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NESHAP — Cooling Towers Chromium

Emission Test Report National Bureau Of Standards Gaithersburg, Maryland

EMISSION TEST REPORT

NATIONAL BUREAU OF STANDARDS
STEAM AND WATER CHILL PLANT
GAITHERSBURG, MARYLAND

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1.0 INTRODUCTION

During the week of August 18, 1986, Entropy Environmentalists, Inc. (Entropy), under contract to the U. S. Environmental Protection Agency, Emission Measurement Branch, conducted an emission measurement program at the National Bureau of Standard's (NBS) Steam and Water Chill Plant in Gaithersburg, Maryland. The purpose of the measurement program was to provide data on chromium emissions from cooling towers in support of a possible chromium standard under the National Emission Standards for Hazardous Air Pollutants (NESHAPS).

Comprehensive testing was conducted on the cooling tower located adjacent to Building 302 of the NBS Steam and Water Chill Plant. This cooling tower was selected for source testing for the following reasons:

- The cooling tower is equipped with a high-efficiency Munters D-15 drift eliminator.
- The facility allowed the addition of chromate-based water treatment compounds to the cooling tower water. The target level for chromate in the cooling water is 15 to 20 parts per million (mg/L); it is added as sodium dichromate. The analysis of the cooling tower water samples collected during the testing program indicated the target level was being maintained.
- The facility also allowed the addition of sodium bromide (NaBr) to the cooling tower water for further evaluation of bromide as a surrogate compound for cooling tower drift emissions testing.
- The cooling tower construction allows good access to the four outlet cell stacks and the stack design permits unobstructed sampling traverses.
- The facility was operating the cooling tower at close to maximum capacity heat loads during the testing program.

The cooling tower emissions were characterized using a Method 13-type impinger train following the draft cooling tower test method (Appendix C) to

collect the drift from the cooling tower exhaust. The impinger contents were analyzed by Research Triangle Institute (RTI) for total chromium content by solubilizing the chromium with nitric acid and using graphite furnace atomic absorbtion (GFAA). The velocity of the airflow through each fan cell was determined using a propeller anemometer following the draft method (Appendix C). The gas temperature and percent moisture were also determined. The corresponding cooling water samples collected during each sampling run were analyzed by RTI for hexavalent chromium using the diphenylcarbazide wet chemical method and by North Carolina State University (NCSU) for total chromium in the filtered residue using Neutron Activation Analysis (NAA). Sampling was also conducted using an "aligned nozzle train" and a "disc train" (see Chapter 4), to determine the percentage of chromium emissions associated with drift particles smaller than a certain particle size (approximately 15 um).

An independent determination of the drift rate and drift size distribution was conducted by personnel from Environmental Systems Corporation (ESC) using their Sensitive Paper (SP) system and microscopic analysis. ESC personnel also conducted the water flow measurements in the recirculating water pipe serving the four riser cells. For this, ESC used calibrated pitot tubes and a methodology similar to EPA Methods 1 and 2 for air velocity measurements.

A sampling protocol using absorbent paper (AP) in a sensitive paper holder was evaluated as part of an effort to develop a potential screening technique for cooling tower emission testing and to determine the percentage of chromium emissions associated with particles greater than a certain particle size (approximately 30 um). These AP's were analyzed for total chromium content by NCSU using NAA.

Mr. David Randall and Mr. Rodney Gibson of Midwest Research Institute (MRI) monitored the operating conditions of the cooling tower and determined when

conditions were suitable for sampling. Mr. Dan Bivins (EPA Task Manager) and Mr. Ed McCarley of the Emission Measurement Branch (EMB) were present to observe the testing program. Mr. Robert Moore of NBS served as the contact for the facility.

This report is organized into several sections that address the various aspects of the testing program. Immediately following this introduction is the "Process Operation" section describing the process involving the cooling tower tested, the cooling tower system, and the control equipment in the tower. Following the "Process Operation" section is the "Summary of Results" section presenting tables summarizing the test conditions, the calculated emission and drift rates, the drift size distribution, and the analytical results. The next section, "Sampling Locations and Test Methods" describes and illustrates the various sampling locations for the emissions testing program and then explains the sampling strategies used. The final section, "Quality Assurance", describes the procedures used to ensure the integrity of the sampling and analysis program. The Appendices present the Test Results and Example Calculations (Appendix A); Field and Analytical Data (Appendix B); Sampling and Analytical Procedures (Appendix C); Calibration and Quality Assurance (Appendix D); MRI Process Data (Appendix E); and Test Participants and Observers (Appendix F).

2.0 PROCESS OPERATION

2.1 PROCESS DESCRIPTION

The NBS is a Federal government research facility near Gaithersburg, Maryland. On the grounds are seven laboratory/office buildings with a total floor area of 625,000 square feet (ft^2). There are also a number of support buildings that add another 675,000 feet. Comfort cooling and cooling for laboratory processes (lasers, ovens, etc.) are both provided by a 4-cell Marley tower located near the western boundary of the facility. The tower was installed in the early 1960's.

A sketch of the cooling tower system is provided in Figure 2.1. The tower is a crossflow design with redwood splash fill and one fan per cell. Propeller fans measuring 22 feet (ft) in diameter are located in the stack of each cell. Last year, the tower was retrofitted with high-efficiency Munters D-15 drift eliminators.

The capacity of the water basin is about 500,000 gallons (gal). Four pumps, each rated for 8,800 gal/min circulate the water to the chillers. The water from the chillers is combined and returned to the tower through a 42-inch riser pump. Above the tower, the flow is split into four branches and distributed to each of the cells. The water distribution decks are located directly above the fill and are equipped with gravity flow nozzles. In winter, heated water is sprayed up into the rear of the tower to prevent icing conditions.

A solution of molybdate and polyacrylate is used to inhibit corrosion in the heat exchangers. The target concentration of molybdate in the

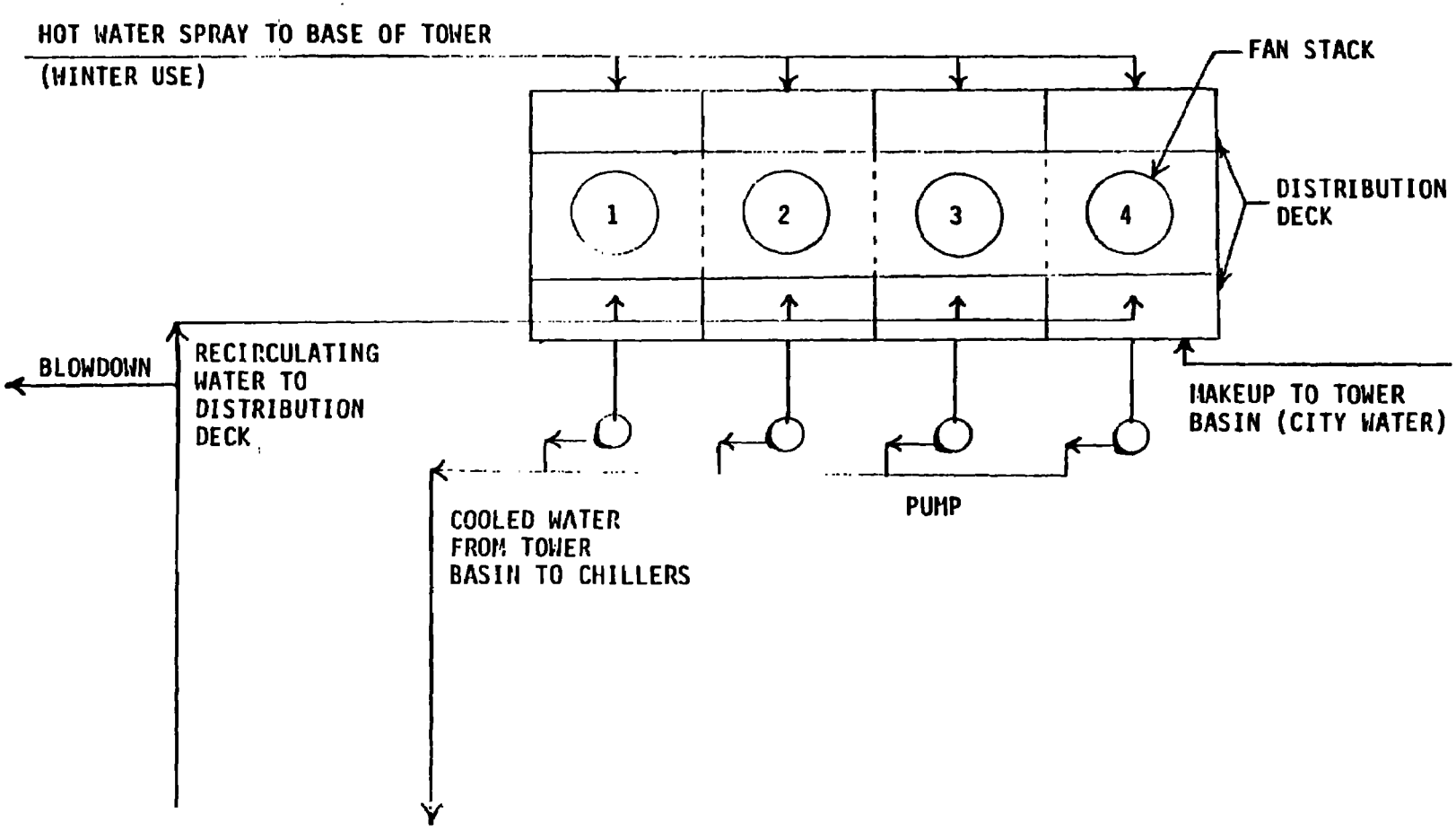


Figure 2-1. Cooling tower at NBS facility in Gaithersburg, Maryland.

recirculating water is about 15 parts per million. Conductivity and pH are monitored continuously, and blowdown occurs automatically when the conductivity reaches 1,800 umhos. Blowdown averages about 60,000 gallons per day (gal/day) in summer and about 2,000 gal/day in winter.

