas for 2 hr, and appears to be an outlier.

7.2.3 Impinger Train Sampling

All sampling train glassware and Teflon components and sample containers were precleaned initially with soap and water followed by a DI water rinse, an 0.1 N nitric acid rinse, and a final DI water rinse. During on-site testing, all sampling train glassware was capped with Parafilm or Teflon tape prior to and immediately after each test run. A clean, dust-free environment was maintained on-site for sampling train assembly and sample recovery.

For the first test series, the impinger reagent (80% IPA/20% 2 N NaOH) was spiked with native and $^{51}Cr^{+6}$, respectively, at a concentration of 18.83 μg and less than 1 millicurie per 200 mL. Samples of the spiked reagent were collected as field blanks for analysis with the field samples.

From the control sample, 95.5% and 99.9% of the native and $^{51}Cr^{+6}$, respectively, were recovered. The recoveries of spiked hexavalent chromium and $^{51}Cr^{+6}$ from the field samples averaged 65.4% and 99.7%, respectively. This difference may have been due to the assumption that, after 0.45 μm filtration of the extraction solution, all of the soluble radioactivity was $^{51}Cr^{+6}$ (see Section 7.2.4).

7-4

For the second test series, the impinger reagents (80% IPA/20% 1.0 N NaOH and 0.5 M phosphate buffer) were spiked with native and $^{51}Cr^{+6}$, respectively, at a concentration of 10.8 μg and less than 1 millicurie per 200 mL. Control samples and field blanks of each reagent were collected and analyzed with the field samples. Radiochromatography was employed to measure $^{51}Cr^{+6}$ in the sample filtrate.

The IPA/NaOH control sample had recoveries of 82.5% and 89.8% of the native and $^{51}Cr^{+6}$ spikes. The IPA/NaOH field blank had recoveries of 45.4% and 79.1% of the native and $^{51}Cr^{+6}$ spikes. The exposed samples had average recoveries of 78.3% and 78.4%, respectively, of the native and $^{51}Cr^{+6}$ spikes.

The phosphate buffer control sample had recoveries of 103.5% and 93.2% of the native and $^{51}Cr^{+6}$ spikes. The phosphate buffer field blank had recoveries of 84.7% and 90.3% of the native and $^{51}Cr^{+6}$ spikes. The exposed samples had average recoveries of 27.4% and 13.8%, respectively, of the native and $^{51}Cr^{+6}$ spikes.

7.2.4 Native Hexavalent Chromium and $^{51}Cr^{+6}$ Analysis

The analysis of filter extracts and impinger sample for native hexavalent chromium was performed by IC/PCR following the procedures in the draft EPA method, "Determination of Hexavalent Chromium from Stationary Sources." A three-point calibration curve from 23-to-108 ppb was established. The deviation of the standard responses from the linear regression line ranged from -8.6% to 5.7%. The largest deviation calculated, -8.6%, was for the 23 ppb standard where the predicted concentration was 21 ppb, a difference of 2 ppb.

The discrepancy between the recoveries of the spiked hexavalent chromium and $^{51}Cr^{+6}$ for the first test series led to the development of the radiochromatography technique for analysis of the samples from the second test series. Upon analysis of the samples from the second test series, the assumption that all soluble radioactivity was present as $^{51}Cr^{+6}$ was found to be false. Of the soluble radioactivity in the NaOH extracts of pretest spiked Method 5-type filters exposed to flue gas, an average of 87%

was found to elute from the IC/PCR with native hexavalent chromium. For the IPA/NaOH impinger samples, an average of 83% of soluble radioactivity was found to elute from the IC/PCR with native hexavalent chromium. For the phosphate buffer impinger samples, an average of 14% of soluble radioactivity was found to elute from the IC/PCR with native hexavalent chromium. In each case the radiochromatographic determinations of $^{51}Cr^{+6}$ were in good agreement with the recoveries of native hexavalent chromium spikes.

REFERENCES

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2. Majiam, T.T. Kasakura, N. Naruse and M. Hiraoka. 1977. Studies of Pyrolysis Process of Sewage Sludge. Prog. Wat. Tech. Vol. 9, 381-396. Great Britain: Pergamon Press.

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Appendix A
Analytical Data

Chromium Analytical Data Sheet
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Job Name: Chromium Impingers PEI   Job Num.   4181
Analyst: E. Coppedge/A. Carver   Date: June 19, 1989
===
Chromium Standard Calibration Curve   6

Conc. (ppb)	Peak Area Run 1	Run 2	Average	Percent Deviation	Predicted Conc. (ppb)	Percent Deviation from Actual
23	2296400	2190500	2243450	2.4%	23.72	4.6%
54	4389800	4377300	4383550	0.1%	52.35	-3.0%
108	8626100	8550400	8588250	0.4%	108.60	0.6%

Standard Curve   Slope 74748.28 Intercept   470246
===

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Chromium Conc. ppb	Volume (ml)	Total Catch (ug)	Spiked (ug)	R (%)
C-108	7710700	7396700	7553700	2.1%	94.76	100	9.48		
C-216	14534000	14552000	14543000	0.1%	188.27	100	18.83		
C-324	23593000	25001000	24297000	2.9%	318.76	100	31.88		
C-I-9	16992000	17162000	17077000	0.5%	222.17	81	18.00	18.83	95.6
I-1	7925400	8034000	7979700	0.7%	100.46	163	16.38	18.83	87.0
I-2	4376200	4320500	4348350	0.6%	51.88	214	11.10	18.83	59.0
I-3	2229700	2235900	2232800	0.1%	23.58	196	4.62	18.83	24.5
I-4	5355600	5364800	5360200	0.1%	65.42	212	13.87	18.83	73.7
I-5	5598700	5492500	5545600	1.0%	67.90	192	13.04	18.83	69.2
I-6	6123800	5960700	6042250	1.3%	74.54	188	14.01	18.83	74.4
I-7	6450300	6393100	6421700	0.4%	79.62	175	13.93	18.83	74.0
I-8*	1962100	2201400	2081750	5.7%	21.56	184	3.97	18.83	21.1
F-A	1255300	1206900	1231100	2.0%	10.18	247	2.51	13.18	19.1
F-B	1798400	1814400	1806400	0.4%	17.88	253	4.52	13.18	34.3
F-C	1977900	1957400	1967650	0.5%	20.03	253	5.07	13.18	38.5
F-D	1684300	1683700	1684000	0.0%	16.24	210	3.41	13.18	25.9

NOTES:
C-108--C-324 are dilutions of the solution used to spike the impinger
solutions. The actual spiking amount is equal to c-108.
C-I-9 was a control impinger solution sent to the field.
All impinger solutions were vaccum filtered through 0.45um Teflon
filter paper. The samples were then boiled to remove the IPA for analysis,
and a cation resin was used to remove the Na+.
Stack gas was drawn through the solution for indicated minutes.
I-8 contained some silica gel in the recovered solution.
F-A--F-D filters were spiked with 13.18 ug. Stack gas was drawn through the filter for
60 min. Filters were digested with 0.1N NaOH and vaccum filtered.

