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

VOLUME I: SUMMARY REPORT

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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 have sponsored a program to monitor the emissions of metals and organics from a series of municipal wastewater sludge incinerators. The following document presents a summary of the results and testing procedures from all five test sites (Sites 5, 6, 7, 8, and 9).[1,2,3,4,5,6,7,8]

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ABSTRACT

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 publication in the Federal Register in January 1992.

EPA sponsored testing at five sewage sludge incinerators under this study (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. At three of the five incinerators in the present project, a wide range of data on emissions of metals, hexavalent chromium, nickel subsulfide, polychlorinated dibenzodioxins and furans (PCDD/PCDFs), semivolatile and volatile organic compounds, carbon monoxide (CO), and total hydrocarbon (THC) were determined. Two multiple hearth incinerators and one fluidized bed incinerator were tested. All three of these incinerators employed venturi/scrubbers for controlling air emissions. On the fluidized bed unit a pilot-scale wet electrostatic precipitator (ESP) was installed. A full-scale wet ESP was installed on one of the multiple hearth units. Feed sludge was tested for metals, moisture, and carbon and hydrogen content. The other two test sites included an evaluation of hexavalent chromium methods (Site 5) and an evaluation of continuous emission monitoring systems for carbon monoxide and total hydrocarbon (Site 7).

Of the metals measured, chromium, lead, and nickel consistently had the highest feed rate to the incinerators. Cadmium and lead had the highest emission factors of the metals fed to the incinerators. The emission control devices at the multiple hearth incinerators had similar removal efficiencies for particulate matter, chromium, and nickel, with lead and cadmium removal efficiencies being less than particulate matter. At the fluidized bed incinerator, the venturi/scrubber had the highest removal efficiency by a scrubber system without discriminating between metals and particulate matter. The wet ESPs were effective in further removal of the metals and particulate matter emitted from the venturi/scrubbers.

The hexavalent chromium test method developed for this program provided acceptable results for the measurement of hexavalent chromium without artifact formation at the outlet locations. The ratio of hexavalent chromium to total chromium was highest (8.3 - 42%) when lime was used for sludge conditioning, during good combustion conditions, and with the long residence times required for combustion of

sludge in a multiple hearth incinerator. The ratio of hexavalent chromium to total chromium in the emissions from a fluidized bed incinerator (despite relatively high total chromium levels) was very low (<2%), probably due to the short sludge retention time in the incinerator and the absence of alkaline material in the sludge.

The ratio of nickel subsulfide to total nickel was extremely low (<10%) under both normal combustion and improved combustion conditions.

PCDD/PCDFs, semivolatile organic compounds, and volatile organic compounds were measured in the controlled emissions from both types of incinerators. The wet ESP was effective in controlling the emissions of these compounds.

The combustion efficiency at both multiple hearth incinerators was improved during the test programs. The process operating conditions established for the second series of test runs at Site 6 and Site 9 greatly reduced the concentrations of carbon monoxide (CO) and total hydrocarbon (THC) emissions. A good correlation was seen between CO emissions and the THC emissions. The fluidized bed incinerator displayed better combustion efficiency than could be achieved with the multiple hearth incinerators.

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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 publication in the Federal Register 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 increased 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.[9] This speculation is based on hexavalent chromium being 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.[9] One-hundred percent conversion of trivalent chromium to hexavalent chromium was observed in several of the tests.[9] 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 full-scale sludge incinerators.[10,11] 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." As previously stated, EPA assumed that 100%

of the nickel emissions are in the subsulfide form to calculate a RSC. Since the Agency had no nickel subsulfide emission data from sewage sludge incinerators, it took the most conservative approach in conducting the nickel risk analysis and assumed that all emitted nickel compounds cause the same health effects as nickel subsulfide. Again, the Technical Support Document stated: "As additional data become available on the form of chromium and nickel emissions from combustion sources, the Agency will consider what changes, if any, would be appropriate for these proposed regulations."

To collect additional data, a comprehensive test program was developed to determine the ratios of hexavalent-to-total chromium and nickel subsulfide-to-total nickel for a typical sewage sludge incinerator under normal combustion conditions (higher concentrations of carbon monoxide and total hydrocarbons) and improved combustion conditions (lower concentrations of carbon monoxide and total hydrocarbons).

Seven secondary objectives also beneficial to the overall test program were established.

(1) Implement sampling and analytical procedures for chromium and nickel in uncontrolled and controlled flue gas emissions from municipal sewage sludge incinerators.

(2) Compare the ratios of emissions of (1) hexavalent-to-total chromium and (2) nickel subsulfide-to-total nickel for various types of municipal sewage sludge incinerators and for different operating conditions.

(3) Compare the emission results for chromium and nickel subspecies determined by different analytical procedures.

(4) Gather data on other metals and organic and inorganic gaseous components (as cited in the Federal Register, Volume 54, No. 23, February 6, 1989) in uncontrolled and controlled incinerator emissions to obtain background data on the effect of operating conditions on these emissions.

(5) Evaluate application of a wet electrostatic precipitator as a retrofit control system on existing facilities to meet the new sewage sludge emission regulations.

Five municipal wastewater sludge incinerators (designated Sites 5, 6, 7, 8, and 9) were selected for testing. (Four incinerators tested, Sites 1, 2, 3, and 4, under a previous project conducted by Radian Corporation are included in the Site numbering convention used here). Methods evaluation for the hexavalent chromium methods were conducted at Site 5. Continuous emissions monitoring evaluations for total hydrocarbon (THC) and carbon monoxide (CO) were conducted at Site 7. The full scale testing for metals, chromium and nickel speciation, and organics were conducted at Sites 6, 8, and 9. The general characteristics of Site 6, 8, and 9 are summarized in Table 1.

At the start of the test program, no published EPA emission measurement test methods for the sampling and analysis of hexavalent chromium or nickel subsulfide were available. Testing conducted at Site 5 was used primarily to develop a satisfactory test method for hexavalent chromium. Previous test methods for hexavalent chromium were shown to result in significant and unquantified conversion of chromium from the hexavalent to trivalent state. The hexavalent chromium test method developed and used for this test program minimized the hexavalent to trivalent conversion and conversion that occurred was quantified.

The test program conducted at Site 7 was intended only, to evaluate continuous emission monitoring systems (CEMSs) for carbon monoxide (CO) and total hydrocarbon (THC) and investigate if a correlation between CO and THC emissions exist at municipal wastewater sludge incinerators. CO and THC were also measured at Sites 6, 8, and 9 during the comprehensive testing for hexavalent chromium, nickel species, metals, and volatile and semivolatile organics.

At Site 6, combined thickened sludge was dewatered with four filter presses. Lime slurry and ferric chloride solution are used to condition the sludge for dewatering. The incinerator tested was one of the two identical multiple (eight) hearth furnaces. The air pollution control system associated with this furnace consists of an afterburner (which was not used during the test program), a water injection venturi, and an impingement tray scrubber.