Makeup water is provided by the City of Gaithersburg. The conductivity is generally about 300 umhos, but after heavy rains and after salt has been applied to the roads in the winter, the conductivity increases. Makeup requirements in summer average about 300,000 gal/day, and in winter average about 55,000 gal/day. Most of the water has first been used for once-through cooling of oil and air compressors.

Biological growth is controlled by manually adding 6.5 gal of a solution containing disodium cyanodithiodocarbonate (7.35 percent) and potassium methyldithiocarbonate (10.15 percent) once a week.

2.2 PROCESS CONDITIONS DURING TESTING

Eight test series were conducted Tuesday through Friday, August 19-22, 1986. The cooling tower operating parameters that were monitored during each test series to ensure that acceptable conditions existed included the recirculating water temperatures into and out of the chiller, recirculating water flow rate, daily blowdown and water makeup, wind speed, and wind direction. Meteorological data were also obtained from the National Weather Service (NWS) at Washington National Airport. This NWS Station is the one closest to NBS.

The design water flow was achieved on each of the test days, but one chiller was not operated; water simply circulated through it. The low ambient temperature and low demand all day on August 21 and early in the morning on August 22 necessitated turning off a second chiller and one fan. Table 2.1 is

TABLE 2.1. SUMMARY OF OPERATING PARAMETERS AND METEOROLOGICAL DATA DURING TESTS

Parameter	Test series No. 1	Test series No. 2	Test series No. 3	Test series No. 4	Test series No. 5	Test series No. 6	Test series No. 7	Test series No. 8
Date	8-19-86	8-19-86	8-20-86	8-20-86	8-21-86	8-21-86	8-22-86	8-22-86
Recirculating water flow in riser, gal/min[a]	36,108	36,108	36,428	36,428	36,383	36,383	35,761	35,761
Fans	All 4 high	All 4 high	All 4 high	All 4 high	3 high, 1 off	3 high, 1 off	All 4 high	All 4 high
Blowdown, gal/day	93,400	93,400	50,200	50,200	31,800	31,800	45,200	45,200
Makeup, gal/day	336,600	336,600	254,400	254,400	201,00	201,000	162,500	162,500
Chillers	3 on, 1 off	3 on, 1 off	3 on, 1 off	3 on, 1 off	2 on, 2 off	2 on, 2 off	2 on, 2 off for 1 h 3 on, 1 off for 1 h	3 on, 1 off
Water temperature, °F								
Entering condenser, avg.	75-78	79-80	77-78	78-79	75-77	77-78	73-75	75-76
Leaving condenser, avg.	81-85	85-86	83-84	84-85	80-82	82-83	77-81	81-82
Water chemistry								
pH	--	--	--	--	--	--	8.5	8.6
Conductivity, umhos	1,700	1,700	1,700	1,700	1,700	1,700	1,750	1,750
Biocide addition, gal	0	0	6.5	6.5	0	0	0	0
Meteorological data								
Wind speed, mph	0-5	0-6	0-14	0-11	0-5	0-5	0-11	0-5
Wind direction (00-360)	0-75	15-90	45-90	90-105	0	0-90	270-360	270-360

[a]As measured by ESC personnel.

a summary of the cooling tower operating parameters and meteorological data recorded during the test period.

Crystalline sodium dichromate was added to the recirculating water (200 pounds on Monday, August 18, and lesser amounts on the following days). The concentration in the water was not determined during the testing and daily variations may have resulted. Sodium bromide also was added to the recirculating water for evaluation of bromide as a surrogate for chromium in drift emissions testing.

A pretest walk-through of the tower was conducted on Tuesday, August 19. Inspection of the drift eliminators revealed a number of water leaks into the fan side of the eliminator sections. This was most significant in the first cell, but in no case did the airflow appear to be shearing droplets away from the water stream. Inspection of the water flow along the outside of the tower revealed an unequal distribution that was most pronounced on the windiest days. The strongest winds were evident on Wednesday, August 20 when the anemometer mounted atop a nearby building indicated gusts of up to 14 miles per hour (mph). On the tower itself, an anemometer indicated 14 mph and the NWS reported winds of 10 to 15 mph for that day. In no instance, however, was drift observed from the sides of the tower. All tests were completed under acceptable conditions with respect to the test plan and Cooling Tower Institute guidelines.

3.0 SUMMARY OF RESULTS

Tests were conducted to determine the mass emission rates of hexavalent chromium and total chromium from the Steam and Chill Plant cooling tower at the National Bureau of Standards (NBS) in Gaithersburg, Maryland. The mass emission rate tests involved using a Method 13-type impinger train to sample four fan stacks on four riser cells equipped with high-efficiency drift eliminators. The testing schedule that was followed for the NBS cooling tower is presented in Table 3.1. The results of these tests are discussed briefly below and in detail in Section 3.1.

The pollutant mass rate for hexavalent chromium, calculated by the ratio of areas (PMR_a) method, for the four riser cells equipped with high-efficiency drift eliminators averaged 1,342 milligrams per hour (mg/hr).

The drift size distribution (drift being defined here as cooling water entrained in the exit air and emitted to the atmosphere in droplet form), along with the drift rate, was determined by Environmental Systems Corporation (ESC) using their sensitive paper (SP) technique. The results of the SP testing suggest that the drift emissions from the fan cells equipped with high-efficiency drift eliminators had an average mass mean diameter of 377 um.

Another method was evaluated for determining the percentage of the mass of hexavalent chromium associated with particles smaller than a certain size (approximately 15 um under these sampling conditions). The sampling protocol involved using a set of paired trains; one, referred to as the "disc train," was designed to capture only the smaller particles and the other, a Method 13-type train with the nozzle aligned directly into the flow of the fan exhaust

TABLE 3.1. TESTING SCHEDULE FOR STEAM AND CHILL PLANT COOLING TOWER AT NATIONAL BUREAU OF STANDARDS, GAITHERSBURG, MARYLAND

Date (1986)	Sample Type	Riser Cell A		Riser Cell B		Riser Cell C		Riser Cell D	
		Run No.*	Test Time 24 h clock	Run No.*	Test Time 24 h clock	Run No.*	Test Time 24 h clock	Run No.*	Test Time 24 h clock
8/19	Chromium	A-1	09:59-12:15						
	Chromium	A-2	12:47-14:49						
	Particle size	DI-A-1	10:10-14:23						
	Particle size	NZ-A-1	10:10-14:23						
8/20	Chromium			B-1	09:45-11:48				
	Chromium			B-2	12:10-14:13				
	Particle size			DI-B-2	10:10-14:24				
	Particle size			NZ-B-2	10:10-14:24				
8/21	Chromium					C-1	09:19-11:22		
	Chromium					C-2	11:43-13:46		
	Particle size					DI-C-3	09:40-13:40		
	Particle size					NA-C-3	09:40-13:40		
8/22	Chromium							D-1	09:23-11:48
	Chromium							D-2	12:05-14:08
	Particle size							DI-D-4	09:25-13:30
	Particle size							NZ-D-4	09:25-13:30

*Run numbers for chromium runs indicate: Riser Cell - Run.
Run numbers for particule size runs indicate: Technique - Riser Cell - Run.

(referred to as the "aligned nozzle train"), was designed to capture all sizes of drift particles. Data from a screening technique being evaluated utilizing absorbent paper (AP), was also used for particle sizing purposes. The data were used based on collection by the AP in a sensitive paper holder of particles over 30 um (under these sampling conditions).

The paired train particle sizing data suggest that most of the hexavalent chromium emissions from the four fan cells equipped with high-efficiency drift eliminators are associated with particles less than 15 um. The AP data for the four cells suggest that only 2.9 to 8.9 percent of the chromium emissions are associated with particles greater than 30 um. The particle sizing results and the differences between the two methods are discussed in detail in Section 3.2.

The analytical results for hexavalent chromium and residue chromium for cooling water samples and the total chromium in the impinger samples are presented in Section 3.3 along with the analytical results of the blanks and quality assurance samples. The results of the analysis of the absorbent papers, which are being evaluated as a screening technique for cooling tower emissions, are also presented in Section 3.3, and the technique is discussed in Section 3.4.