Chromium Analytical Data Sheet
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Job Name:Chromium Filters PEI/SRI   Job Num.   4181
Analyst: E. Coppedge/A. Carver   Date: June 14, 1989
===

Chromium Standard Calibration Curve   6

Conc. (ppb)	Peak Area			Percent Deviation	Predicted Conc. (ppb)	Percent Deviation from Actual
	Run 1	Run 2	Average			
23	1124200	1150800	1137500	1.2%	21.92	-4.7%
54	3598100	3688000	3643050	1.2%	55.70	3.1%
108	7429600	7524200	7476900	0.6%	107.38	-0.6%

Standard Curve   Slope 74180.23 Intercept -488631
===

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Chromium Conc. ppb	Volume (ml)	Total Catch (ug)	Spiked (ug)	R (%)
C-6	1173100	1027300	1100200	6.6%	21.42	278	5.95	10.8	55.1
C-7	NO PEAK	NO PEAK							
C-8	2419600	2376300	2397950	0.9%	38.91	220	8.56	10.8	79.3
C-9	4383900	4422400	4403150	0.4%	65.94	136	8.97	10.8	83.0
F-1	688600	672130	680365	1.2%	15.76	505	7.96	10.8	73.7
F-2	815170	722990	769080	6.0%	16.95	427	7.24	10.8	67.0

NOTES:
Instrument Setting AU: 0.5
C-6 was sent to the field as a control sample.
It was digested with water.
C-7 was sent to the field as a control sample,
a 0.2M phosphate buffer was used for digestion.
C-8 was a laboratory control digested with water.
C-9 was a laboratory control digested with the
0.1 N NaOH
F-1 was an actual field sample. Stack gas was
pulled for 15 min. The filter was digested
in 0.1 N NaOH.
F-2 was an actual field sample with gas pulled for
30 min, also digested in 0.1N NaOH. The ash
on this filter was a yellow chalky color and very
light compared to the other filters.

Chromium Analytical Data Sheet
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                    Job Name:Chromium Filters SRI   Job Num.   4181
                    Analyst: E. Coppedge/A. Carver   Date: June 15, 1989
==
                    Chromium Standard Calibration Curve   6

| | | Peak Area | | Percent | Predicted | | Percent | |
| Conc. | --- | --- | --- | Deviation | Conc. | | Deviation | |
(ppb)	Run 1	Run 2	Average		(ppb)		from Actual	
23	1945300	1977100	1961200	0.8%	21.03		-8.6%	
54	5481100	5212600	5346850	2.5%	57.10		5.7%	
108	9967400	10069000	10018200	0.5%	106.87		-1.0%	

Standard Curve   Slope 93861.74 Intercept -12724
==

Sample ID	Run 1 Area	Run 2 Area	Average	Percent Deviation	Chromium Conc. ppb	Volume (ml)	Total Catch (ug)	Spiked (ug)	R (%)
F-3*	1288700	1233190	1260945	2.2%	13.57	513	6.96	10.8	64.5
F-4	2068600	1927000	1997800	3.5%	21.42	500	10.71	10.8	99.2
F-5	1703700	1640200	1671950	1.9%	17.95	462	8.29	10.8	76.8

NOTES:
Instrument Setting AU: 0.5

All samples were digested in 0.1 N NaOH, sonicated for 50 minutes,
and vaccum filtered.
F-3 approximately 15 ml of sample was lost during digestion.
F-3 1 hour interupted sample.
F-4 120 min sample.
F-5 1 hour uninterupted sample.

A-4

Radioactive Chromium Analytical Data
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Sample ID	CT #	Count 1	Count 2	Average	Sample Vol (ml)	Vol Cor.	R (%)
C-I-9:Filter after digestion	117	2431		2431	81	2431	
C-I-9: 5 ml filtrate	118	199650		199650	5	3234330	99.9
I-1: Filter after digestion	101	4736		4736	163	4736	
I-1: 5 ml filtrate	102	89463		89463	5	2916494	99.8
I-2: Filter after digestion	103	3972		3972	214	3972	
I-2: 5 ml filtrate	104	58276		58276	5	2494213	99.8
I-3: Filter after digestion	105	4376		4376	196	4376	
I-3: 5 ml filtrate	106	78579		78579	5	3080297	99.9
I-4: Filter after digestion	107	5940		5940	214	5940	
I-4: 5 ml filtrate	108	69401		69401	5	2970363	99.8
I-5: Filter after digestion	109	7949		7949	192	7949	
I-5: 5 ml filtrate	110	58276		58276	5	2237798	99.6
I-6: Filter after digestion	111	10850		10850	188	10850	
I-6: 5 ml filtrate	112	75480		75480	5	2838048	99.6
I-7: Filter after digestion	113	4234		4234	175	4234	
I-7: 5 ml filtrate	114	83306		83306	5	2915710	99.9
I-8: Filter after digestion	115	5011824		5011824	184	5011824	
I-8: 5 ml filtrate	116	21542		21542	5	792746	13.7
F-A: Filter after digestion	145	107705		107705	247	107705	
F-A: 15 ml filtrate	146	66428		66428	15	1093848	91.0
F-B: Filter after digestion	147	929795		929795	253	929795	
F-B: 15 ml filtrate	148	75442		75442	15	1272455	57.8
F-C: Filter after digestion	149	809712		809712	253	809712	
F-C: 15 ml filtrate	150	82366		82366	15	1389240	63.2
F-D: Filter after digestion	151	114805		114805	210	114805	
F-D: 15 ml filtrate	152	84082		84082	15	1177148	91.1