At Site 8, approximately 15 to 17 tons of solids were dewatered by one filter press and fed to the fluidized bed incinerator. The air pollution control system associated with

TABLE 1. CHARACTERISTICS OF INCINERATORS AND SLUDGES AT THE FIVE SITES

	Site 6 - Normal	Site 6 - Low CO	Site 8 - Normal	Site 9 - Normal	Site 9 - Improved
Furnace type	Multiple Hearth	Multiple Hearth	Fluidized Bed	Multiple Hearth	Multiple Hearth
Control device	Venturi Scrubber	Venturi Scrubber	Venturi Scrubber/ Pilot Wet ESP	Venturi Scrubber/ Wet ESP	Venturi Scrubber/ Wet ESP
Sludge feed rate (#/hr)	3733	3460	4968	7482	7460
Inlet* stack gas parameters:					
Gas temperature (°C)	469	555	604	433	688
Gas oxygen (%)	13.0	11.5	8.3	12.9	10.4
Gas flow (dscmm)	468	430	2947	4191	4169
Midpoint* stack gas parameters:					
Gas temperature (°C)			35	27	33
Gas oxygen (%)	No midpoint location at Site 6		7.8	11.2	10.4
Gas flow (dscmm)			2982	3691	4169
Outlet* stack gas parameters:					
Gas temperature (°C)	63	65	28	52	68
Gas oxygen (%)	14.1	13.3	7.8	14.9	12.4
Gas flow (dscmm)	513	531	1405	5530	5175
Sludge characteristics:					
% solids	26	27	20	21	22
% volatiles	59	56	68	63	78
Heating value (btu/#)	6094	5481	8299	8481	8601

*"Inlet" and "Outlet" refer to inlet and outlet of the pollution control systems, "Midpoint" is between Wet ESP and Scrubber Systems.

this incinerator consists of a water injection venturi, and an impingement tray scrubber. A pilot-scale wet electrostatic precipitator was evaluated during testing at Site 8.

At Site 9, the sludge incinerator is a multiple (seven) hearth furnace. At the present time, the sludge is polymer conditioned and dewatered by two belt presses and then deposited onto a series of inclined and horizontal conveyor belts for feeding into the incinerator. The testing at Site 9 was to evaluate a furnace that did not use lime conditioning for the sludge filtration. It was discovered at the completion of the program that some of the Site 9 sludge that was trucked in had some lime added. Also a small amount of lime was added to the wastewater entering the plant facilities. The total amount of lime present was about 2.5% of the solids in the sludge, which is less than a typical amount of lime used for sludge conditioning but more than normally found in sludge at a typical plant that does not use lime. The air pollution control system associated with this incinerator consists of an adjustable throat venturi scrubber and three plate tray scrubber with a Chevron mist eliminator. A full-scale upflow, wet electrostatic precipitator was evaluated during the test program at Site 9.

This document is labelled Volume I in a series of nine volumes. Volume I presents a summary of the results and testing procedures from all five test sites (Sites 5, 6, 7, 8, and 9). Test data is presented in the Results and Discussion (Section 2.0) and briefly summarized in the Conclusions (Section 4.0). Volumes II through IX document results and procedures from each individual test site. (Volumes IV, VII, and IX are the appendices to Reports for Sites 6, 8, and 9, respectively).

2.0 SAMPLING AND ANALYTICAL PROCEDURE

At Site 5, tests were only conducted for hexavalent chromium methods development purposes. At Site 6, emissions were measured at the inlet and outlet of the control device. At Site 7, an evaluation of CO and THC CEMSs was performed. At Sites 8 and 9, emissions were measured at the inlet of the venturi scrubber, at the midpoint located between the venturi scrubber and the wet ESP, and at the outlet of the wet ESP. For Sites 6, 8, and 9, midpoint and outlet air emission samples were collected and analyzed for particulate matter, for metals, for polychlorinated dibenzodioxins and furans (PCDD/PCDFs), volatile and semivolatile compounds (except Site 6), and for hexavalent chromium and nickel species listed in Table 2. Inlet samples were collected and analyzed for metals, chromium, and nickel species. Due to the difficult sampling conditions at the inlet locations, only the concentrations of metals in the collected particulate matter and the ratios of hexavalent chromium to total chromium and nickel species to total nickel were determined. Continuous emission monitoring was conducted for O_2, CO_2, CO, SO_2, and NO_x at the control system inlet and O_2 (except Site 6), CO_2 (except Sites 6 and 9), CO, SO_2 (except Sites 6 and 9), NO_x (except Sites 6 and 9), and THC at the control system outlet stack. The monitoring data were used principally to determine process and control equipment operating conditions during the chromium and nickel speciation tests. Process samples consisting of sludge feed, scrubber inlet and discharge water, and bottom ash (except Site 8) were collected. Process samples were analyzed for the metals listed in Table 2 and were subjected to ultimate and proximate analysis. The heating value of the sludge feed was calculated from the carbon and hydrogen content.

Particulate matter and metals sampling was conducted following the procedures in the draft EPA method, "Methodology for the Determination of Trace Metals Emissions

TABLE 2. SPECIFIC ELEMENTS AND COMPOUNDS OF INTEREST

I. Metal Speciation

A. Trivalent Chromium
B. Hexavalent Chromium
C. Soluble Nickel
D. Sulfidic Nickel
E. Oxidic Nickel

II. Total Metals

A. Arsenic
B. Beryllium
C. Cadmium
D. Chromium
E. Lead
F. Mercury
G. Nickel

III. Combustion Gases and Criteria Pollutants

A. O_2
B. CO_2
C. CO
D. SO_2
E. NO_x
F. THC

IV. PCDDs/PCDFS

PCDDs

A. Mono-CDD
B. Di-CDD
C. Tri-CDD
D. 2378-TCDD
E. Other TCDD
F. 12378-PCDD
G. Other PCDD
H. 123478-HxCDD
I. 123678-HxCDD
J. 123789-HxCDD
K. Other HxCDD
L. 1234678-HpCDD
M. Other HpCDD
N. Octa-CDD

PCDFs

O. Mono-CDF
P. Di-CDF
Q. Tri-CDF
R. 2378-TCDF
S. Other TCDF
T. 12378-PCDF
U. 2378-PCDF
V. Other-PCDF
W. 123478-HxCDF
X. 123678-HxCDF
Y. 234678-HxCDF
Z. 123789-HxCDF
AA. Other HxCDF
BB. 1234678-HpCDF
CC. 1234789-HpCDF
DD. Other HpCDF
EE. Octa-CDF

V. Semivolatile Organics

A. Bis (2-ethylhexyl)phthalate
B. 1,2-Dichlorobenzene
C. 1,3-Dichlorobenzene
D. 1,4-Dichlorobenzene
E. Phenol
F. Naphthalene

VI. Volatile Organics

A. Acrylonitrile
B. Benzene
C. Carbon tetrachloride
D. Chlorobenzene
E. Chloroform
F. 1,2-dichloroethane
G. Trans1,2-dichloroethane
H. Ethylbenzene
I. Methylene chloride
J. Tetrachloroethane
K. Toluene
L. 1,1,1-Trichloroethane
M. Trichloroethane
N. Vinyl chloride

in Exhaust Gases from Stationary Source Combustion Processes." A diagram of the multiple metals sampling train used in this test program is shown in Figure 1 and a copy of the draft method is reproduced in Appendix B found in Volume IX: Site 9 Draft Test Report, Appendices. The sampling train and procedures used are similar to those for EPA Method 5 (40 CFR Part 60) with the following exceptions:

- A glass or quartz nozzle and probe liner are used;
- A Teflon filter support is used;
- A low metals background quartz fiber filter is used;
- 5% nitric acid/10% hydrogen peroxide solution replaced water in the first two impingers and $KMnO_4$ in the third impinger;
- The glassware is cleaned according to the procedure in the draft method; and
- The sample is recovered as shown in Figure 2.