Drift rate calculations based on the water flow to the riser cells, the concentration of chromium in the cooling water, and the mass emission rates calculated for the impinger train samples and the AP samples are presented in Section 3.5. Drift rate calculations from the SP data are also presented and the drift rates calclulated by the various methods are compared.

3.1 HEXAVALENT CHROMIUM AND TOTAL CHROMIUM EMISSIONS

The mass emission rates for hexavalent chromium and total chromium from the four riser cells equipped with high-efficiency drift eliminators were determined.

Sampling was conducted isokinetically with the isokinetic values for the eight sampling runs ranging from 99.2% to 101.9% (see Table 3.2). The sampling runs were typically 2 hours in length, with a single traverse on each fan stack cell comprising a single sample.

The hexavalent chromium emissions in the drift were calculated using the values for the total chromium emissions and the ratio of hexavalent-to-total chromium in the cooling water. The assumption was made that the chromium emissions from the cooling tower fan stack maintained the same ratio of hexavalent-to-total chromium as measured in the cooling water.

The concentration of hexavalent and total chromium in milligrams per dry standard cubic meter (mg/dscm), in micrograms per gallon of water flow to the fan cell (ug/gal), and in milligrams per million Btu's of heat removed (mg/10^6Btu), and the mass emission rates of hexavalent and total chromium, in milligrams per hour (mg/hr) are presented in Table 3.3 for each sampling run. These results are based on the total chromium analysis conducted by RTI using GFAA with the hexavalent chromium values being calculated using the ratio of hexavalent-to-total chromium in the cooling water sample for that run. The hexavalent and total chromium values are representative of the emissions from a single fan stack on the corresponding fan cell. The mass emission rates were calculated using the ratio of the fan stack area to the sampling nozzle area, the catch weight of total chromium, the calculated catch weight of hexavalent chromium, and the sampling time (see Appendix A for example calculations).

3.1.1 Flue Gas Conditions and Isokinetic Sampling Rate

A summary of the flue gas conditions for the fan cells tested is presented in Table 3.2. The volumetric flow rates were fairly constant on all the fan cells tested. For fan cell A, the volumetric flowrate averaged 1,121,000 actual cubic

TABLE 3.2. SUMMARY OF FLUE GAS CONDITIONS

Run No.	Date (1986)	Test Time 24 h clock	Volumetric Flow Rate Actual[a] acmh x 10^6	Actual[a] acfh x 10^6	Standard[b] dscmh x 10^6	Standard[b] dscfh x 10^6	Stack Temperature °C	Stack Temperature °F	Moisture %	Isokinetic %
Riser Cell A										
A-1	8/19	9:59-12:15	1.121	39.58	1.062	37.50	27	80	3.4	101.0
A-2	8/19	12:47-14:49	1.121	39.58	1.054	37.23	28	82	3.7	101.9
Average			1.121	39.58	1.058	37.37	27	81	3.5	101.5
Riser Cell B										
B-1	8/20	9:45-11:48	1.254	44.28	1.201	42.41	25	77	3.1	100.5
B-2	8/20	12:10-14:13	1.308	46.18	1.244	43.92	26	79	3.4	100.1
Average			1.281	45.23	1.223	43.16	26	78	3.2	100.3
Riser Cell C										
C-1	8/21	9:19-11:22	1.163	41.06	1.117	39.46	24	76	3.0	99.4
C-2	8/21	11:43-13:46	1.161	40.98	1.116	39.42	24	76	3.0	99.2
Average			1.162	41.02	1.117	39.44	24	76	3.0	99.3
Riser Cell D										
D-1	8/22	9:23-11:48	1.241	43.82	1.196	42.22	25	76	3.0	98.8
D-2	8/22	12:05-14:08	1.212	42.79	1.162	41.02	26	78	3.2	99.6
Average			1.227	43.81	1.179	41.62	25	77	3.1	99.2

TABLE 3.3. SUMMARY OF HEXAVALENT AND TOTAL CHROMIUM EMISSIONS BASED ON GRAPHITE FURNACE ATOMIC ABSORPTION (GFAA)

Run No.	Date	Hexavalent Chromium				Total Chromium			
		concentration			mass emissions	concentration			mass emissions
		(mg/dscm) x 10^{-3}	ug/gal	mg/10^6 Btu	mg/hr	(mg/dscm) x 10^{-3}	ug/gal	mg/10^6 Btu	mg/hr
Riser Cell A, High-Efficiency Drift Eliminators									
A-1	8/19	0.606	1.20	4.88	650	0.606	1.20	4.88	650
A-2	8/19	4.207	8.35	34.61	4521	4.208	8.35	34.61	4521
Average		2.406	4.78	19.75	2586	2.407	4.78	19.75	2586
Riser Cell B, High-Efficiency Drift Eliminators									
B-1	8/20	0.575	1.27	4.46	694	0.576	1.27	4.47	695
B-2	8/20	0.285	0.65	2.51	355	0.285	0.65	2.51	355
Average		0.430	0.96	3.49	524	0.431	0.96	3.49	525
Riser Cell C, High-Efficiency Drift Eliminators									
C-1	8/21	0.568	1.16	5.21	631	0.569	1.16	5.22	632
C-2	8/21	2.647	5.37	25.17	2930	2.649	5.38	25.19	2932
Average		1.608	3.26	15.19	1780	1.609	3.27	15.21	1782
Riser Cell D, High-Efficiency Drift Eliminators									
D-1	8/22	0.375	0.83	3.40	443	0.375	0.87	3.40	443
D-2	8/22	0.448	0.97	3.77	518	0.448	0.97	3.78	519
Average		0.412	0.90	3.59	480	0.412	0.92	3.59	481

meters per hour (39,580,000 actual cubic feet per hour), for fan cell B it averaged 1,281,000 actual cubic meters per hour (45,230,000 actual cubic feet per hour), for fan cell C, it averaged 1,162,000 actual cubic meters per hour (41,020,000 actual cubic feet per hour), and for fan cell D, it averaged 1,227,000 actual cubic meters per hour (43,810,000 actual cubic feet per hour). The stack temperature averaged 27°C (81°F), 26°C (78°F), 24°C (76°F), and 25°C (77°F) for fan cells A, B, C, and D, respectively. The moisture content averaged 3.5%, 3.2%, 3.0%, and 3.1% for fan cells A, B, C, and D, respectively. The isokinetic sampling rates were well within the allowable limits for all eight runs.

3.1.2 Hexavalent Chromium Emissions

The emission concentrations and the mass emission rates for hexavalent chromium for the test runs on the four fan cells are presented in Table 3.3. The hexavalent chromium concentrations for fan cells A, B, C, and D averaged 0.0024, 0.0004, 0.0016, and 0.0004 milligrams per dry standard cubic meter of exhaust gas; 4.78, 0.96, 3.26, and 0.90 micrograms per gallon of water flow to the fan cells; and 19.75, 3.49, 15.19, and 3.59 milligrams per million Btu's of heat removed; respectively. The mass emission rates of hexavalent chromium for fan cells A, B, C, and D averaged 2586, 524, 1780, and 480, respectively.

3.1.3 Total Chromium Emissions

The emission concentrations and the mass emission rates for total chromium are also presented in Table 3.3. The total chromium concentrations averaged 0.0024, 0.0004, 0.0016, and 0.0004 milligrams per dry standard cubic meter of exhaust gas; 4.78, 0.96, 3.27, and 0.92 micrograms per gallon of water flow to the fan cells; and 19.8, 3.45, 15.2, and 3.6 milligrams per million Btu's of heat removed for fan cells A, B, C, and D, respectively.

3.2 SIZE DISTRIBUTION OF DRIFT AND CHROMIUM

3.2.1 Size Distribution of Drift

The drift size distribution, as well as the drift rate, was measured by ESC, using their sensitive paper (SP) technique, for each fan cell tested by Entropy. The total flux, the mean particle diameter for mass and particle count, the mass emission rate, and a drift rate expressed as a percent of water flow to the fan cell are presented in Table 3.4 for the four fan cells. The drift rates calculated using the SP data as a percent of water flow ranged from 0.0001% to 0.0004%.

The mass mean diameter of the drift is that particle diameter at which half the drift mass is composed of particles with diameters larger than the mean diameter and half the mass is composed of particles with diameters smaller than the mean diameter. For the four riser cells, the mass mean diameter for the drift particles ranged from 348 to 407 micrometers (um) and averaged 377 um.

3.2.2 Size Distribution of Chromium

Two methods were used for estimating the percent of hexavalent chromium in two particle size ranges. The first method involved the use of paired trains with an "aligned nozzle train" and a "disc train" (described in Section 4.9). The aligned nozzle train, which was used as a reference measurement, was designed to collect all particle sizes isokinetically. The disc train was operated at the same sampling rate as the nozzle train and was designed to collect primarily the smaller particles (less than about 15 um). The purpose of the paired train particle sizing was to determine the percent of the chromium emissions associated with the smaller particles.