Radioactive Chromium Analytical Data

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===========================================================================
        SRI Filter Analysis        Job. Number: 4181
        Anna C. Carver             Date: June 15, 1989
===========================================================================
```

Sample ID	CT #	Count 1	Count 2	Average	Sample Vol (ml)	Vol Cor.	R (%)
F-1: Filter after digestion	47-50	681038		681038	504	681038	
F-1: 9 ml filtrate	51	24752		24752	9	1386112	67.1
F-2: Filter after digestion	52-54	496081		496081	427	496081	
F-2: 9 ml filtrate	55	33961		33961	9	1611261	76.5
F-3:Filter after digestion	69-72	410934		410934	513	410934	
F-3: 8 ml filtrate	73	19553		19553	8	1253836	75.3
F-4: Filter after digestion	74-76	236544		236544	500	236544	
F-4: 8 ml filtrate	77	25906		25906	8	1619125	87.3
F-5: Filter after digestion	78-80	390074		390074	462	390074	
F-5: 8 ml filtrate	81	28497		28497	8	1645702	80.8

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TO: W. G. DeWees

FROM: Scott Steinsberger

DATE: August 20, 1989

SUBJECT: Results From Second Methods Development Effort

This memorandum is to summarize the results from the second methods development effort conducted by PEI and Entropy. The results of the spiked impinger experiments are summarized in Table 1. Recoveries of spiked native chromium (10.8) from two 80% IPA/20% 1.0 N NaOH impinger reagent samples exposed to 2 hours of flue gas were 81.7% and 74.8%. For the IPA/NaOH reagent relative to a spiked IPA/NaOH control sample where 8.9 ug was recovered, the recoveries were 99.0% and 90.6% for the two samples. The recovery of spiked $^{51}Cr^{+6}$ in the two samples were in agreement with the native Cr recovery, at 75.7% and 81.1%, with recovery in the control sample being 89.8%. The $^{51}Cr^{+6}$ analysis protocol involves filtering the whole sample followed by IC separation of the filtrate. With this protocol, only the soluble radioactivity in the filtrate that coelutes with the native hexavalent chromium is considered to be hexavalent ^{51}Cr. The radiochromatograms for the IPA/NaOH samples are shown at the top of Figure 1. Note that the majority of the radioactivity elutes from the IC between 4.5 and 6 minutes, where the native hexavalent chromium elutes.

A field blank sample was also collected with the IPA/NaOH set. Unexplainably, the field recovery was about 50%, and the total recovered radioactivity was low also.

The 0.5 M phosphate buffer resulted in very low recoveries; about 25% for native Cr^{+6} and about 15% for $^{51}Cr^{+6}$. Both control and filed blank samples should good recoveries of both Cr^{+6} and $^{51}Cr^{+6}$. While the phosphate buffer did not prevent conversion during sampling, the radiochromatograms (see the bottom of Figure 1) for the control sample and the field samples (P-1 and P-2) graphically demonstrate the ability of the IC to separate soluble ^{51}Cr species.

The results for the Method 5-type filters sample are presented in Table 2. A set of four unspiked filters were exposed to flue gas for 2 hours to obtain a representative particulate loading. Two of the samples were extracted and analyzed for Cr^{+6}. Note that 2.8 and 2.9 ug were found on the unspiked filters. The remaining two samples and two blank filters were spiked with a mixture of $^{51}Cr^{+6}$ and native Cr^{+6}, and the four filters were extracted. Recoveries for the blank filters were 87 % and 82.4 % for native Cr^{+6}, with 98% of the recovered ^{51}Cr being Cr^{+6}. For the flue-gas exposed, spiked filters, the recoveries were 66.1% and 67.3% for native Cr^{+6} with 91% of the recovered ^{51}Cr being Cr^{+6}. The expected amount of native Cr (13.7 ug) was calculated as the sum of the spike amount (10.8 ug) and the amount found on the unspiked exposed filters (2.87 ug).

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The results for the filter spiked with native Cr^{+6} and $^{51}Cr^{+6}$ prior to exposure for 2 hours to flue gas are also presented in Table 2. The recoveries for three exposed filter samples, relative to the expected value of 13.7 ug, were 47% to 48.3%. Relative to the spiked blank filter control samples, the recoveries were 70% to 72%. Of the recovered ^{51}Cr, 61.5% to 73.3% was found to $^{51}Cr^{+6}$.

In summary, the IPA/NaOH appeared to be the best collection media for this test series, with both the native and radioactive Cr numbers agreeing quite well. The precisions of the measurements were also good. The filter experiments indicate that conversion during sampling and/or matrix effects on recovery by extraction do occur, and can be measured, semi-quantitatively, with $^{51}Cr^{+6}$ and/or native Cr^{+6} spikes.

TABLE 1   RECOVERY OF NATIVE AND LABELED HEXAVALENT CHROMIUM SPIKE IN IMPINGER REAGENT

| Sample Identity | Native Hexavalent Chromium | | | | Spiked Hexavalent ^{51}Chromium (total counts) | | | | | | |
	Expected (ug)	Found (ug)	% of Expected	% of Control	Total	Residue	Soluble	IC Separation $^{51}Cr^{+3}$	IC Separation $^{51}Cr^{+6}$	Percent of Total $^{51}Cr^{+3}$	Percent of Total $^{51}Cr^{+6}$
Spiked 80% IPA/20% 1.0 N NaOH Impinger Reagent Exposed to 2 Hours of Flue Gas											
IPA/NaOH Control	10.8	8.9	82.5%	NA	536845	450	536395	54571	481824	10.2%	89.8%
IPA/NaOH Sample (1-2)	10.8	8.8	81.7%	99.0%	414468	26458	388010	74057	313953	24.3%	75.7%
IPA/NaOH Sample (1-3)	10.8	8.1	74.8%	90.6%	398358	15750	382608	59632	322976	18.9%	81.1%
IPA/NaOH Field Blank	10.8	4.9	45.4%	55.0%	230848	284	230564	47979	182585	20.9%	79.1%
Spiked 0.5 M Phosphate Buffer Impinger Reagent Exposed to 2 Hours of Flue Gas											
0.5 M PO4 Control	10.8	11.2	103.5%	NA	NC	NC	NC	11100	151300	6.8%	93.2%
PO4 Sample (P-1)	10.8	2.8	26.2%	25.3%	563977	5579	558398	487509	70889	87.4%	12.6%
PO4 Sample (P-2)	10.8	3.1	28.5%	27.5%	541406	6654	534752	453351	81401	85.0%	15.0%