After gravimetric analysis of the front half portion of the train, the samples were digested according to the procedure and total metals determined using inductively-coupled argon plasma spectroscopy and atomic absorption spectroscopy for total Cr, Ni, As, Pb, Cd, and Be. A sample preparation and analytical flow chart is presented in Figure 3. Mercury sampling was included in Sites 8 and 9 testing program using the multiple metals train. It was later determined by EPA that the sample should be filtered and the solids be digested. Since the need for this procedure was not know at the time of the mercury sample preparation and analysis, the mercury results are considered invalid and are not presented.

Flue gas sampling and analysis for hexavalent chromium followed the procedures in the draft EPA method, "Determination of Hexavalent Chromium from Stationary Sources." Either quadruplicate or duplicate sampling trains were employed. A diagram of the recirculating reagent sampling train, shown in Figure 4, was used at the midpoint and outlet locations for Sites 6, 8, and 9. The draft method is reproduced in Appendix B of Volume IX: Site 9 Draft Test Report, Appendices. This procedure is based on EPA Method 5 with the following modifications:

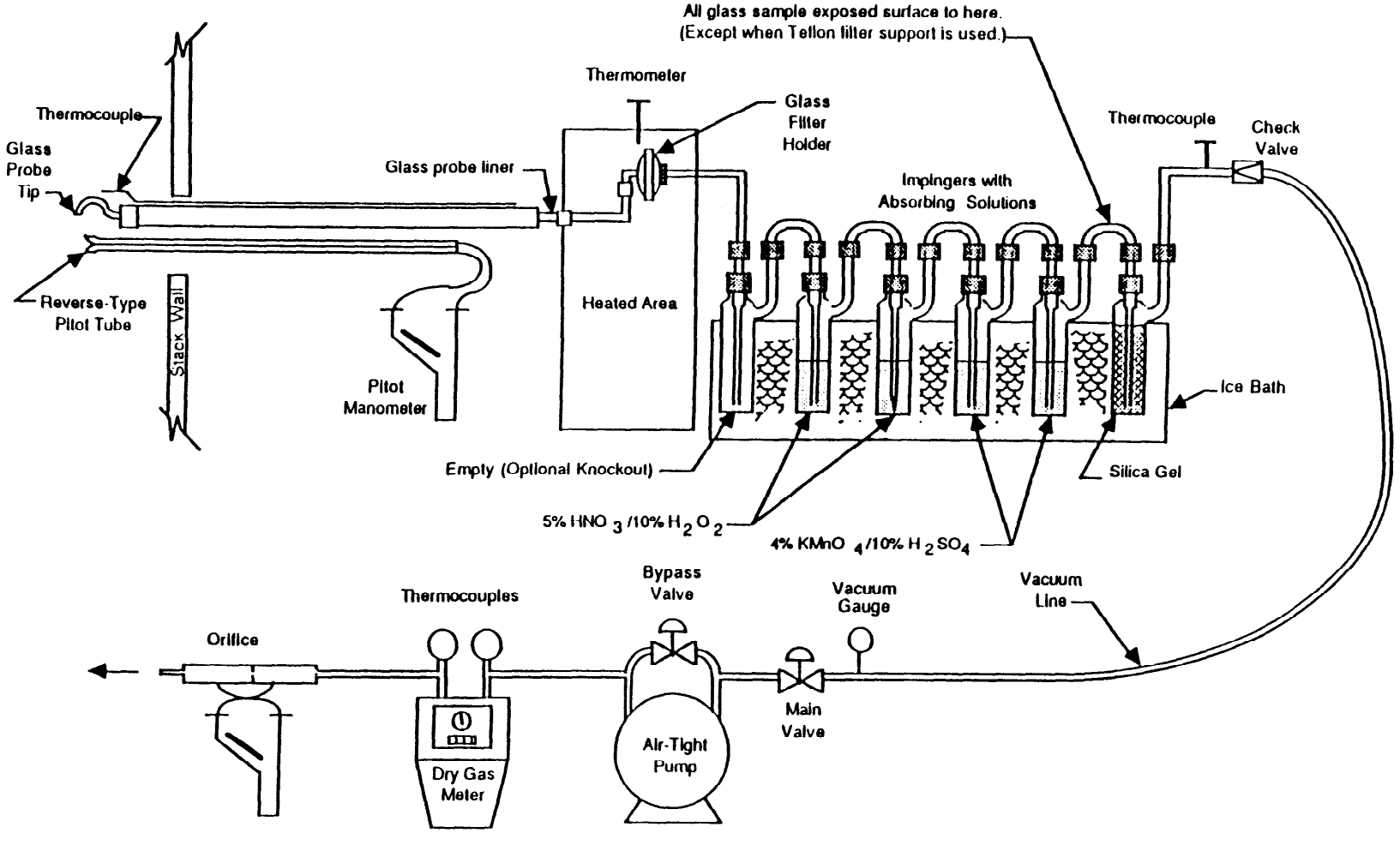
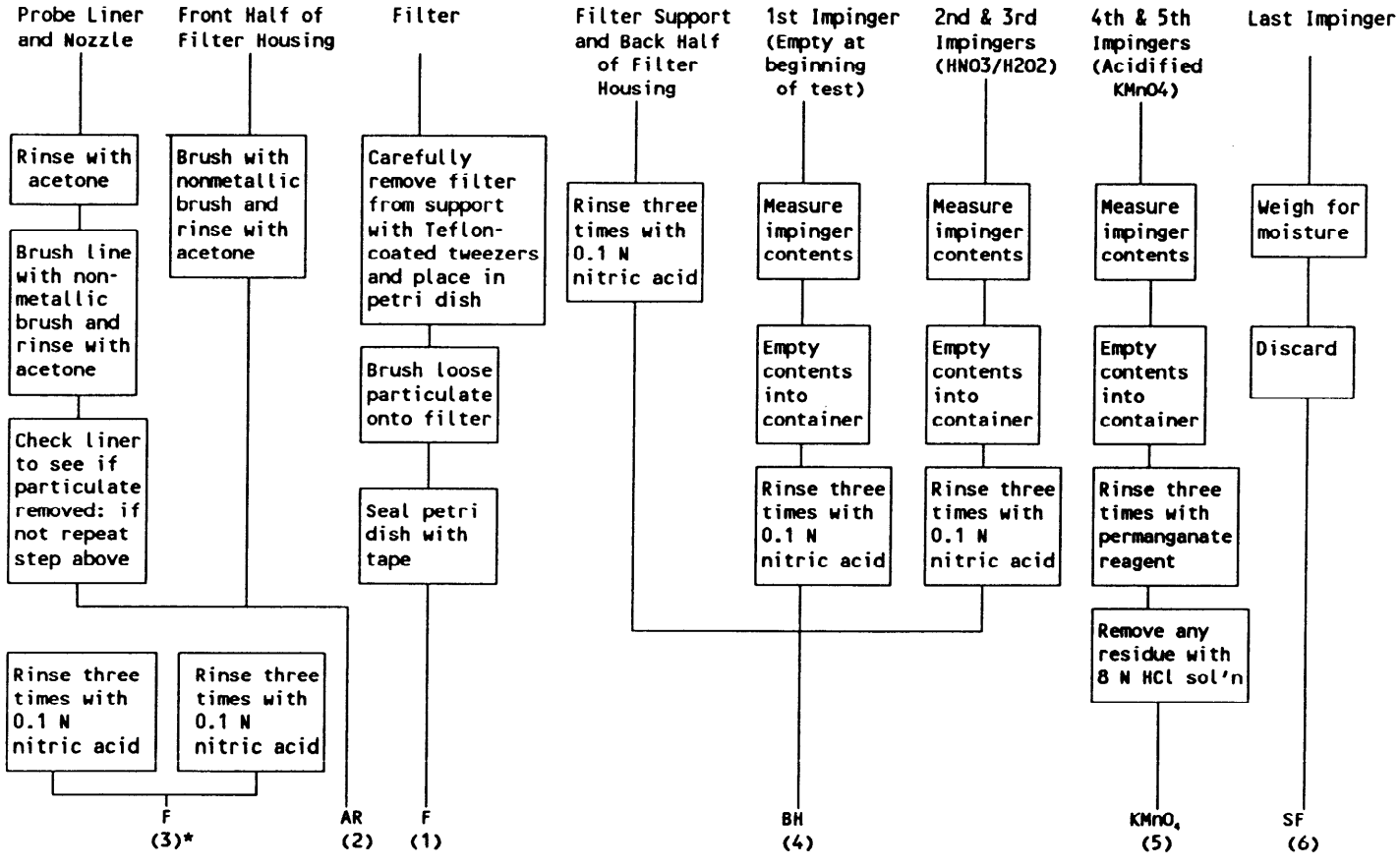