The second method used for particle sizing, the absorbent paper (AP) technique, was, in addition, being evaluated as a screening method for cooling tower testing. Southern Research Institute's (SoRI) Aerosol Science Division

TABLE 3.4. SUMMARY OF SENSITIVE PAPER (SP) DRIFT SIZE DATA

Date	Total Flux		Mean Diameter		Mass Emission Rate	Water Flow*	Drift Rate
	mass ($ug/m^2/sec$) x 10^6	count ($\#/m^2/sec$) x 10^6	mass um	count um	grams/sec	gpm	%
Riser Cell A							
8/19	0.031	1.83	407	56	1.17	9027	0.0002
Riser Cell B							
8/20	0.067	1.97	348	79	2.49	9095	0.0004
Riser Cell C							
8/21	0.020	7.04	355	37	0.758	9094	0.0001
Riser Cell D							
8/22	0.016	1.76	397	39	0.584	8939	0.0001
Average	0.034	3.15	377	53	1.251	9039	0.0002

*Water flow to individual risers calculated by dividing total water flow to tower by four.

calculated the cut sizes for both particle sizing methods. Using the fan cell gas velocity and the inside diameter of the disc train probe, SoRI calculated the diameter of particles collected at 50 percent efficiency (D_{50}) by the disc train. The D_{50} for the disc train runs ranged from 13.1 to 14.9 um (see Appendices A and C) with particles less than this size range being collected. The D_{50} for the AP sampling device, which collected primarily larger particles (i.e., 30 um and up), ranged from 25.1 to 28.5 um with particles larger than this size range being collected.

The ratio of the emission rates of hexavalent chromium measured by the paired trains for runs 1, 2, 3, and 4 for fan cells A, B, C, and D, respectively, are shown in Table 3.5. With to the nozzle train collection value used as the reference, the disc train collected over 100% of the hexavalent chromium. This suggests that most or all of the chromium emissions from the fan cells equipped with high-efficiency drift eliminators are associated with particles less than 15 um.

The second particle sizing method involved using the AP device attached to the traversing impinger train. The percent of chromium associated with particles greater than the 30 um cut size was calculated using the ratio of the PMR_a values for the AP device and the corresponding impinger (IMP) train run values (see Table 3.5). The ratio of the AP to impinger train values ranged from 2.9% to 8.9% for the four fan cells. This suggests that only a small portion of the chromium emissions are associated with particles larger than 30 um.

3.3 SUMMARY OF ANALYTICAL RESULTS FOR HEXAVALENT CHROMIUM AND TOTAL CHROMIUM

3.3.1 Cooling Water Samples

Two analytical techniques (see Figure 4.3) were used for the analysis of hexavalent chromium and total chromium in the cooling water samples. A portion

TABLE 3.5. SUMMARY OF PARTICLE SIZING DATA USING DISC TRAIN AND ABSORBENT PAPER

Run Number	Hexavalent Chromium PMRc (mg/hr)	Percent Ratio of Disc to Nozzle	Run Number	Hexavalent Chromium PMRa mg/hr	Hexavalent Chromium PMRa Avg.	Percent Ratio of AP to IMP train
RISER CELL A, HIGH-EFFICIENCY DRIFT ELIMINATORS						
DI-A-1	809	207%	A-1(AP) A-2(AP)	86.7 62.4	74.6	2.9%
NZ-A-1	391		A-1(IMP) A-2(IMP)	650 4,521	2,586	
RISER CELL B, HIGH-EFFICIENCY DRIFT ELIMINATORS						
DI-B-2	370	146%	B-1(AP) B-2(AP)	18.6 40.7	29.7	5.7%
NZ-B-2	253		B-1(IMP) B-2(IMP)	694 355	525	
RISER CELL C, HIGH-EFFICIENCY DRIFT ELIMINATORS						
DI-C-3	3058	1353%	C-1(AP) C-2(AP)	90.7 89.5	90.1	5.1%
NZ-C-3	226		C-1(IMP) C-2(IMP)	631 2,930	1,781	
RISER CELL D, HIGH-EFFICIENCY DRIFT ELIMINATORS						
DI-D-4	742	209%	D-1(AP) D-2(AP)	73.4 12.5	43.0	8.9%
NZ-D-4	355		D-1(IMP) D-2(IMP)	443 518	481	

of each cooling water sample was analyzed by RTI for hexavalent chomium using the diphenylcarbazide colorimetric procedure. Another 10-ml aliquot of each cooling water sample (approximately 350 ml) was filtered through a Teflon filter with a 1.0-um pore size. The filter, which was used to collect the insoluble trivalent chromium (Cr^{+3}) residue, was then analyzed for total chromium by NAA. The sum of the hexavalent chromium (Cr^{+6}) and the residue on the filter (Cr^{+3}) represents the total chromium content of the cooling water.

The hexavalent chromium results for the diphenylcarbazide analysis of the cooling water samples presented in Table 3.6 show a range of 16.9 to 18.2 micrograms per milliliter (ug/ml) of hexavalent chromium. The levels of trivalent chromium determined using NAA shown in Table 3.6 range from <0.0001 to 0.0222 ug/ml. The ratio of hexavalent chromium-to-total chromium (sum of hexavalent and trivalent chromium) in the cooling water ranged from 0.999 to 1.00 (99.9% to 100.0% hexavalent chromium). The percent hexavalent chromium value determined for each water sample collected was used to calculate the hexavalent chromium emissions from the total chromium emissions measured by the impinger train for that corresponding run.

The first and last cooling water samples collected during testing and a third cooling water sample collected prior to the addition of sodium dichromate and sodium bromide to the cooling water (NBS-Prespiked) were also analyzed for calcium (Ca), magnesium (Mg), manganese (Mn), and sodium (Na) content, and pH. The results of these analyses are presented in Table 3.7.

TABLE 3.7. MINERAL CONTENT AND pH OF SELECTED COOLING WATER SAMPLES

Sample No.	Cr ug/ml	Ca ug/ml	Mg ug/ml	Mn ug/ml	Na ug/ml	Cr+6 ug/ml	pH
A-1	17.5	177	48.7	<0.02	127	16.9	8.15
D-2	18.4	208	53.9	<0.02	140	17.0	8.49
NBS-Prespiked	<0.015	203	57.8	<0.02	130	NA	8.36

TABLE 3.6. SUMMARY OF ANALYTICAL RESULTS FOR COOLING WATER SAMPLES

Run No.	Sample Type	Sample No. Analyzed	Chromium (ug/ml)
	Riser Cell A		
A-1	Cooling Water (Cr+6)	A-1	16.90
A-1	Cooling Water (Cr+3)	A-1-R	<0.0001
A-1	Cooling Water (Total Cr)		16.90 *
A-2	Cooling Water (Cr+6)	A-2	17.00
A-2	Cooling Water (Cr+3)	A-2-R	0.0004
A-2	Cooling Water (Total Cr)		17.00 *
	Riser Cell B		
B-1	Cooling Water (Cr+6)	B-1	17.20
B-1	Cooling Water (Cr+3)	B-1-R	0.0222
B-1	Cooling Water (Total Cr)		17.22 *
B-2	Cooling Water (Cr+6)	B-2	17.50
B-2	Cooling Water (Cr+3)	B-2-R	0.0130
B-2	Cooling Water (Total Cr)		17.51 *
	Riser Cell C		
C-1	Cooling Water (Cr+6)	C-1	17.20
C-1	Cooling Water (Cr+3)	C-1-R	0.0082
C-1	Cooling Water (Total Cr)		17.21 *
C-2	Cooling Water (Cr+6)	C-2	17.20
C-2	Cooling Water (Cr+3)	C-2-R	0.0091
C-2	Cooling Water (Total Cr)		17.21 *
	Riser Cell D		
D-1	Cooling Water (Cr+6)	D-1	18.20
D-1	Cooling Water (Cr+3)	D-1-R	0.0053
D-1	Cooling Water (Total Cr)		18.21 *
D-2	Cooling Water (Cr+6)	D-2	18.10
D-2	Cooling Water (Cr+3)	D-2-R	0.0153
D-2	Cooling Water (Total Cr)		18.12 *

* This value represents the total chromium content of the cooling water and is the sum of the hexavalent chromium (Cr+6) measured by the diphenylcarbizide wet chemical method and the trivalent chromium (Cr+3) which is the chromium measured by NAA in the filtered residue of the cooling water sample.

3.3.2 Impinger Train Samples

The analytical results for the samples from each impinger train run and each paired train particle sizing run are presented in Table 3.8. The impinger train and paired train samples, consisting of the impinger contents and rinses, the probe rinses, and a filter, were analyzed principally by RTI using graphite furnace atomic absorption (GFAA). Each result was blank corrected using the results of a DI water or a DI water/filter blank. The chromium in each sample was first solubilized using nitric acid so that the GFAA analysis, which measures only soluble chromium, would yield results for total chromium. A small correction factor was added to the sample results to account for a prior NAA analysis of a small aliquot of each sample (see example calculations in Appendix A).

Prior to analysis, each sample was concentrated down in a glass beaker and then transferred to another container. Each beaker used was then treated with aqua regia to solubilize any residual chromium remaining after sample transfer. This aqua regia solution (beaker residue) was also analyzed by GFAA. Thus, the analytical results presented for total chromium in each impinger sample is the sum of the total chromium for the sample measured by GFAA (with the NAA correction factor) and the residual chromium recovered from the sample concentration beakers measured by GFAA (see example calculations in Appendix A).