PO4 Field Blank	10.8	9.2	84.7%	81.8%	435957	908	435049	41561	393488	9.7%	90.3%

TABLE 2 RECOVERY OF NATIVE AND LABELED HEXAVALENT CHROMIUM SPIKE ON GLASS FIBER FILTERS

Sample Identity	Native Hexavalent Chromium				Spiked Hexavalent ^{51}Chromium (total counts)						
	Expected (ug)	Found (ug)	% of Expected	% of Control	Total	Residue	Soluble	IC Separation		Percent of Total	
								$^{51}Cr^{+3}$	$^{51}Cr^{+6}$	$^{51}Cr^{+3}$	$^{51}Cr^{+6}$
Post Test Spiked Quartz Method 5-Type Filters Exposed to 2 Hours of Flue Gas											
Spiked Control	10.8	9.4	87.0%	NA	867869	1619	866250	18261	847989	2.3%	97.7%
Spiked Control	10.8	8.9	82.4%	NA	858487	3962	854525	8804	845721	1.5%	98.5%
Post Test Spike (B 2)	13.7	9.0	66.1%	98.8%	866047	17997	848050	81345	766705	11.5%	88.5%
Post Test Spike (B-4)	13.7	9.2	67.3%	100.5%	872866	21841	851025	56920	794105	9.0%	91.0%
Exposed Filter (B-1)	0	2.9	NA	NA	394	9	385	NA	NA	NA	NA
Exposed Filter (B-3)	0	2.8	NA	NA	292	12	280	NA	NA	NA	NA
Pretest Spiked Quartz Method 5-Type Filters Exposed to 2 Hours of Flue Gas											
Spiked Filt. (I-1)	13.7	6.4	47.0%	70.3%	458210	113495	344715	63106	281609	38.5%	61.5%
Spiked Filt. (I-2)	13.7	6.4	47.0%	70.2%	441934	126759	315175	38554	276621	37.4%	62.6%
Spiked Filt. (I-4)	13.7	6.6	48.3%	72.1%	444449	91019	353430	27489	325941	26.7%	73.3%
Spiked Filt. FB	10.8	0.6	5.3%	6.2%	430161	176761	253400	118253	135147	68.6%	31.4%

FIGURE 1. 51Cr RADIOCHROMATOGRAMS OF SPIKED IMPINGER SOLUTIONS EXPOSED TO FLUE GAS FOR 2 HOURS

■ IPA control   ◄ IPA Sample (I-3)   △ IPA Sample (I-2)

■ PO4 Control   ◄ PO4 Sample (P-1)   △ PO4 Sample (P-2)

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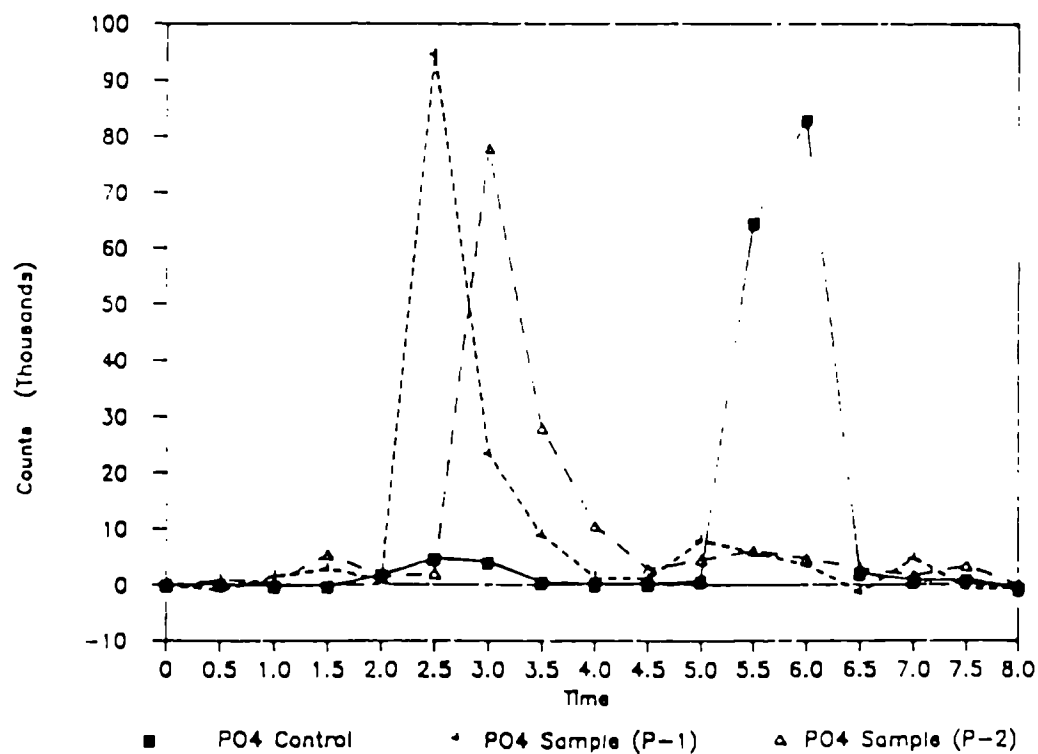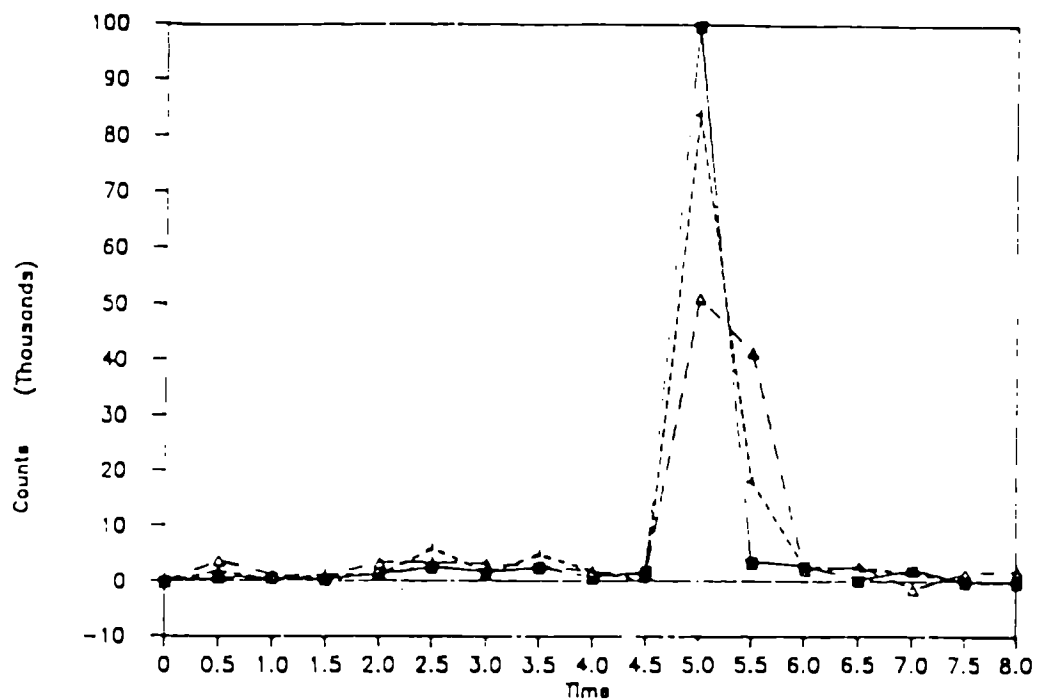# FIGURE 2. 51Cr RADIOCHROMATOGRAMS OF SPIKED METHOD 5 FILTERS EXPOSED TO FLUE GAS FOR 2 HOURS

○   Spiked Filter 1   △   Spiked Filter 2   ▽   Spiked Filter Field Blank

■   Control Filter 1   +   Control Filter 2   ○   Post Spiked Filter 2   △   Post Spiked Filter 4

A-12
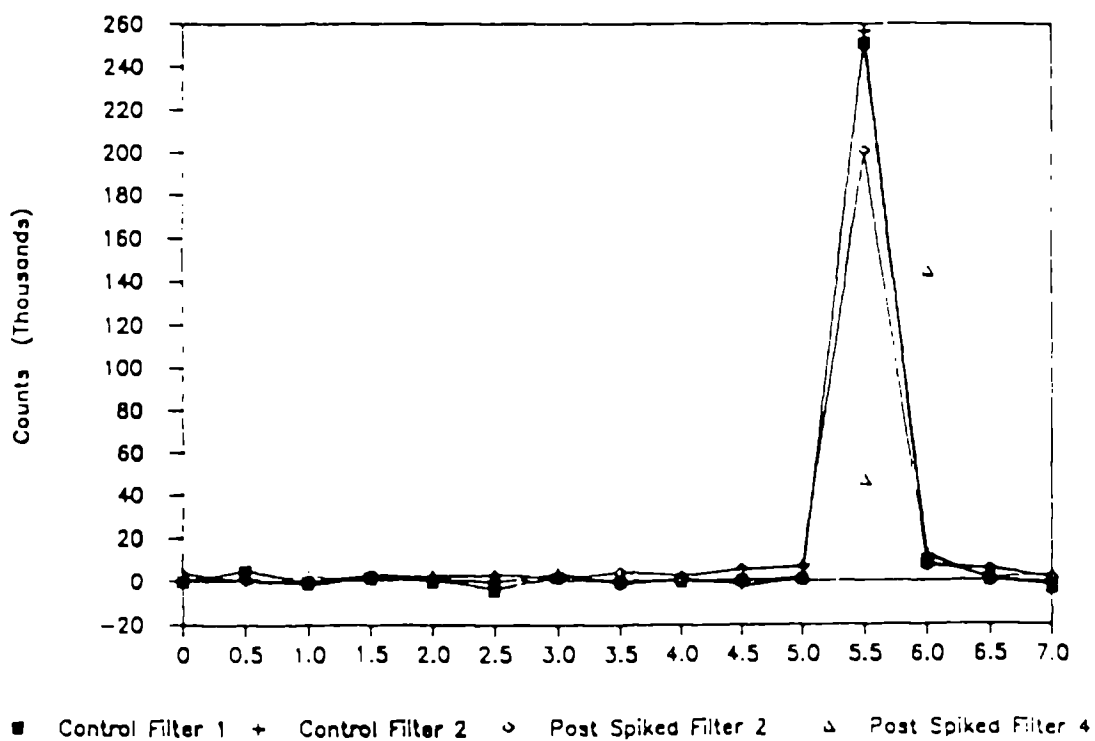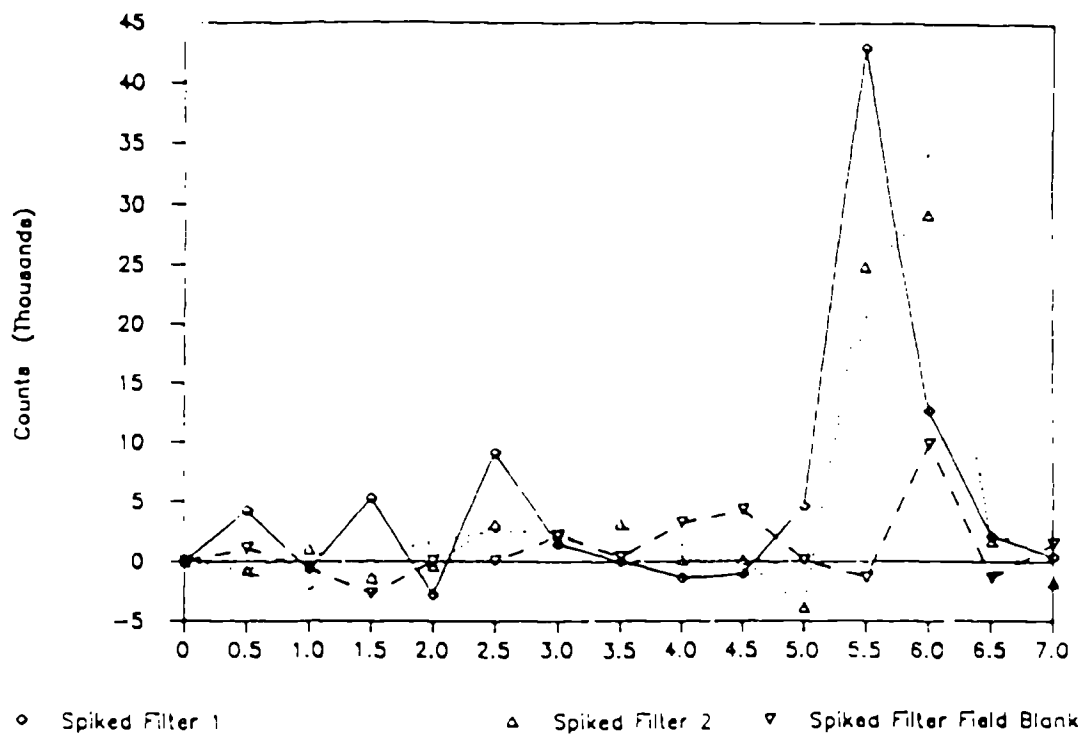
Appendix B
Method for Determination of Hexavalent Chromium
using Recirculating Reagent Impinger Train

METHOD Cr^{+6} - DETERMINATION OF HEXAVALENT CHROMIUM FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of hexavalent chromium (Cr^{+6}) emissions from cooling towers, hazardous waste incinerators, municipal waste combustors, and sewage sludge incinerators. The method, while not designed to capture insoluble forms of chromium, may, with the approval of the Administrator, be used to measure total chromium.

1.2 Principle. For cooling towers, the Cr^{+6} emissions are collected isokinetically from the exit plane of the tower. For incinerators and combustors, the Cr^{+6} emissions are collected isokinetically from the source. The emission samples are collected with a recirculatory train where the impinger reagent is continuously recirculated to the nozzle. The impinger train samples are analyzed for Cr^{+6} on an ion chromatograph equipped with a post-column reactor and a visible wavelength detector (IC/PCR). The IC/PCR separates the Cr^{+6} as chromate ($CrO_4^{=}$) from other components in the sample matrix that may interfere with the Cr^{+6}-specific diphenylcarbazide reaction that occurs in the post-column reactor.

2. Range, Sensitivity, Precision, and Interference

2.1 Range. Employing a preconcentration procedure, the lower limit of the range can be extended to 7.5 nanograms per liter (ng/l) of impinger sample. With sample dilution, there is no upper limit.

2.2 Sensitivity. A minimum detection limit of 2.4 ng/l of impinger sample can be achieved by preconcentration.

2.3 Precision. The overall precision of sample collection and analysis for a cooling tower containing 250 micrograms per liter (ug/l) of Cr^{+6} in the cooling water and emitting 2.5 micrograms per dry standard cubic meter (ug/dscm) is 31 percent. The precision of the IC/PCR with sample preconcentration is 9 percent. No precision measurements have been made for cooling towers emitting less Cr^{+6} or for incinerators or combustors.

2.4 Interference. Components in the sample matrix may cause Cr^{+6} to convert to trivalent chromium (Cr^{+3}) or cause Cr^{+3} to convert to Cr^{+6}. Conversion of Cr^{+6} to Cr^{+3} is more likely to occur. Radioactive Cr^{+6} ($^{51}Cr^{+6}$) can employed to monitor conversion within the train. For the IC/PCR analysis, only compounds that coelute with Cr^{+6} and affect the diphenylcarbazide reaction will cause interference. The known interferents to the diphenylcarbazide reaction will not coelute with Cr^{+6} on a properly operated ion chromatograph.

3. Apparatus

3.1 Sampling Train. A schematic of the recirculatory sampling train employed in this method is shown in Figure Cr^{+6}-1. The recirculatory train is readily assembled from commercially available components. All portions of the train that will come into contact with the sample are either glass or plastic, and are to be cleaned with 0.1 N nitric acid (HNO_3) and rinsed thoroughly with distilled, deionized water (DI H_2O) before and after each sampling run.

The metering system is identical to Method 5 with the exception of the use of a propeller anemometer for cooling tower testing. The sampling train consists of the following components:

3.1.1 Probe Nozzle. Glass or Teflon with a sharp, tapered leading edge. The angle of taper shall be $\leq 30°$ and the taper shall be on the outside to Figure

TEFLON
IMPINGERS

TEFLON
LINES

ASPIRATOR

RECIRCULATING
LIQUID

NOZZLE

TO
METHOD S-TYPE
METERBOX

250 ml
0.1 N KOH/
80% IPA

100 ml
0.1 N KOH/
80% IPA

100 ml
0.1 N KOH/
80% IPA

SILICA
GEL

ICE BATH

B-3
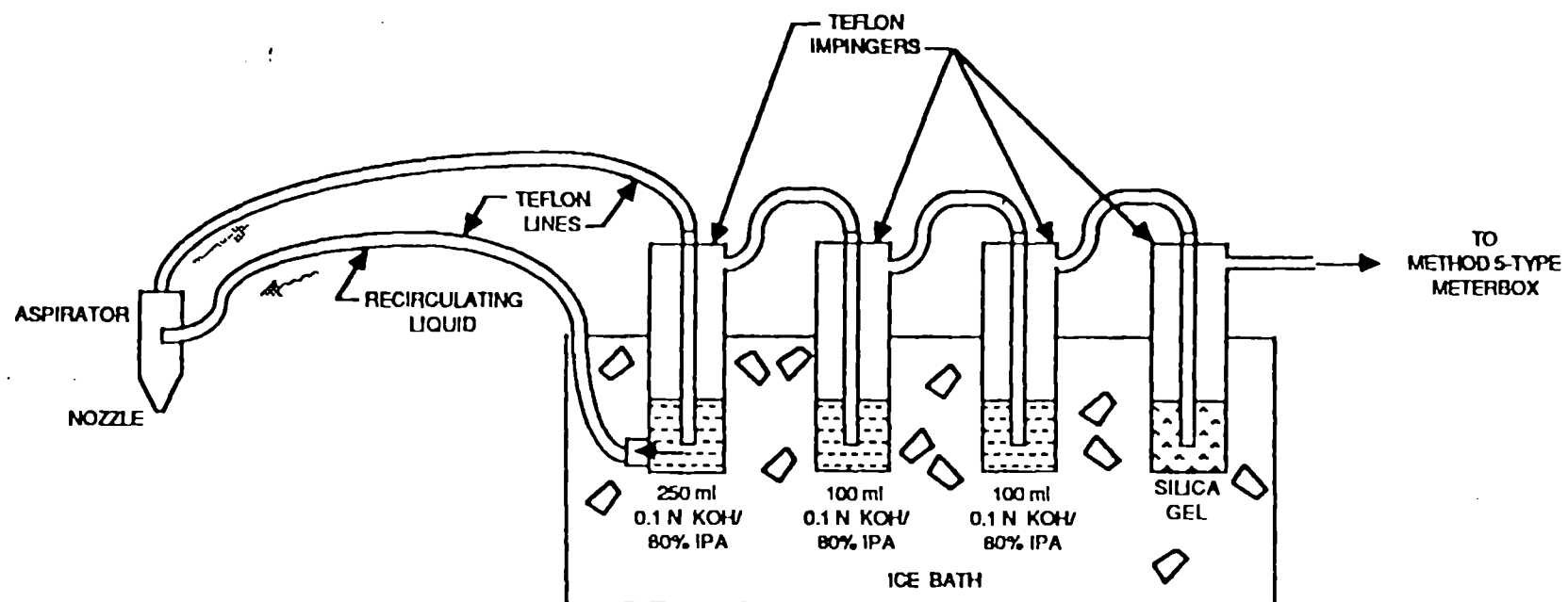
Schematic of recirculatory sampling train.

preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) (larger if higher volume sample trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 6.

3.1.2 Teflon Aspirator. Teflon aspirator capable recirculating absorbing reagent at 50 ml/min while operating at 0.75 cfm. Teflon fittings, Teflon ferrules, and stainless steel nuts to connect glass nozzle, Teflon recirculation, and Teflon sample line to aspirator.

3.1.3 Teflon Sample Line. Teflon, 3/8" outside diameter (O.D.) and 1/4" inside diameter (I.D.), of suitable length to connect aspirator to first Teflon impinger.

3.1.4 Teflon Recirculation Line. Teflon tubing, 1/4" O.D. and 1/8" I.D., of suitable length to connect first impinger to aspirator. The recirculation line should be fitted with a non-restricting shut-off device constructed out of Teflon or equivalent inert material.

3.1.5 Recirculation Control Valve. Inert valve system with 1/8" I.D. flow path constructed of plastic, Teflon, and/or glass installed at a convenient point in the Teflon recirculation line.

3.1.6 Teflon Impingers. Three Teflon impingers, 2" diameter by 8", with vacuum-tight 3/8" O.D. Teflon compression fittings. Inlet fittings on impinger top to be bored through to accept 3/8" O.D. tubing as impinger stem. Impinger stem to extend to 1/2" from impinger bottom. First impinger to have bottom cap with 1/4" O.D. Teflon compression fitting for recirculation line. An optional knockout impinger may be used for high moisture sources.

3.1.7 Silica Gel Impinger and Thermometer. Vacuum-tight impinger, capable of containing 200 g of silica gel, with compatible fittings. Thermometer, at the outlet of the silica gel impinger, to monitor the exit temperature of the gas.

3.1.8 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Section 2.1.8 through 2.1.10, respectively.

3.2 Sample Recovery. Clean all items for sample handling or storage with 8 N HNO_3 solution by soaking, where possible, and rinse thoroughly with DI H_2O before use. THe following items are needed:

3.2.1 Wash Bottles. Two polyethylene wash bottles, for DI H_2O and HNO_3 rinse solution.

3.2.2 Sample Storage Containers. Polyethylene, with leak-free screw cap, 500-ml or 1000-ml size.

3.2.3 Graduated Cylinder and/or Balance.

3.2.4 Plastic Storage Containers. Air tight containers to store silica gel.

3.2.5 Funnel and Rubber Policeman. To aid in transfer of silica gel from impinger to storage container; not necessary if silica gel is weighed directly in the impinger.

3.3 Sample Preparation for Analysis. Sample preparation prior to analysis includes pretreatment with phosphate buffer and aluminum sulphate, if total Cr is to be determined, followed by filtration to remove particulate matter and precipitate caused by the phosphate buffer and aluminum sulphate treatment. Additional sample pretreatment to remove hydroxide ion will be necessary if sample preconcentration is required.

3.3.1 Beakers, Funnels, Volumetric Flasks, Volumetric Pipets, and Graduated Cylinders. Assorted sizes, plastic or glass, for preparation of samples, sample dilution, and preparation of calibration standards. Prepare initially following procedure described in Section 5.1.3 and rinse between use with 0.1 N HNO_3 and DI H_2O.

3.3.2 Filtration Apparatus. Teflon, or equivalent, for filtering samples. Teflon impinger components have been found to be satisfactory as a sample reservoir for pressure filtration using nitrogen.

3.4 Analysis.

3.4.1 IC/PCR System. High performance liquid chromatograph pump, sample injection valve, post column reagent delivery and mixing system, and a visible detector, capable of operating at 530 nm, all with a non-metallic flow path. An electronic recording integrator operating in the peak area mode is recommended, but other recording devices and integration techniques are acceptable provided the repeatability criteria and the linearity criteria for the calibration curve described in Section 5.5 can be satisfied. A sample loading system will be required if preconcentration is employed.

3.4.2 Analytical Column. A Dionex AS-7, or equivalent non-metallic column with anion separation characteristics provided resolution described in Section _._. A non-metallic guard column with the same ion-exchange material is recommended.

3.4.3 Preconcentration Column. A Dionex AG-7, or equivalent non-metallic column with acceptable anion retention characteristics and sample loading rates as described in Section _._.

4. Reagents

All reagents should, at a minimum, conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. All prepared reagents should be checked by IC/PCR analysis for $Cr^{.6}$ to assure that contamination is below the analytical detection limit for direct injection or, if selected, preconcentration. If total Cr is also to be determined, the reagents should also be checked by the analytical technique selected to assure that contamination is below the analytical detection limit.

4.1 Sampling

4.1.1 Water. Deionized and/or distilled water. It is recommended that water blanks be checked prior to preparing reagents sampling to ensure that the $Cr^{.6}$ content of is less than the analytical detection limit.

4.1.2 Potassium Hydroxide Solution, 1.0 N. Dissolve 56.1 g of potassium hydroxide (KOH) in 1000 ml of water.

4.1.3 80% Alkaline Isopropanol (IPA/KOH). Mix 800 ml of 100% isopropanol (IPA) with 200 ml of 1.0 N KOH. It is recommended that 80% IPA/KOH reagent blanks be checked prior to sampling to ensure that the $Cr^{.6}$ content of is less than the analytical detection limit.

4.2 Sample Recovery. The reagents used in sample recovery are as follow:

4.2.1 Water. Approximately 300 to 400 ml of water for rinsing the sampling train; significant levels of $Cr^{.6}$ must not be present in the water. (See Section 4.1.1.)

4.2.2 Nitric Acid, 0.1 N. Add 6.3 ml of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 ml of water. Dilute to 1000 ml with water, and mix well.