Figure 1. Schematic of multiple metals/particulate sampling train.



* Number in parentheses indicates container number.

Figure 2. Sample recovery procedures for multiple metals train.

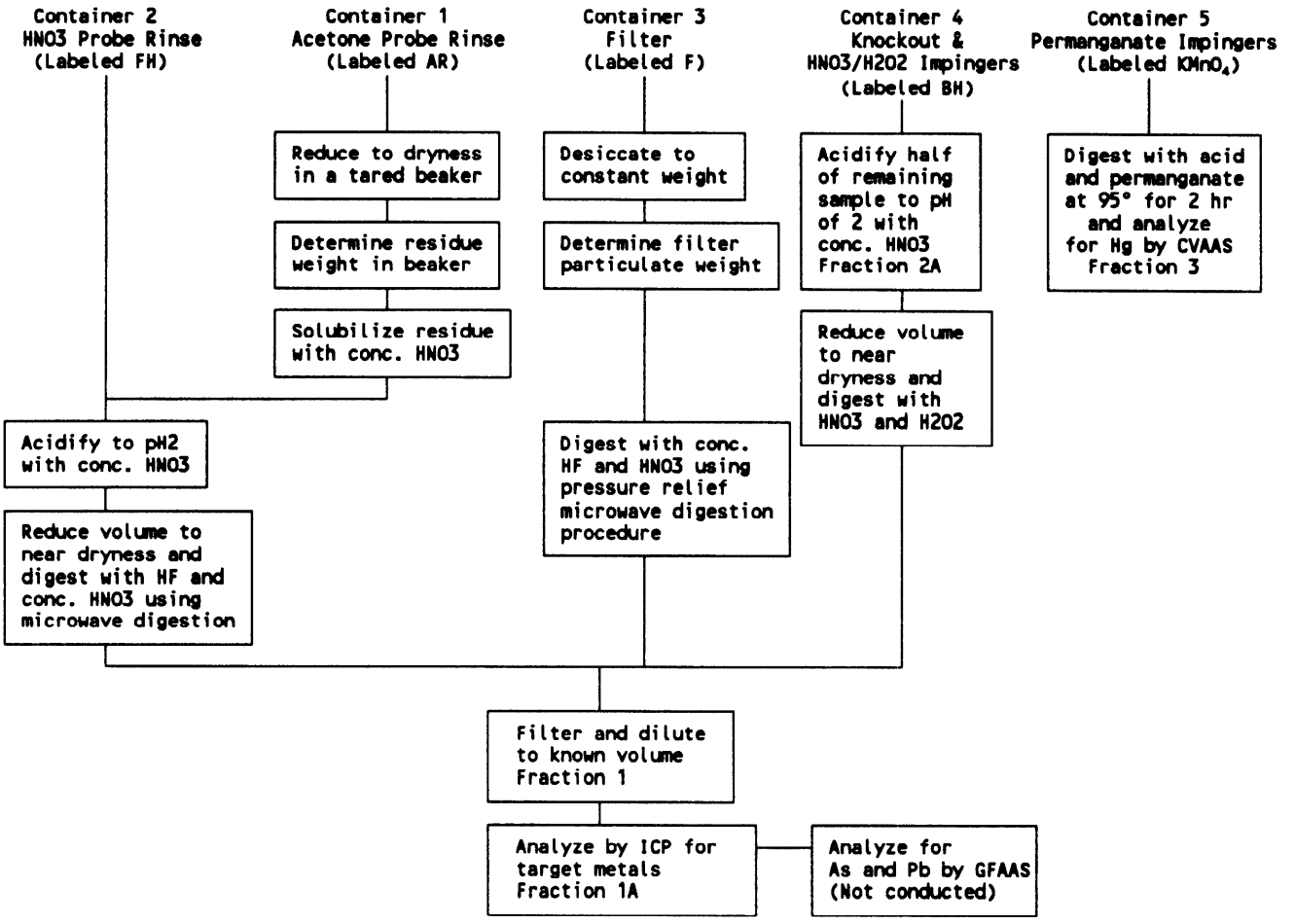


Figure 3. Sample preparation and analysis scheme for multiple metals trains.