The collection efficiencies for the sampling train (for runs A-2, C-2, and PS-DI-4) are presented in Table 3.9. The collection efficiency for runs A-2, C-2, and PS-DI-4 show 95.9%, 92.9% and 85.6%, respectively, of the chromium being collected in the first and second impingers.

TABLE 3.9. SAMPLE TRAIN (IMPINGER) COLLECTION EFFICIENCY

Date (1986)	Run No.	1st Imp. Catch, ug	Cumulative % of Catch	2nd Imp. Catch, ug	Cumulative % of Catch	3rd Imp. Catch, ug	Cumulative % of Catch
8/19	A-2	10.3645	87.1	1.0438	95.9	0.4884	100%
8/21	C-2	5.8704	76.1	1.2993	92.9	0.5453	100%
8/22	PS-DI-4	2.2331	41.7	2.3517	85.6	0.7718	100%

TABLE 3.8. SUMMARY OF ANALYTICAL RESULTS FOR CHROMIUM

Run Number	Sample Number	Sample Type	Sample Size	Total Chromium by NAA (ug)	Total Chromium by GFAA (ug)
		Riser Cell A			
A-1	A-1-abc	Impinger Contents & Filter	20.5103 ml		1.772
A-1	A-1-AP	Traversing Absorbent Paper	13.2 sq.cm	6.103	
A-2	A-2-a	1st Impinger & Probe Rinse	22.7763 ml		10.365
A-2	A-2-b	Second Impinger Contents	23.3437 ml		1.044
A-2	A-2-c	Third Impinger and Filter	22.6116 ml		0.488
A-2	A-2-AP	Traversing Absorbent Paper	13.2 sq.cm	4.394	
		Riser Cell B			
B-1	B-1-abc	Impinger Contents & Filter	23.1403 ml		1.842
B-1	B-1-AP	Traversing Absorbent Paper	1.32 sq.cm	1.309	
B-2	B-2-abc	Impinger Contents & Filter	24.3555 ml		0.934
B-2	B-2-AP	Traversing Absorbent Paper	1.32 sq.cm	2.867	
		Riser Cell C			
C-1	C-1-abc	Impinger Contents & Filter	21.7093 ml		1.673
C-1	C-1-AP	Traversing Absorbent Paper	13.2 sq.cm	6.386	
C-2	C-2-a	1st Impinger & Probe Rinse	19.4799 ml		5.870 *
C-2	C-2-b	Second Impinger Contents	21.6142 ml		1.299
C-2	C-2-c	Third Impinger and Filter	25.8687		0.545 *
C-2	C-2-AP	Traversing Absorbent Paper	13.2 sq.cm	6.309	
		Riser Cell D			
D-1	D-1-abc	Impinger Contents & Filter	18.6235 ml		1.173
D-1	D-1-AP	Traversing Absorbent Paper	13.2 sq.cm	5.167	
D-2	D-2-abc	Impinger Contents & Filter	24.4623 ml		1.365
D-2	D-2-AP	Traversing Absorbent Paper	13.2 sq.cm	0.883	
		Particle Sizing, Riser Cells A, B, C, and D			
DI-A-1	PS-DI-1-p	Disc Train Probe Rinse	18.984 ml		2.186
DI-A-1	PS-DI-1	Disc Train Imp. & Filter	27.637 ml		2.653
DI-B-2	PS-DI-2-p	Disc Train Probe Rinse	17.227 ml		1.301
DI-B-2	PS-DI-2	Disc Train Imp. & Filter	26.063 ml		1.326
DI-C-3	PS-DI-3-p	Disc Train Probe Rinse	17.467 ml		21.566
DI-C-3	PS-DI-3	Disc Train Imp. & Filter	12.707 ml		0.602
DI-D-4	PS-DI-4-p	Disc Train Probe Rinse	17.502 ml		1.3144
DI-D-4	PS-DI-4-a	Disc Train, First Imp.	16.508 ml		0.9187
DI-D-4	PS-DI-4-b	Disc Train, Second Imp.	15.907 ml		2.3517
DI-D-4	PS-DI-4-c	Disc Train, Third Imp.	17.963 ml		0.7718
DI-D-4	PS-DI-4-f	Disc Train Filter	Total		0.000
NZ-A-1	PS-NZ-1	Nozzle Train Imp. & Filter	25.888 ml		2.4894
NZ-B-2	PS-NZ-2	Nozzle Train Imp. & Filter	21.144 ml		1.9333
NZ-C-3	PS-NZ-3	Nozzle Train Imp. & Filter	16.860 ml		1.7775
NZ-D-4	PS-NZ-4	Nozzle Train Imp. & Filter	17.090 ml		2.8096

(continued)

TABLE 3.8 (continued)

Run Number	Sample Number	Sample Type	Sample Size	Total Chromium by NAA (ug)	Total Chromium by GFAA (ug)
		Blanks and Quality Assurance Samples			
	**	Imp. & Filter - Blank Value			0.1
	**	Imp. 1 & Rinse - Blank Value			0.1
	**	Imp. 2 - Blank Value			0.04
	**	Imp. 3 & Filter - Blank Value			0.02
	Blank-AP	Adsorbent Paper Blank	1.32 sq.cm	0.164	
	QA-1	QA Sample 1	1.0 ug Cr	0.221	
	QA-2	QA Sample 2	1.0 ug Cr		1.0
	QA-3	QA Sample 3	1.0 ug Cr	0.551	
	QA-4	QA Sample 4	0.1 ug/ml Cr		0.096 ug/ml
	QA-5	QA Sample 5	0.1 ug Cr	0.225	0.085

* Values were exchanged to correct for sample mislabelling.
** Blank values calculated from GFAA results for samples: P-42, P-43, Blank-f, Blank, Blank 1, and Blank 2.

3.3.3 Absorbent Papers

The analytical results for the absorbent paper measurements are also presented in Table 3.8. For these samples, the entire 47 mm paper was submitted directly to NCSU for NAA. The results in Table 3.8 are also blank corrected using the analytical results for a blank paper (Sample Blank-AP).

3.3.4 Blanks and Quality Assurance Samples

The results of the analyses for the blanks and the quality assurance samples are also presented in Table 3.8. Blanks for the cooling water analysis consisted of a DI water blank filtered through a Teflon filter having a 1.0-um pore size, with the filtrate being collected for analysis. The filter and a 1.0-ml aliquot of the DI water filtrate were submitted separately for analysis. The blanks for the Method 13-type impinger trains and paired particle sizing trains consisted of a blank Teflon filter identical to the ones used in the sampling trains and 500 ml of DI water concentrated to approximately 25 milliliters or just 500 ml of DI water concentrated (for collection efficiency samples). Each analytical result was blank corrected using the appropriate blank value.

The results of the analyses of the quality assurance samples are also presented in Table 3.8 and discussed in Section 5.0.

3.4 ABSORBENT PAPER SAMPLING

A sampling protocol using absorbent paper (filter paper) was evaluated as part of an effort to develop a screening method for cooling tower emission testing. The absorbent paper, held in a device similar to the SP holder, was exposed to the rising drift emissions by being attached to the traversing impinger train. The traversing AP allowed the use of the impinger train results as a reference to determine the sample collection efficiency of the

AP's. The AP catch of total chromium was determined by placing the AP directly into a 2-ml vial and submitting the sample for NAA.

A pollutant emission rate using the ratio of areas calculation (PMR_a) for each of the AP tests was calculated using the exposed area of the paper (exposed diameter of 41 mm). These results are presented in Table 3.10 for comparison with the PMR_a's calculated for the impinger train samples. The PMR_a values for the AP's are significantly lower than the PMR_a's calculated for the impinger trains. This low bias may be explained by the 30 um cut size calculated for the AP device, with only particles greater than 30 um being collected, and the association of the majority of the chromium emissions with particles less than 15 um (see Section 3.2.2).

The evaluation of this screening method will continue on future cooling tower tests and a separate report will be produced summarizing the results of the screening tests. The evaluation of the use of sodium bromide as a surrogate for cooling tower emission tests will also be discussed in the screening test summary report.

3.5 DRIFT RATE DETERMINATION

Drift rates for each sampling run were calculated as a percent of water flow to the individual fan cells being tested (see Appendix A). The water flow measurements, made by ESC, are presented in Table 3.4. The water flow values used to calculate the drift rate were determined by dividing the total water flow to the tower by the number of individual fan cells (four), because the PMR_a values used to calculate the drift rates were for individual fan cells. The drift rates from the impinger train results and the AP results were calculated using the PMR_a for total chromium and the total chromium in the cooling water at the time of the sampling run. It was assumed that the concentration of chromium in the drift was the same as the concentration of

TABLE 3.10. COMPARISON OF MEASUREMENT METHODS FOR TOTAL CHROMIUM EMISSIONS

Run Number	Pollutant Mass Rate by Ratio of Areas (mg/hr)	
	Total Chromium by Impinger Train (GFAA)	Total Chromium by Absorbent Papers (NAA)
	Riser Cell A	
A-1	650	86.7
A-2	4,521	62.4
Average	2,586	74.6
	Riser Cell B	
B-1	695	18.6
B-2	355	40.7
Average	525	29.7
	Riser Cell C	
C-1	632	90.7
C-2	2,932	89.6
Average	1,782	90.2
	Riser Cell D	
D-1	443	73.4
D-2	519	12.5
Average	481	43.0
Tower Average	1,343	59.3

chromium in the cooling water. The drift rates for the impinger train samples and the AP samples were calculated using the following formula:

$$\% \text{ Drift Rate} = \frac{\text{Cr PMRa (mg/hr) x 1 hour/60 minutes}}{\text{Cr in water (mg/l) x water flow (gpm) x 3.785 L/gal}} \times 100\%$$

The calculated drift rates for each run are presented in Table 3.11.