4.3 Sample Preparation

4.3.1 Water. Same as Section 4.1.1.

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4.3.2 Phosphate Buffer, 2 M at pH 9 (for total Cr determination). Dissolve 34.84 g of anhydrous dipotassium hydrogen phosphate (K_2HPO_4) in 60 ml or 45.65 g of dipotassium hydrogen phosphate hydrate ($K_2HPO_4 \cdot 3H_2O$) in 50 ml. Adjust volume to 95 ml with DI water. Adjust the pH to 9 with concentrated phosphoric acid, and make a final volume adjustment to 100 ml.

4.3.3 Aluminum Sulphate, 0.74 M (for total Cr determination). Dissolve 49.32 g of hydrated aluminum sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$) in 50 ml of water, and adjust the final volume to 100 ml.

4.3.4 Filters. Teflon membrane, or equivalent, filters with 0.45-micron or smaller pore size to remove insoluble material.

4.4 Analysis

4.4.1 Chromatographic Eluent. An effective eluent for use with the Dionex AS-7 analytical column is a pyridine dicarboxylic acid (PDCA)-based solution. Heat 3.34 g of pyridine-2,6-dicarboxylic acid (PDCA) in 500 ml of degassed, deionized water. Continue heating until the PDCA is completely dissolved. Add 5.36 g of disodium hydrogen phosphate heptahydrate. Add 15.0 g of sodium iodide. Add 38.5 g of ammonium acetate. Add 1.10 g of lithium hydroxide monohydrate. Dilute to 1 liter with degassed, deionized water. Pipet 100 ml of this stock eluent into 500 ml of degassed, deionized water and dilute to 1 liter. Other combinations of eluents and/or columns may also be employed provided peak resolution, as described in Section _._, repeatability and linearity, as described in Section _._, and analytical sensitivity are acceptable.

4.4.2 Post Column Reagent. An effective post column reagent for use with the PDCA-based chromatographic eluent described in Section 4.3.1 is a diphenylcarbazide (DPC)-based system. Dissolve 0.5 g of 1,5-diphenylcarbazide (DPC) in 100 ml of HPLC-grade methanol. Add to 500 ml of degassed, deionized water containing 25 ml of 96% spectrophotometric grade sulfuric acid. Allow 30 minutes for the above to come to solution. Dilute to 1 liter with degassed, deionized water.

4.4.3 Cation Exchange Resin. Bio-Rad AG 50W-X8, 200-400 mesh, or equivalent, in the hydrogen ion (H^+) form for sample treatment prior to preconcentration. Sample pretreatment is necessary remove hydroxide anions that interfere with the anion retention capacity of the preconcentration column. Prepacked, disposable resin cartridges can be employed to treat up to 10 ml of sample. Larger sample aliquots can be treated by slurrying with the cation exchange resin.

4.4.4 Cr^{+6} Calibration Standard. Prepare Cr^{+6} standards from hydrated sodium chromate (Na_2CO_4) that has been desiccated to dryness prior to use. To prepare a 1000 ug/ml Cr^{+6} stock solution, dissolve 3.461 g of $Na_2CrO_4 \cdot 4H_2O$ in 1 liter of 18 M-ohm deionized water. To prepare working standards, dilute the stock solution, to the chosen standard concentrations for instrument calibration with IPA/KOH reagent and water to achieve a matrix similar to the actual field samples.

4.4.5 Performance Audit Sample. A performance audit sample shall be obtained from the Quality Assurance Division of EPA and analyzed with the field samples. The mailing address to request samples is:

U. S. Environmental Protection Agency
Atmospheric Research And Exposure Assessment Laboratory
Quality Assurance Division
Source Branch, Mail Drop 77-A
Research Triangle Park, North Carolina 27711

The audit sample should be prepared in a suitable sample matrix at a concentration similar to the actual field samples.

5. Procedure

    5.1 Sampling. The complexity of this method is such that to obtain reliable results, testers should be trained and experienced with test procedures.

    5.1.1 Pretest Preparation. All components shall be maintained and calibrated according to the procedures described in APTD-0576, unless otherwise specified herein.

    Rinse all sample train components from the glass nozzle up to the silica gel impinger and sample containers with hot tap water followed by washing with hot soapy water. Next, rinse the train components and sample containers three times with tap water followed by three rinses with distilled or deionized water. All the components and containers should then be soaked overnight, or a minimum of 4 hours, in a 10 percent (v/v) nitric acid solution, then rinsed three times with distilled or deionized water. Allow the components to air dry prior to covering all openings with Parafilm, or equivalent.

    5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

    5.1.3 Preparation of Sampling Train. Place 250 ml of IPA/KOH reagent in the first impinger. If a knockout impinger is to be used for high moisture sources (collection of more than 150 ml), the impinger should be sized to hold the entire amount of flue gas condensate plus an additional 50% to contain the recirculation liquid. The volume of IPA/KOH added to the knockout impinger will be equal to half of the anticipated volume of flue gas condensate. Place 50 ml of IPA/KOH in the second impinger and, if the knockout impinger is used, place 50 ml of IPA/KOH in the third impinger. The next Teflon impinger is left dry. Place a preweighed 200- to 300-g portion of indicating silica gel in the final impinger.

    Retain reagent blanks of the IPA/KOH equal to the volumes used with the field samples.

    5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

    5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. At the start of the sampling, open the recirculation line shut off device. The shut-off device must be closed prior to any interruption in the flow of sample gas through the aspirator to the first impinger to prevent loss of sample. Approximately one minute before the completion of the sampling run, close the shut-off device to permit the recirculating liquid to be cleared from the sample line.