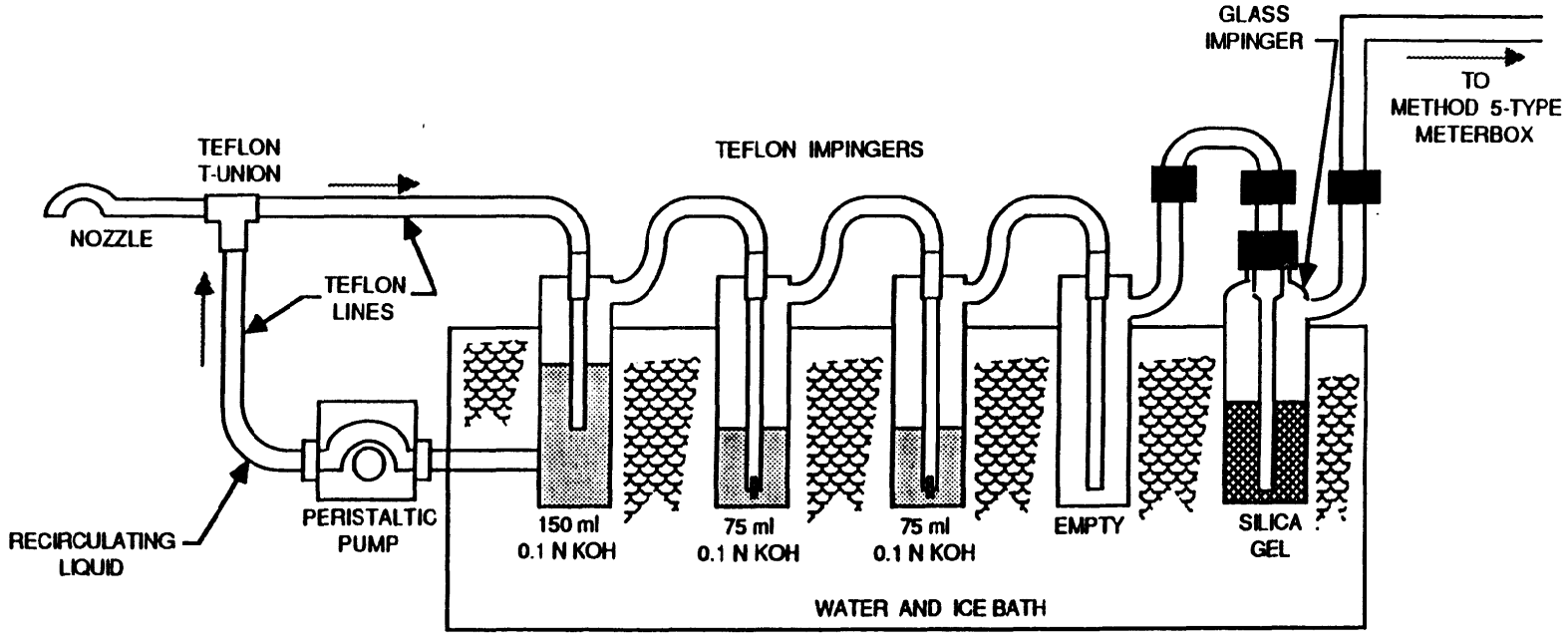


Figure 4. Schematic of recirculating reagent impinger train for hexavalent chromium.

- The train does not have a filter section;
- 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;
- 0.1 N KOH replaces water in the impingers;
- The entire surface exposed to sample is constructed of Teflon and/or glass;
- The glassware cleaning procedure includes a 10 hour soak in 10% HNO_3; and
- The sample is recovered as shown in Figure 5.

Sampling for hexavalent chromium at the inlet locations was performed essentially with a Method 5-type train at Site 6. At Site 8, the train was modified by eliminating the filter and collecting the sample directly in a 1.0 N KOH solution. At Site 9, a peristaltic pump was used to spray a 1.0 N KOH solution into the probe directly behind the sampling nozzle during sampling. A schematic of the inlet hexavalent sampling train employed at Site 9 is shown in Figure 6.

Hexavalent chromium samples were analyzed by ion chromatography coupled to a diphenylhydrazine post-column reaction (IC/PCR) on the filtered impinger samples. To determine the recovery of the radioactive hexavalent chromium spike, 0.5 ml fractions of the IC/PCR discharge were collected at regular time intervals during the IC/PCR analysis, and the gamma emissions measured for each fraction. For samples with the ^{51}Cr spike, the gamma emissions from the filter residue and the HNO_3 rinses were measured before combining them for digestion and total Cr analysis. A sample preparation and analytical flow diagram is presented in Figure 7.

Flue gas sampling and analysis for nickel species followed the draft EPA method, "Methodology for the Determination of Nickel Compound Emissions from Stationary Sources." A diagram of the nickel sampling train is shown in Figure 8 and the method description is presented in Appendix B found in Volume IX: Site 9 Draft Test Report, Appendices. Typically the sample trains collected for nickel speciation were paired with

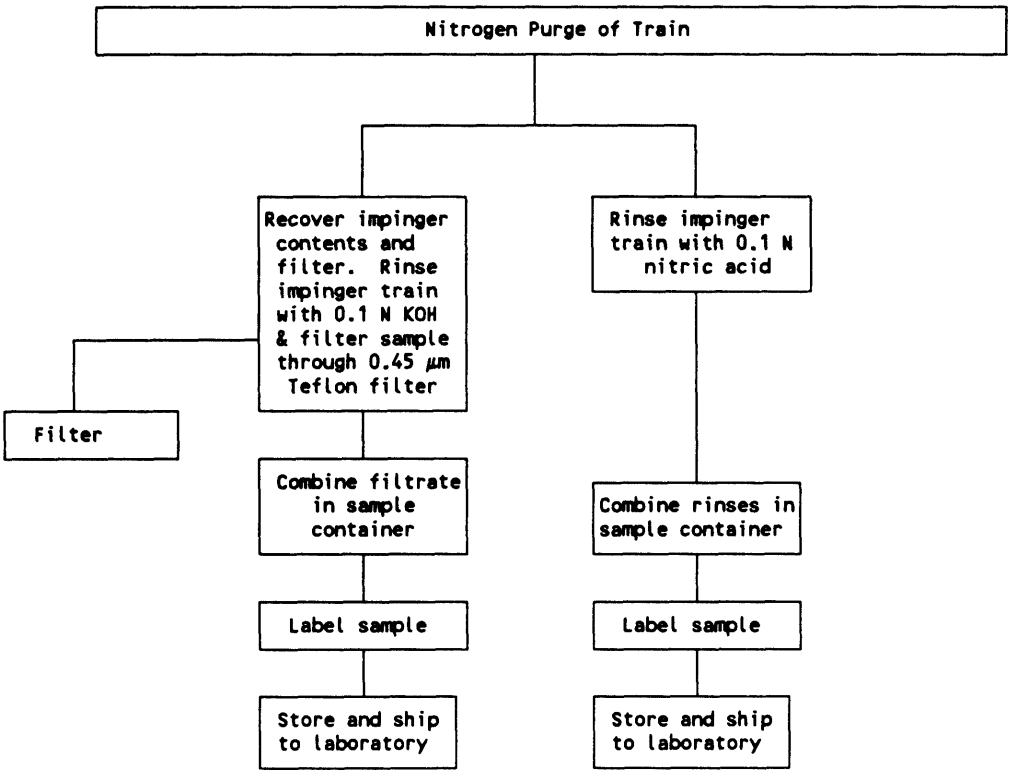


Figure 5. Sample recovery scheme for hexavalent chromium impinger train.