Drift rate as a percent of water flow was also calculated using the mass emission rate of drift (not chromium) determined by the ESC SP method. The ESC method is used here for comparison purposes only, as it is not being considered for use as an EPA reference method. The drift was assumed to have a specific gravity of 1 gram per milliliter (g/ml). The drift rate was calculated from the ESC data using the following formula:

$$\% \text{ Drift Rate} = \frac{\text{mass emission rate (g/sec) x 60 sec/min}}{\text{1 g/ml x water flow (gpm) x 3785.3 ml/gal}} \times 100\%$$

The calculated drift rates from the SP results are presented in Table 3.11 as the average fan cell drift rates for each riser cell tested.

The drift rates calculated using the AP data and the SP results show a low bias compared to the impinger results and good agreement between the two methods themselves. The differences between the AP and SP results and the impinger results may be explained based on the observations made by SoRI (see Section 3.2.2). The SP and AP technique may significantly underestimate the small droplet flux downstream of high-efficiency drift eliminators.

TABLE 3.11. COMPARISON OF MEASUREMENT METHODS FOR DRIFT RATES

Run Number	Drift Rate as a Percent of Water Flow		
	Impinger Train (GFAA)	Absorbent Paper (NAA)	Sensitive Paper
Riser Cell A			
A-1	0.0019%	0.0003%	
A-2	0.0130%	0.0002%	
Average	0.0074%	0.0003%	0.0002%
Riser Cell B			
B-1	0.0020%	0.0001%	
B-2	0.0010%	0.0001%	
Average	0.0015%	0.0001%	0.0004%
Riser Cell C			
C-1	0.0018%	0.0003%	
C-2	0.0082%	0.0002%	
Average	0.0050%	0.0003%	0.0001%
Riser Cell D			
D-1	0.0012%	0.0002%	
D-2	0.0014%	0.00003%	
Average	0.0013%	0.0001%	0.0001%
Tower Average	0.0038%	0.0002%	0.0002%

4.0 SAMPLING LOCATIONS AND TEST METHODS

This section describes the sampling locations and test methods used to characterize emissions from the mechanical draft crossflow cooling tower at the National Bureau of Standard's (NBS) Steam and Water Chill Plant in Gaithersburg, Maryland. Four fan cell stacks of the cooling tower adjacent to Building 302 were sampled to measure chromium emission and drift rates, drift size distribution, and exhaust gas velocity. In addition, the water flow was measured in the single riser pipe serving the four fan cells tested, and cooling water samples were taken from the water trough for analysis of hexavalent and trivalent chromium. Meteorological conditions were monitored and data collected using instruments on site that are owned and operated by NBS. The relative positions and the type of testing conducted at each location are shown in the simplified process flow diagram (see Figure 4.1) and accompanying Table 4.1. The subsections which follow further describe each sampling location and the applicable test methods.

4.1 COOLING TOWER CELL STACK OUTLETS (SAMPLING LOCATIONS A, B, C AND D)

Emissions testing for chromium and drift emissions, and drift size distribution determinations by several methods were conducted at each of four fan cells on the crossflow cooling tower adjacent to Building 302. All sampling on the first day was performed on the first fan cell (Sampling Location A), the second day at Sampling Location B, the third day at Sampling Location C, and the fourth day at Sampling Location D.

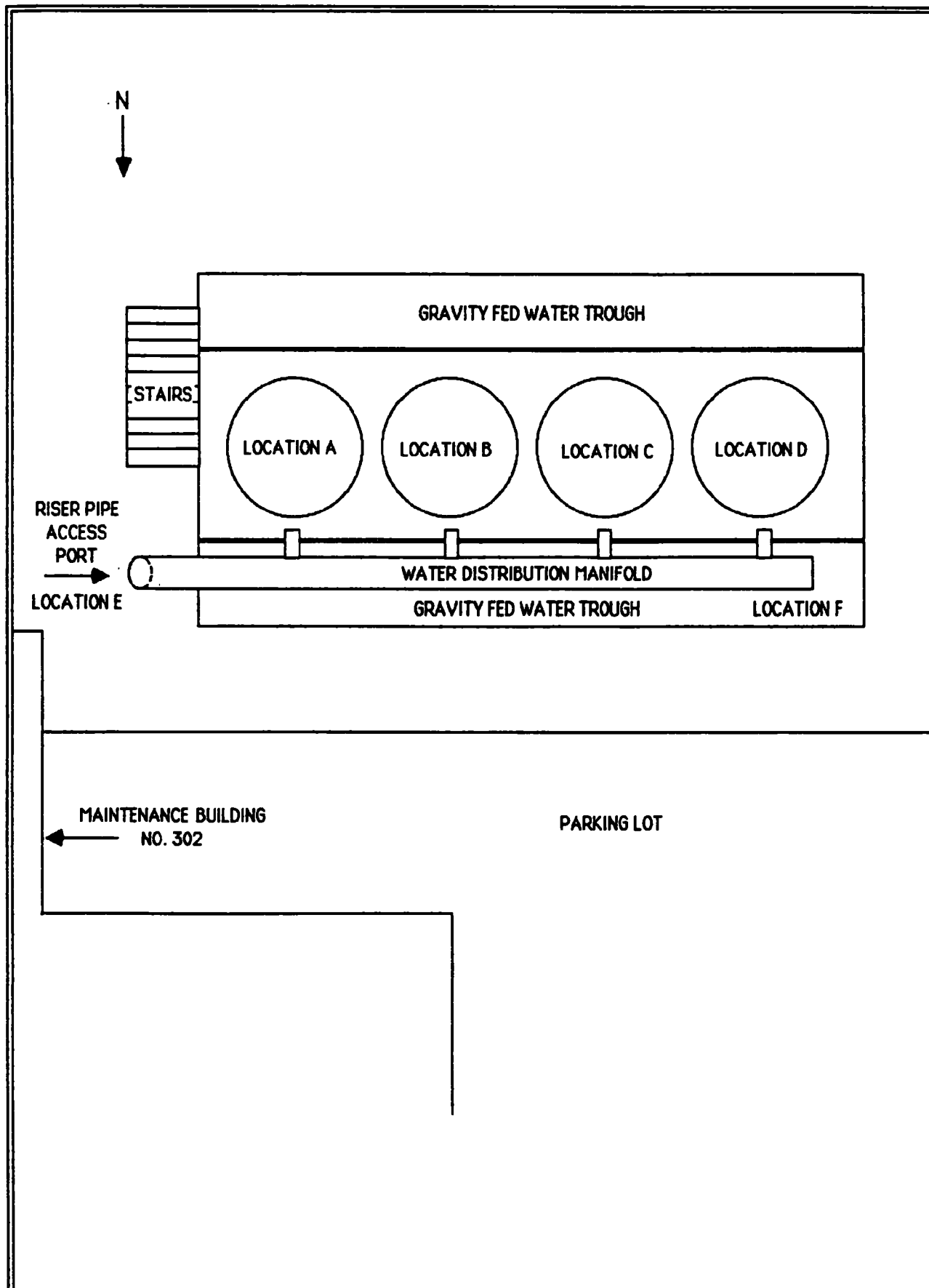


FIGURE 4.1. SKETCH OF NBS COOLING TOWER NEAR BUILDING NO. 302, SHOWING RISER PIPE, DISTRIBUTION MANIFOLD, WATER TROUGHS, AND SAMPLING LOCATIONS.