    For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

    5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

5.2 Sample Recovery. Begin cleanup procedures as soon as the probe assembly is removed from the stack at the end of the of the sampling run.

    The probe assembly should be allowed to cool prior to sample recovery. Disconnect the umbilical cord from the sampling train. When the probe assembly can be safely handled, wipe off all external particulate matter near the tip of the nozzle, and cap the nozzle prior to transporting the sample train to a clean up area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

5.2.1 Container No. 1 (Impingers 1 through 3, or 4, if knockout is used) Disconnect the first impinger from the second impinger and disconnect the recirculation line from the aspirator. Through the recirculation line, drain the impinger contents into a precleaned graduated cylinder by opening the shut-off device. Add the contents of the second, third (if used), and dry impinger to the graduated cylinder, and measure the volume of the liquid to within 0.5 ml. Record the volume of liquid present as this information is required to calculate the moisture content of the flue gas sample. Transfer the sample from the graduated cylinder to a precleaned polyethylene sample container. With water, rinse the insides of the glass nozzle, the aspirator, the sample and recirculation lines, the impingers, and the connecting tubing three times, and combine the rinses with the impinger solution in the sample container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination if leakage occurs during transport. Label the container clearly to identify its contents.

5.2.2 Container No. 2 (HNO_3 rinse, optional for total Cr). Repeat the rinse procedure with 0.1 N HNO_3, and combine the rinses in a separate precleaned polyethylene container for possible total Cr analysis, or discard the HNO_3 rinse. Repeat the rinse procedure a final time with water, and discard the water rinses. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination if leakage occurs during transport. Label the container clearly to identify its contents.

5.2.3 Container No. 3 (Silica Gel). Note the color of the indicating silica gel to determine if it has been completely spent, and make a notation of its condition. Quantitatively transfer the silica gel from its impinger to the original container, and seal the container. A funnel and a rubber policeman may be used to aid in the transfer. The small amount of particulate that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or the silica gel plus impinger) to the nearest 0.5 g.

5.2.4 Container No. 4 (IPA/KOH Blank). Once during each field test, place a volume of sampling reagent equal to the volume placed in the sampling train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination if leakage occurs during transport. Label the container clearly to identify its contents.

5.2.5 Container No. 5 (Water Blank). Once during each field test, place a volume of water equal to the volume employed to rinse the sampling train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination if leakage occurs during transport. Label the container clearly to identify its contents.

5.2.6 Container No. 5 (0.1 N HNO_3). Once during each field test, if total Cr is to be determined, place a volume of 0.1 N HNO_3 reagent equal to the volume employed to rinse the sampling train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container

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and record the weight to permit determination if leakage occurs during transport. Label the container clearly to identify its contents.

5.3 Sample Preparation. For determination of Cr^{+6}, the sample should be filtered to remove any insoluble matter. For total Cr determination, the sample is first treated with phosphate buffer, pH adjusted to 9 with phosphoric acid, and treated with aluminum sulphate prior to filtration.

5.3.1 Container 1 (Impinger Sample) For determining total Cr, add 1 ml of phosphate buffer per 100 ml of sample. Check the pH and adjust to 9 with concentrated phosphoric acid, if necessary. Add 0.1 ml of aluminum sulphate solution per 100 ml of sample.

For determining either Cr^{+6} or total Cr, filter the entire impinger sample through the 0.45-um filter, and collect the filtrate. Rinse the sample container with water three separate times and pass these rinses through the filter, and add the rinses to the sample filtrate. Determine the final volume of the filtrate and rinses prior to IC/PCR analysis

Quantitatively recovery the filter and residue, and place them in a vial if total Cr is to be determined.

5.3.2 Container 2 (HNO_3 rinse, optional for total Cr). This sample shall be analyzed in accordance with the selected procedure for total Cr analysis. At a minimum, the sample should be subjected to a digestion procedure sufficient to solubilize all chromium present.

5.3.3 Container 3 (Silica Gel). Weigh the spent silica gel to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

5.4 Sample Analysis. The Cr^{+6} content of the sample filtrate is determined by ion chromatography using a post column reactor (IC/PCR). For trace levels of Cr, a preconcentration system is also used in conjunction with the IC/PCR. After separation from other sample components, Cr^{+6} forms a specific complex in the post column reactor with a sym-diphenylcarbazide, and the complex is then detected by ultraviolet absorbance at a wavelength of 520 nm. The amount of absorbance measured is proportional to the concentration of the Cr^{+6} complex formed. The IC retention time and absorbance of the Cr^{+6} complex is compared with known Cr^{+6} standards analyzed under identical conditions to provide both qualitative and quantitative analyses.