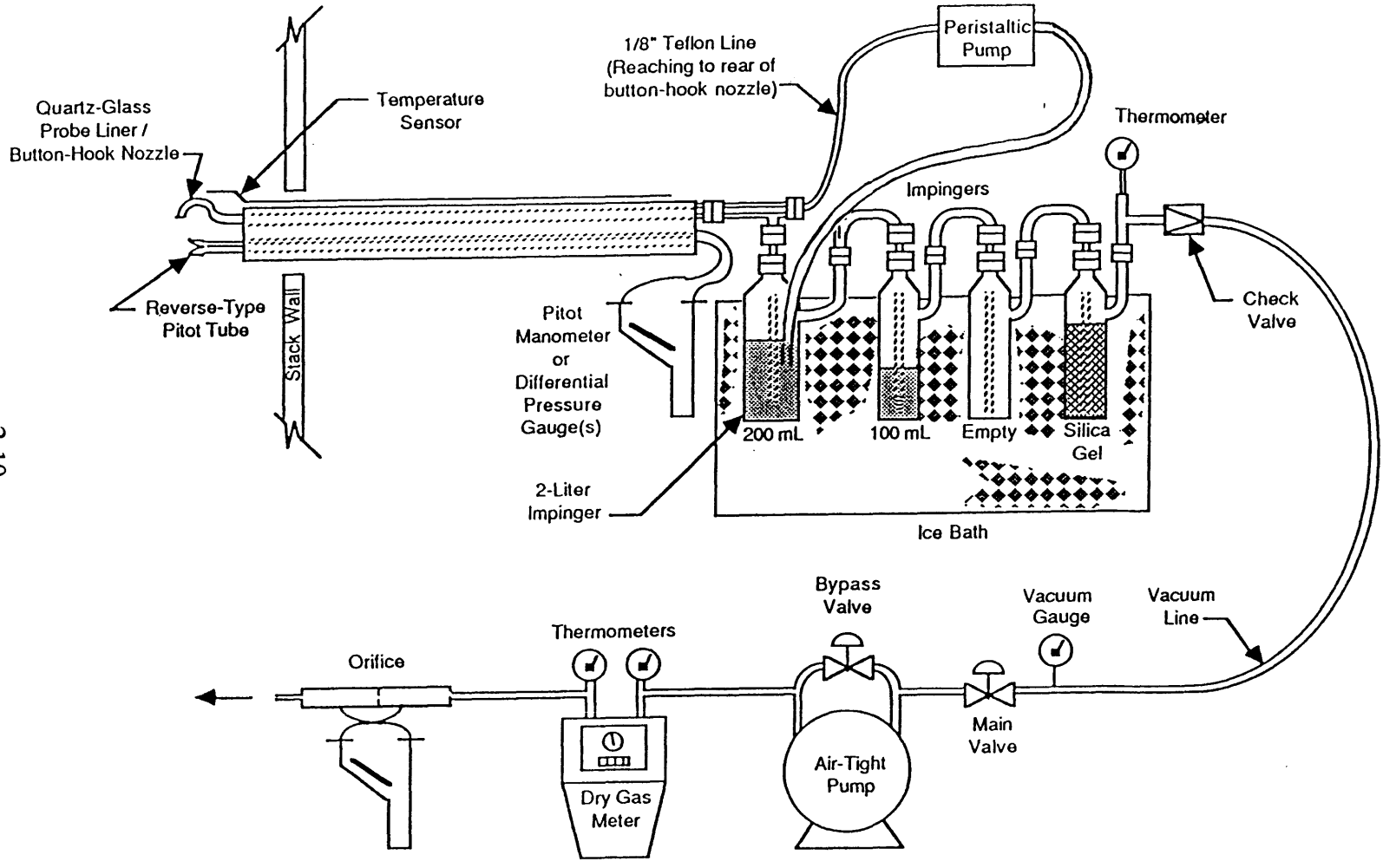


Figure 6. Schematic of inlet location recirculating reagent impinger train for hexavalent chromium.

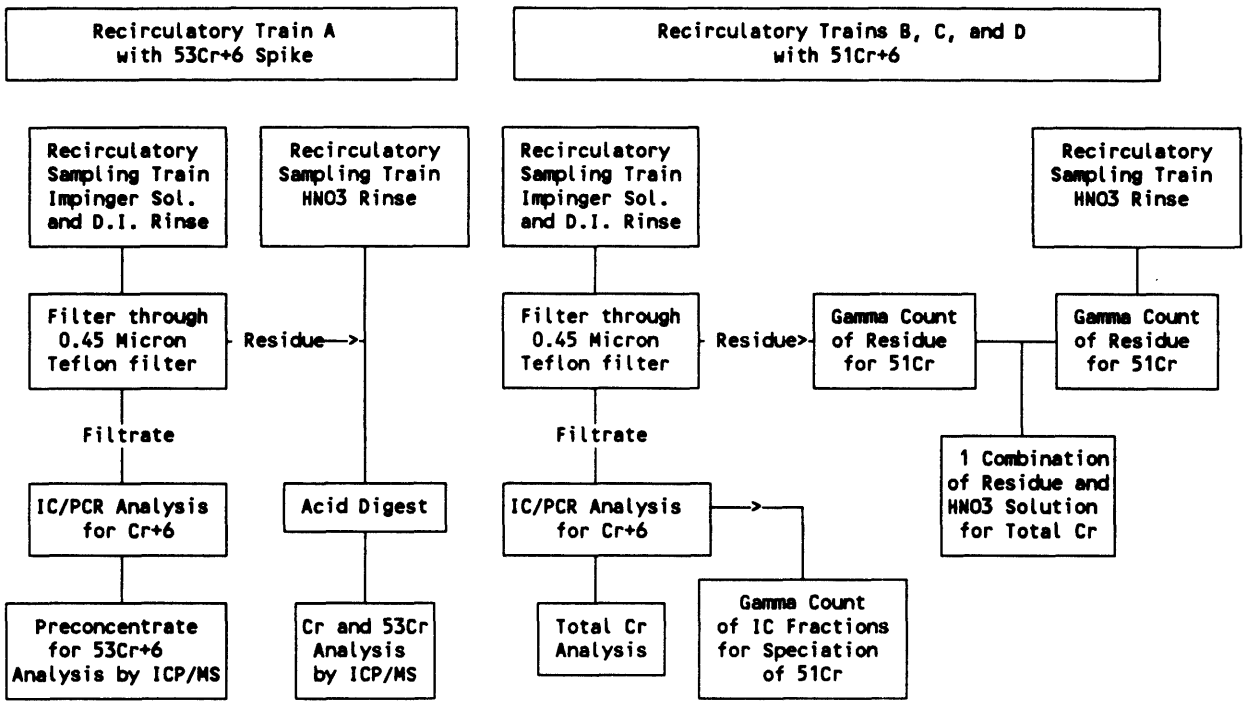


Figure 7. Analytical protocol for quadruplicate recirculatory train hexavalent chromium sampling at midpoint and outlet locations.