TABLE 4.1. SAMPLING PLAN FOR COOLING TOWER ADJACENT TO BUILDING 302
NBS, GAITHERSBURG, MARYLAND

Sample Type	Sampling Location	Number of Runs	Methods
Total Chromium & Drift Emissions	A, B, C, D	2 at each location	EPA Method 13-type impinger train with GFAA analysis; filters and impingers recovered separately for collection efficiency check on two runs
Drift Size Distribution and Drift Rate Determination	A,B,C,D	1 at each	Aligned nozzle train and disc train with GFAA analysis; absorbent paper with NAA analysis; sensitive paper with microscopic analysis
Recirculating Water Flow Rate	E	Single point check before each run; must be within 10% of initial determination by complete traverse	Calibrated pitot tube
Cooling Water Samples	F	3 grab samples per run combined into one composite sample	Cr^{+6} and NAA (Cr^{+3}) analysis
Meteorological Data	NBS Weather Instruments	Hourly	Dry, wet bulb temperatures, humidity, wind speed, and wind direction

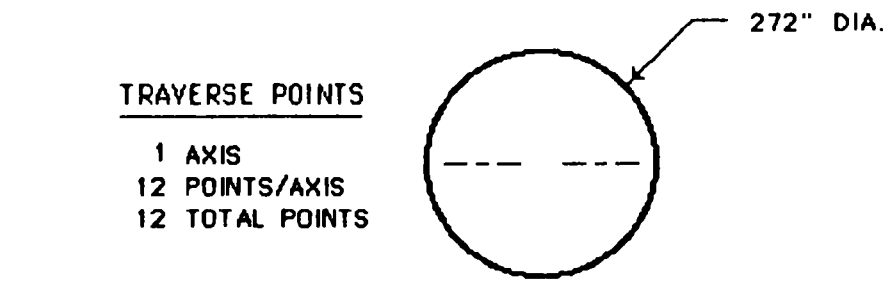
The four fan cell stacks were identical in construction and were all approximately 22.7 feet (272 inches) in diameter at the plane of the nozzle and train (see Figure 4.2). Sampling probes connected to sampling train boxes containing the impingers were introduced into the flow 2.33 feet into the fan cell stack and were suspended from a monorail to facilitate traversing the stack. The propeller anemometer used to measure the axial component of the exhaust flow was located 3 to 5 inches above the tip of the nozzle or the sampling point.

A Method 13-type impinger train was used for chromium and drift emissions sample collection. The fan stack was traversed along one axis at 12 points following the draft method (Appendix C). Each of the 12 points was sampled for 10 minutes for a total of 120 minutes of sampling per run. Propeller anemometer data were taken at each traverse point during sampling to be used in calculating the mass emission rate. Two runs were performed at each sampling location. The impinger contents and filter from one run at Sampling Locations A and C were recovered separately for a collection efficiency check.

Paired train test runs using the "disc" and "aligned nozzle" particle sizing trains (see Section 4.9) were all conducted at a single point at each sampling location. All of the paired train runs were 240 minutes in length.

Absorbent paper (AP) (see Section 4.11) samples were collected during each impinger train run.

Sensitive paper (SP) (see Section 4.10) size distribution testing was conducted once at each sampling location. Sensitive papers of 47 mm diameter were exposed at each of 12 equal area test points along one axis of a fan cell. Exposure times were selected in order to produce samples with a sufficient number of stains to allow confidence in the resultant droplet size distribution, but also to prevent overlapping stains. Local updraft air velocity values were taken at each sampling point using a Gill propeller anemometer and a Fluke digital multimeter.



POINT	% OF DIAMETER	DISTANCE FROM INSIDE WALL
1	2.1	5.750"
2	6.7	18.250"
3	11.8	32.125"
4	17.7	48.125"
5	25.0	68.000"
6	35.6	96.875"
7	64.4	175.125"
8	75.0	204.000"
9	82.3	223.875"
10	88.2	239.875"
11	93.3	253.750"
12	97.9	266.250"

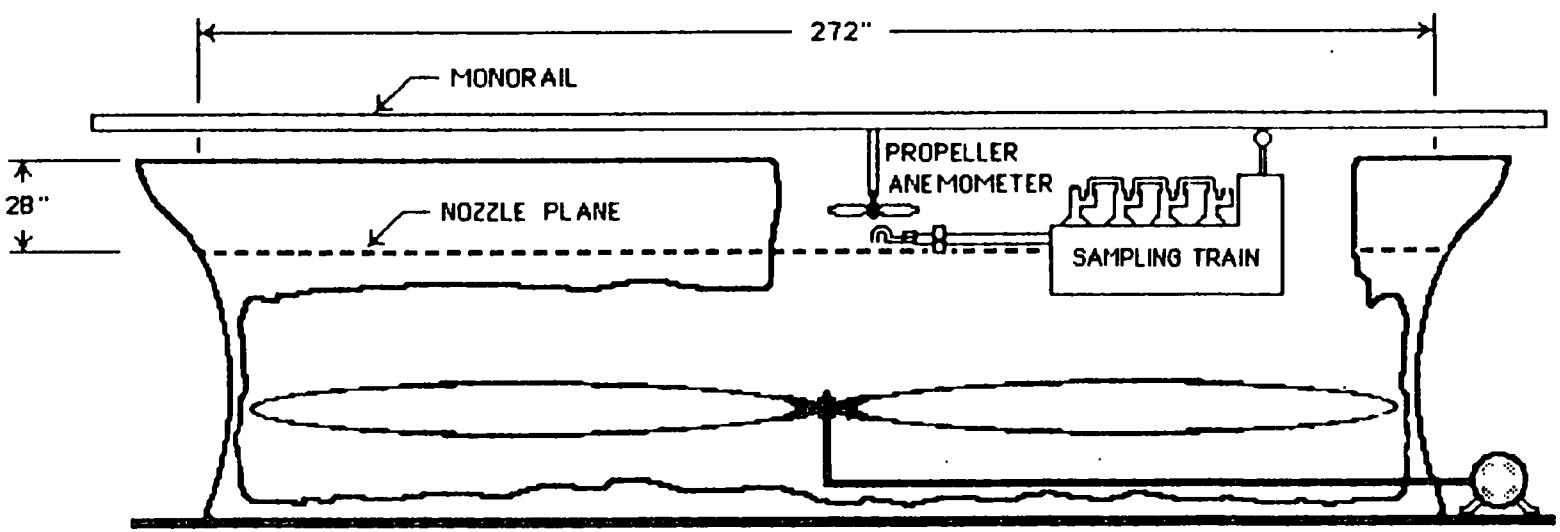


FIGURE 4.2. CUTAWAY VIEW OF FAN CELL STACK ON COOLING TOWER ADJACENT TO BUILDING NO. 302 AT NBS, SHOWING EQUIPMENT LOCATIONS AND NOZZLE TRAVERSE PLANE.

4.2 RECIRCULATING WATER PIPE (SAMPLING LOCATION E)

Circulating water flow rate was determined by traversing the cooling tower riser pipe using the calibrated pitot tube. A complete traverse was made initially on the single riser pipe that supplies all four fan cells. A single point check was then made prior to each testing run. The single point check was considered sufficient if the measured value was within 10% of the value determined by the initial complete traverse. To obtain the flow rate to each individual cell, the measured water flow rate for the one riser water pipe was divided by four, assuming equal distribution of water to each cell.

4.3 WATER TROUGH (SAMPLING LOCATION F)

During each emissions test run, a recirculating water sample was taken from the water trough at a point adjacent to the fan cell being sampled. These samples were taken by hand and stored in 500 ml glass jars. Each sample was analyzed for hexavalent chromium by RTI (wet chemical method). An aliquot of each water sample was also filtered through a 1.0-um pore size Teflon filter to collect the insoluble residue (Cr^{+3}); the filter and residue were then analyzed by NCSU for total chromium (NAA).

4.4 AMBIENT METEOROLOGICAL STATION

Ambient conditions during sampling were monitored and data collected using meterological instruments on site that are owned and operated by NBS. Sufficient data were collected at regular intervals for use in calculations and are summarized in Chapter 2.

4.5 VELOCITY AND GAS TEMPERATURE

A propeller anemometer was used to determine the total flow velocity in the axial direction at each sampling point as described in the draft test method

(see Appendix C). The temperature at each sampling point was measured using a thermocouple and digital readout.

4.6 MOLECULAR WEIGHT

Flue gas composition was essentially that of the ambient air drawn into the cooling tower via the fan. Therefore, the dry molecular weight and composition of air was used.

4.7 CHROMIUM COLLECTED BY IMPINGER TRAINS

Method 5-type sampling procedures, as described in the Federal Register,* were used with the Method 13-type trains to measure chromium and drift emissions at Sampling Locations A, B, C, and D (see the draft test method in Appendix C). Sampling trains consisted of a heated, glass-lined probe and a series of Greenburg-Smith impingers (two containing 100 ml of deionized-distilled water, one empty, and one with silica gel) with a 3-inch nominal Teflon filter located between the third and fourth impinger. A deionized distilled water rinse of the nozzle, probe, appropriate filter holder portions, and impingers of the sampling train was made at the end of each test. This rinse, the impinger contents, and the filter were combined and stored in a 500 ml glass jar, except for the two sampling runs on which collection efficiency checks were made. For these two runs, the rinse, impinger contents, and filter were stored and analyzed separately.

The samples were typically concentrated to approximately 25 ml in a 500 ml glass beaker and then were transferred to another container. The 500 ml beakers used to concentrate the samples were treated with aqua regia to solubilize residual chromium and these solutions were treated as separate

*40 CFR 60, Appendix A, Reference Methods 2, 3, and 5, July 1, 1980.

samples. The total chromium content of the impinger samples (after solubilization of the chromium with nitric acid) and the total chromium content of the solution containing the residual chromium from the beakers was determined by RTI using graphite furnace atomic absorption (GFAA). The total chromium catch for each impinger run is the sum of the total chromium content in the corresponding impinger sample and the total chromium content solublized from the appropriate beaker using aqua regia.