Prior to sample analysis, establish a stable baseline with the detector set at the required attenuation by setting the eluent and post column reagent flow rates to the values recommended by the manufacturer. Inject a sample of water, and determine if any Cr^{+6} appears in the chromatogram. If Cr^{+6} is present, repeat the water injection until no Cr^{+6} appears. At this point, the instrument is ready for use.

First, inject the calibration standards prepared, as described in Section 6.2, to cover the appropriate concentration range, starting with the lowest standard first. Next, inject, in duplicate, the performance audit sample, followed by the IPA/KOH field blank, and the field samples. Finally, repeat the injection of the calibration standards to allow for compensation of instrument drift. Measure areas or heights of the Cr^{+6}/DPC complex chromatogram peak. The response for replicate, consecutive injections of samples must be within 5 percent of the average response, or the injection should be repeated until the 5 percent criterion can be met. Use the average response (peak areas or heights) from the duplicate injections of calibration standards to generate a linear calibration curve. From the calibration curve, determine the concentration of the field samples employing the average response from the duplicate injections.

The results for the analysis of the performance audit sample must be within 10 percent for the field sample analysis to be valid.

6. Calibration

Maintain a written log of all calibration activities.

6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

6.2 Calibration Curve for the IC/PCR. Prepare working standards from the stock solution described in Section 4.4.4 by dilution with a IPA/KOH solution diluted with water to approximate the field sample matrix. Prepare at least four standards to cover one order of magnitude that bracket the field sample concentrations. Analyze the standards with the field samples as described in Section 5.4. For each standard, determine the peak areas (recommended) or the peak heights, calculate the average response from the duplicate injections, and plot the average response against the Cr^{+6} concentration in ug/l. The individual responses for each calibration standard determined before and after field sample analysis must be within 5 percent of the average response for the analysis to be valid. If the 5 percent criteria is exceeded, excessive drift and/or instrument degradation may have occurred, and must be brought under control before further analyses are performed.

Use linear regression to calculate the formula describing the linear curve. Employing the regression equation, calculate a predicted value for each calibration standard with the average response for the duplicate injections. Each predicted value must be within 7 percent of the actual value for the calibration curve to be considered acceptable. Remake and/or reanalyze the calibration standards. If the calibration curve is still unacceptable, reduce the range of the curve.

7. Calculations

7.1 Dry Gas Volume. Using the data from the test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

7.2 Volume of Water Vapor and Moisture Content. Using the date from the test, calculate $V_{w(std)}$ and B_{ws}, the volume of water vapor and the moisture content of the stack gas, respectively, using Equations 5-2 and 5-3 of Method 5.

7.3 Stack Gas Velocity. Using the data from the test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

7.4 Total ug Cr^{+6} Per Sample. Calculate as described below:

$$m = (S-B) \times V_{ls} \times d$$

Where:

m = Mass of Cr^{+6} in the sample, ug,
S = Analysis of sample, ug Cr^{+6}/ml,
B = Analysis of blank, ug Cr^{+6}/ml,
V_{ls} = Volume of sample after filtration, ml, and,
d = Dilution factor (1 if not diluted).

8. Bibliography

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15. SUPPLEMENTARY NOTES

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16. ABSTRACT

At Site 5, three candidate sampling methods and two candidate analytical methods for hexavalent chromium were assessed. The conversion of hexavalent chromium (Cr^{+6}) to other valence states of chromium during sampling and sample storage was of primary concern. Method 5-type samples and impinger train samples were collected by PEI Associates, Inc. Dilution train samples were collected by Southern Research Institute. Method 5-type train samples were analyzed by Technology Applications, Inc.'s (TAI) staff under contract to EPA's Environmental Monitoring Systems Laboratory (EMSL) in Cincinnati, Ohio. Dilution train samples, Method 5-type samples, and impinger train samples were analyzed by Entropy Environmentalists, Inc. TAI used an ion chromatograph with post column reaction (IC/PCR) and inductively coupled argon plasmography/mass spectrometry (ICP/MS) to analyze the Method 5-type samples. A stable chromium isotope ($^{53}Cr^{+6}$) spiked onto the Method 5 filter prior to sample collection was used to assess conversion of Cr^{+6}. The samples analyzed by Entropy were collected using a dilution train on an 8.5 in X 11 in glass fiber filter, a Method 5-type sampling train on an 82 mm quartz fiber filter, and an impinger sampling train with an alkaline impinger reagent, and spiked with native hexavalent chromium and a radioactively-labeled chromium isotope ($^{51}Cr^{+6}$). The samples were analyzed for hexavalent chromium by IC/PCR and for the radioactive isotopes by scintillation (gamma) counting. EMSL has not released the TAI data. The preliminary method evaluation testing demonstrated that all sampling methods had problems with conversion of hexavalent chromium.

17.		KEY WORDS AND DOCUMENT ANALYSIS			
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