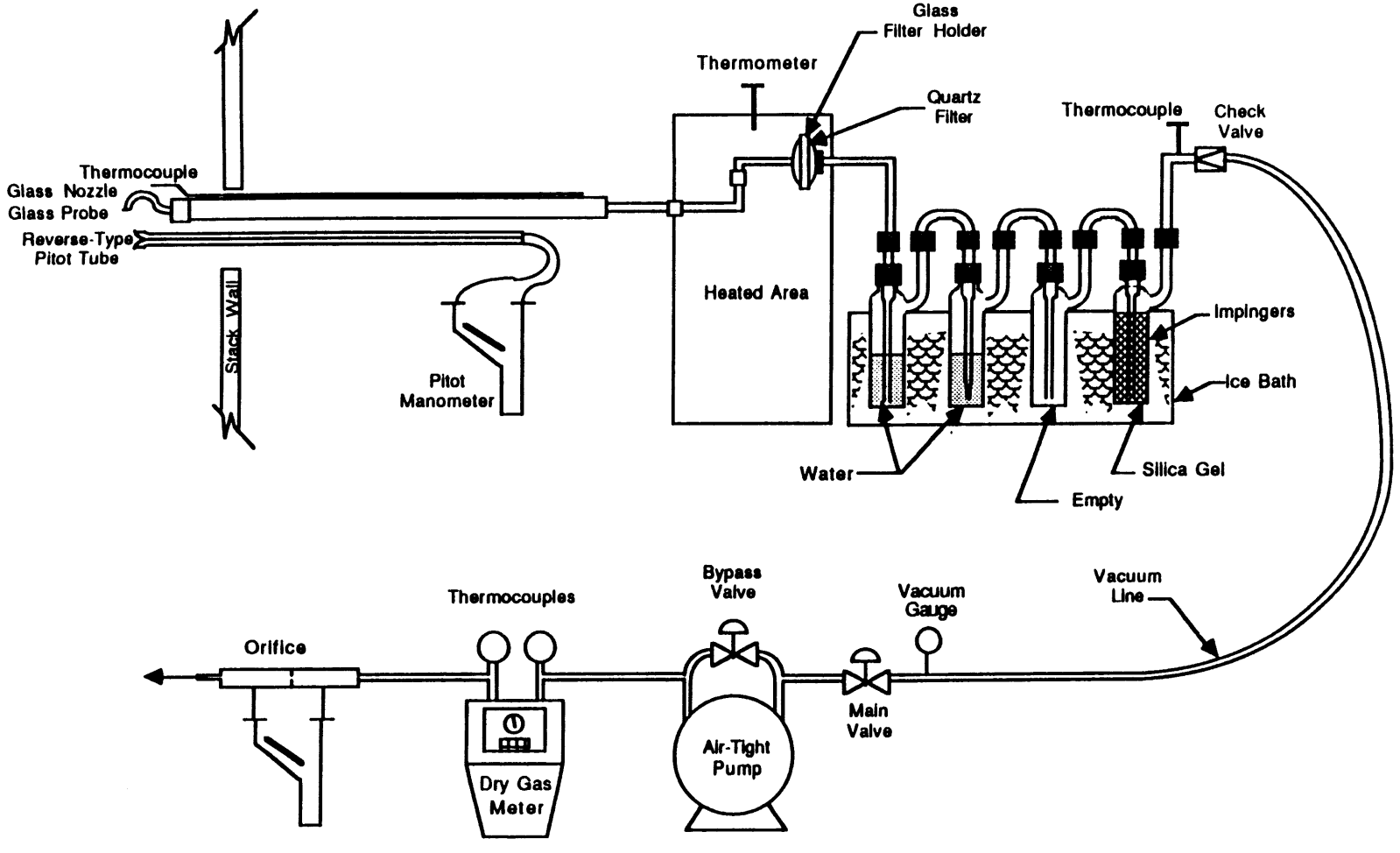


Figure 8. Schematic of nickel/nickel subsulfide sampling train.

a metals sampling train or in a quadruplicate arrangement with one metals sampling train.

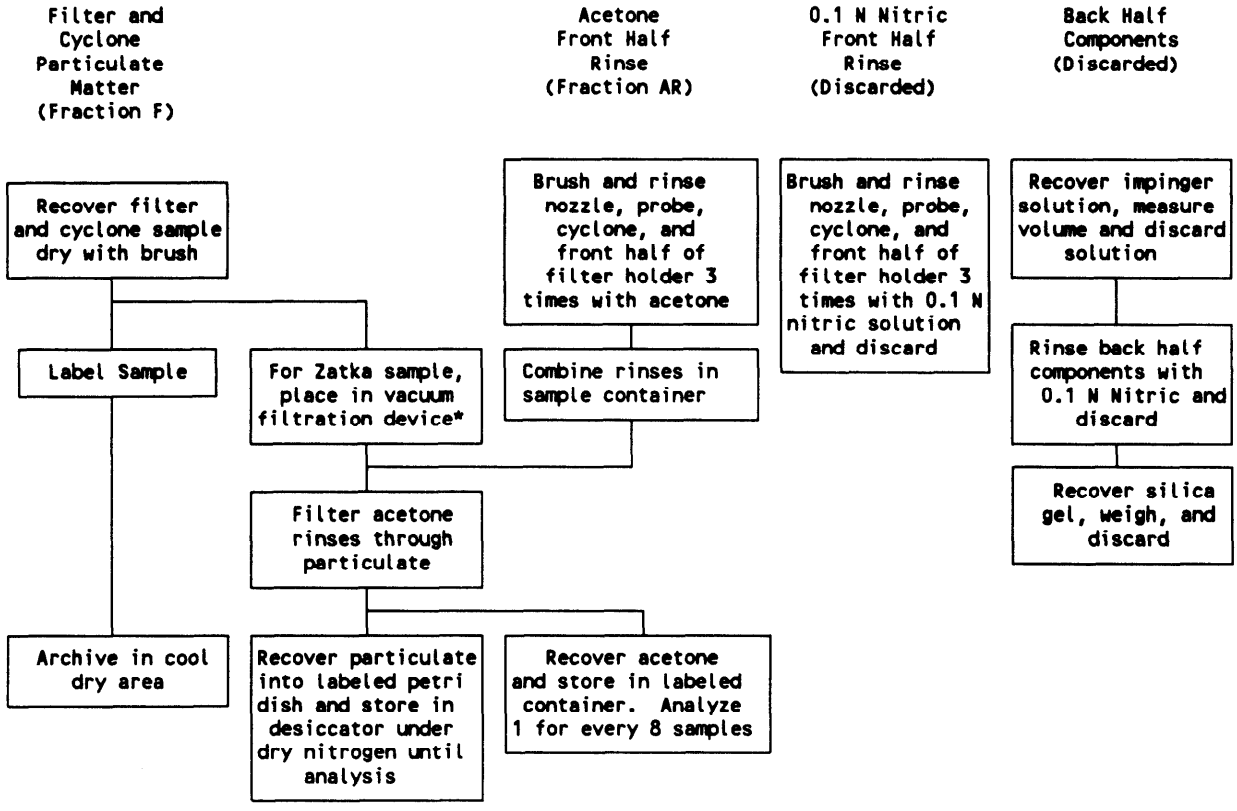
The sampling train and procedures are identical to those of EPA Method 5 (40 CFR Part 60) with the following exceptions:

- A glass or quartz nozzle and probe liner are used;
- A low metals background quartz fiber filter is used;
- The glassware cleaning procedure includes a 10 hour soak in 10% HNO_3; and
- The sample is recovered as shown in Figure 9.