4.8 CHROMIUM IN COOLING WATER

Cooling water samples collected were analyzed for hexavalent chromium by RTI using the diphenylcarbazide wet chemical method. Also, a 10-ml aliquot of the cooling water was filtered through a Teflon filter with a 1.0-um pore size and the residue on the filter (insoluble trivalent chromium) was analyzed for total chromium by NAA. A flow chart for the analysis of the cooling water samples is presented in Figure 4.3.

4.9 DRIFT SIZING USING ALIGNED NOZZLE AND DISC TRAINS

Paired aligned nozzle and disc trains were used to estimate the percent chromium in drift particles smaller than a certain size. The disc train consisted of the impinger train set-up described in Section 4.7 with the exception that no nozzle was attached to the probe and a plexiglass disc was attached in the plane of the flow around the opening of the probe. This configuration was designed to collect the majority of drift particles less than a certain diameter.

The aligned nozzle train was run at the same time as the disc train at the same single sampling point to serve as a reference measurement for collection of all sizes of drift particles. It was identical to the impinger train used. The nozzle was aligned directly with the flow at the point sampled; the exact

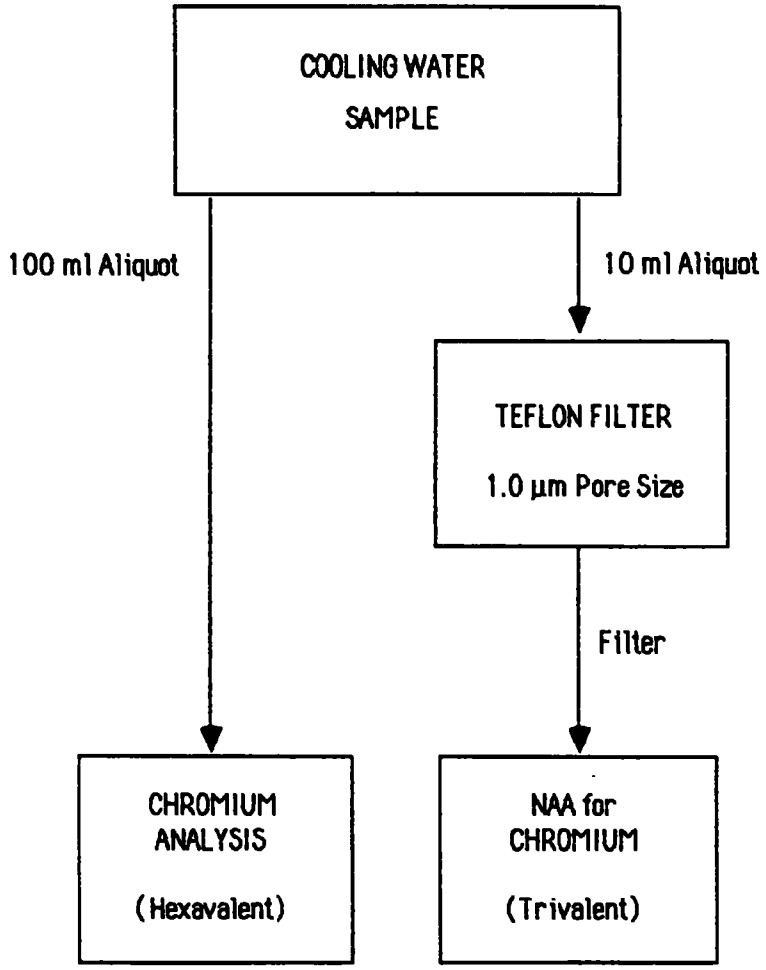


FIGURE 4.3. FLOW CHART FOR ANALYSIS OF COOLING WATER SAMPLES.

flow direction and delta P at that point was determined using a three-dimensional pitot tube.

The catches from each train were analyzed as previously described for the chromium emissions and drift testing.

4.10 SENSITIVE PAPER TESTING

Sensitive paper (SP) testing was used to measure drift rate and size distribution. The SP testing relies on droplet collection by inertial impaction on water-sensitive paper held perpendicular to the flow. This paper is chemically treated so the impinging droplet generates a well-defined blue stain on the pale yellow background of the paper. The size and shape of the stain and the droplet size were correlated by calibrating the SP system with a mono-disperse water droplet generator over a range of droplet sizes and impaction velocities.

Processing of exposed SP's consisted of measuring the stain diameters using a microscrope and a semi-automated GRAF PEN digitizer linked to a microcomputer which groups stain counts by size range. A computer program employing calibration curves for specific droplet sizes and impaction velocities was used to correlate stains with their original droplet sizes. In addition, a correction factor was applied which incorporated the collection efficiency of each droplet size range.

4.11 ABSORBENT PAPER TESTING

Absorbent paper (Whatman™ 541 filter paper) held in a sensitive paper sampling device was attached to each traversing impinger train to collect drift emissions. This was part of an effort to evaluate screening techniques for cooling tower testing. The sensitive paper device and absorbent paper were positioned on the probe of the impinger train and were exposed so as to collect

drift emissions during the 120 minutes of impinger train sampling. Absorbent paper samples were analyzed for total chromium by NAA.

5.0 QUALITY ASSURANCE

Because the end product of testing is to produce representative emission results, quality assurance is one of the main facets of stack sampling. Quality assurance guidelines provide the detailed procedures and actions necessary for defining and producing acceptable data. Two such documents were used in this test program to ensure the collection of acceptable data and to provide a definition of unacceptable data. These documents are the EPA Quality Assurance Handbook Volume III, EPA-600/4-77-027 and Entropy's "Quality Assurance Program Plan," which has been approved by the U. S. EPA, EMB.

Relative to this test program, the following steps were taken to ensure that the testing and analytical procedures produce quality data.

- Calibration of field sampling equipment. (Appendix D describes calibration guidelines in more detail.)
- Checks of train configuration and calculations.
- On-site quality assurance checks of sampling train components.
- Use of designated analytical equipment and sampling reagents.

Pre- and post-test calibrations were performed for each of the meter boxes used for sampling. Calibrations were also performed for the temperature sensing equipment, nozzles, water flow pitot tubes, anemometer sensor, and the entire propeller anemometer apparatus. Appendix D includes the calibration data sheets for each dry gas meter used for testing and data sheets for the calibrations of the other sampling equipment mentioned.

An on-site audit was performed on the meter boxes used for sampling and the data are summarized in Table 5.1. Entropy used the procedures described in the December 14, 1983 Federal Register (48F255670).

TABLE 5.1. METER BOX CALIBRATION AUDIT

Meter Box No.	Pre-Audit Y Value	Allowable Error 0.97Y<Y<1.03Y	Calculated Yc	Within Allowable Limits
N-2	1.0059	0.9757 - 1.0361	1.0214	✓
N-3	1.010	0.9797 - 1.0403	1.028	✓
N-7	1.010	0.9797 - 1.0403	1.0098	✓
N-9	1.003	0.9729 - 1.0331	0.9857	✓

Audit solutions were used to check the analytical procedures of the laboratories conducting the chromium analyses. Table 5.2 presents the results of these analytical audits.

The sampling equipment, reagents, and analytical procedures for this test series were in compliance with all necessary guidelines set forth for accurate test results as described in Volume III of the Quality Assurance Handbook.

TABLE 5.2. AUDIT REPORT CHROMIUM ANALYSIS

Plant: NBS

Task No.: 3505

Date Samples Received: _____

Date Analyzed: 8-27-86

Samples Analyzed By: RTI, NCSU

Reviewed By: P. Grohse, J. Weaver

Date of Review: _____

Sample Number	ug/mL Cr^{+6} or Cr	Source of Sample	Analytical Technique	Audit Value	Relative Error, %
QA-1 AP	.221 µg Cr	QAD/EEI	NAA	1.0 µg Cr	-34.5
QA-2	1.01 µg/ml Cr	QAD/EEI	Cr^{+6}	1.0 µg/ml Cr	1.0
QA-3	0.551 µg Cr	QAD/EEI	NAA	1.0 µg Cr	-45.0
QA-4	0.0986 µg/ml Cr	QAD/EEI	GFAA	0.100 µg/ml Cr	-1.4
QA-5	0.225 µg Cr	QAD/EEI	NAA	0.1 µg Cr	+125.0
QA-5	0.085 µg Cr	QAD/EEI	GFAA	0.1 µg Cr	-15.0

TABLE 5.3. AUDIT REPORT BROMIDE ANALYSIS

Plant: NBS

Task No.: 3505

Date Samples Received: _____

Date Analyzed: 8-27-86

Samples Analyzed By: NAA - NCSU

Reviewed By: J. WEAVER

Date of Review: _____

Sample Number	ug/ml ~~Cr^{+6}~~ or ~~Cr~~ Br	Source of Sample	Analytical Technique	Audit Value	Relative Error, %
QA-1 AP	0.155 µg Br	QAD/EEI	NAA	0.5 µg Br	-34.5
QA-3	0.235 µg Br	QAD/EEI	NAA	0.5 µg Br	-53.0
QA-5	0.008 µg Br	QAD/EEI	NAA	0.05 µg	-84.0