Each day the filters to be analyzed were stored in a desiccator under a dry nitrogen atmosphere and sent to the analytical laboratory at the conclusion of test. The dry nitrogen atmosphere was used because past experience has shown that oxidation of nickel compounds can occur over a several week period.

Analysis of the nickel speciation samples was performed following the NiPERA sequential leaching method. The ratios of sulfidic nickel species, nickel subsulfide (Ni_3S_2) and nickel sulfide (NiS), to total Ni were determined. The method is not capable of speciating between Ni_3S_2 and NiS. Individual nickel phases are extracted out from the solid sample by sequential leachings using a series of solutions with increasing oxidation strength. Four nickel phase groups are determined:

Nickel Groups	Types of Nickel	Leaching Solution
1) soluble nickel	water soluble nickel salts;	0.1M ammonium acetate
2) sulfidic nickel	besides Ni_3S_2 and NiS, also dissolved are arsenides NiAs and $Ni_{11}As_8$, and selenide NiSe;	peroxide-citrate
3) metallic nickel	free or alloyed with iron (ferronickel);	methanol-bromine
4) oxidic nickel	refractory nickel oxide;	nitric/perchloric acid



* Note: Inlet samples were not acetone rinsed.

Figure 9. Schematic of sample recovery procedures for nickel train.

EPA Methods 1, 2, 3, and 4 were used in conjunction with the sampling procedures described above. Method 3 samples were collected as backup for O_2 and CO_2 determination should the CEMSs data be unavailable.

Flue gas sampling for PCDD/PCDFs and semivolatile organic compounds followed procedures in SW-846 Method 0010, except that a final toluene rinse was conducted and analyzed separately for PCDD/PCDF. The samples were analyzed for PCDD/PCDF using SW-846 Method 8290 and for other semivolatile organic compounds using a combination of SW-846 Methods 3540, 3550, 3510, 3520, and 8270. A schematic of the MM5 sampling train is shown in Figure 10 and copies of the relevant SW-846 methods are reproduced in Volume IX: Site 9 Draft Emission Test Report, Appendices. The sample recovery scheme is presented in Figure 11 and the sample extraction scheme is presented in Figure 12.

Flue gas sampling for volatile organic compounds employed the volatile organic sampling train (VOST) shown in Figure 13 in accordance with SW-846 Method 0030, which is reproduced in Volume IX: Site 9 Draft Emission Test Report, Appendices.

The CEMSs used to measure concentrations of CO, CO_2, O_2, NO_x, SO_2, total hydrocarbons (THC as propane) followed the EPA instrumental Methods 10, 3A, 7E, 6C, and 25A, respectively. The primary intent of the continuous monitoring effort was to: (1) determine concentrations of these compounds, and (2) provide a real-time indication of combustion conditions. The continuous monitoring systems were calibrated daily, but no attempt was made to certify the monitors using the EPA instrumental test methods.

The dewatered sludge samples were analyzed for the target metals after determination of their moisture and ash content, heating value, and proximate and ultimate analyses following ASTM Methods D3174, D3175, D3177, D3178, D3179, and D2361 (not reproduced in Appendices because they are standard methods). A dried portion of the sludge sample was subjected to microwave HNO_3/HF digestion in a pressure relief vessel identical to the flue gas particulate samples described above. This digestion procedure was chosen to provide for comparison of the metals in the sludge with the flue gas samples and the bottom ash samples (see below). The digestion

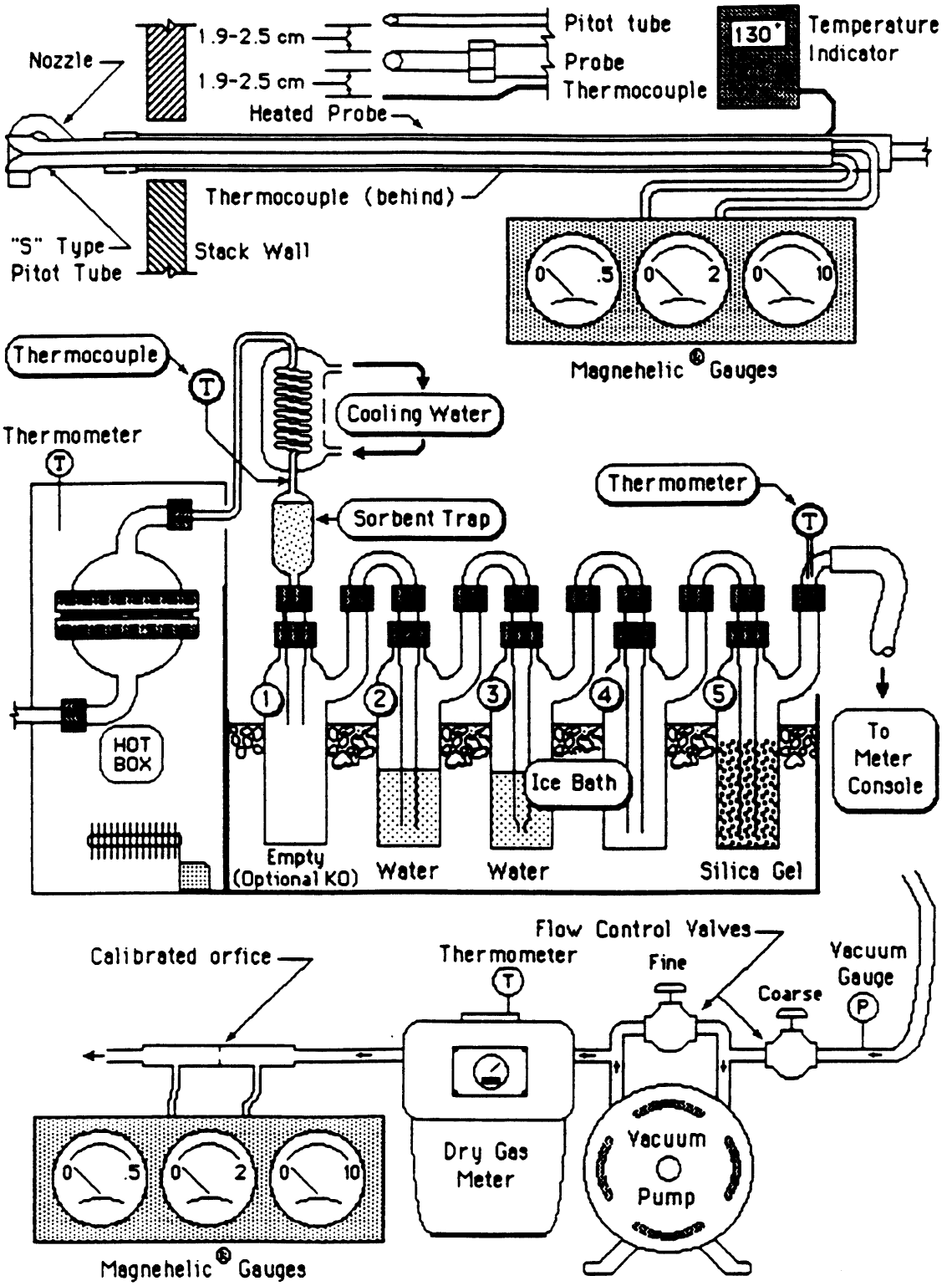
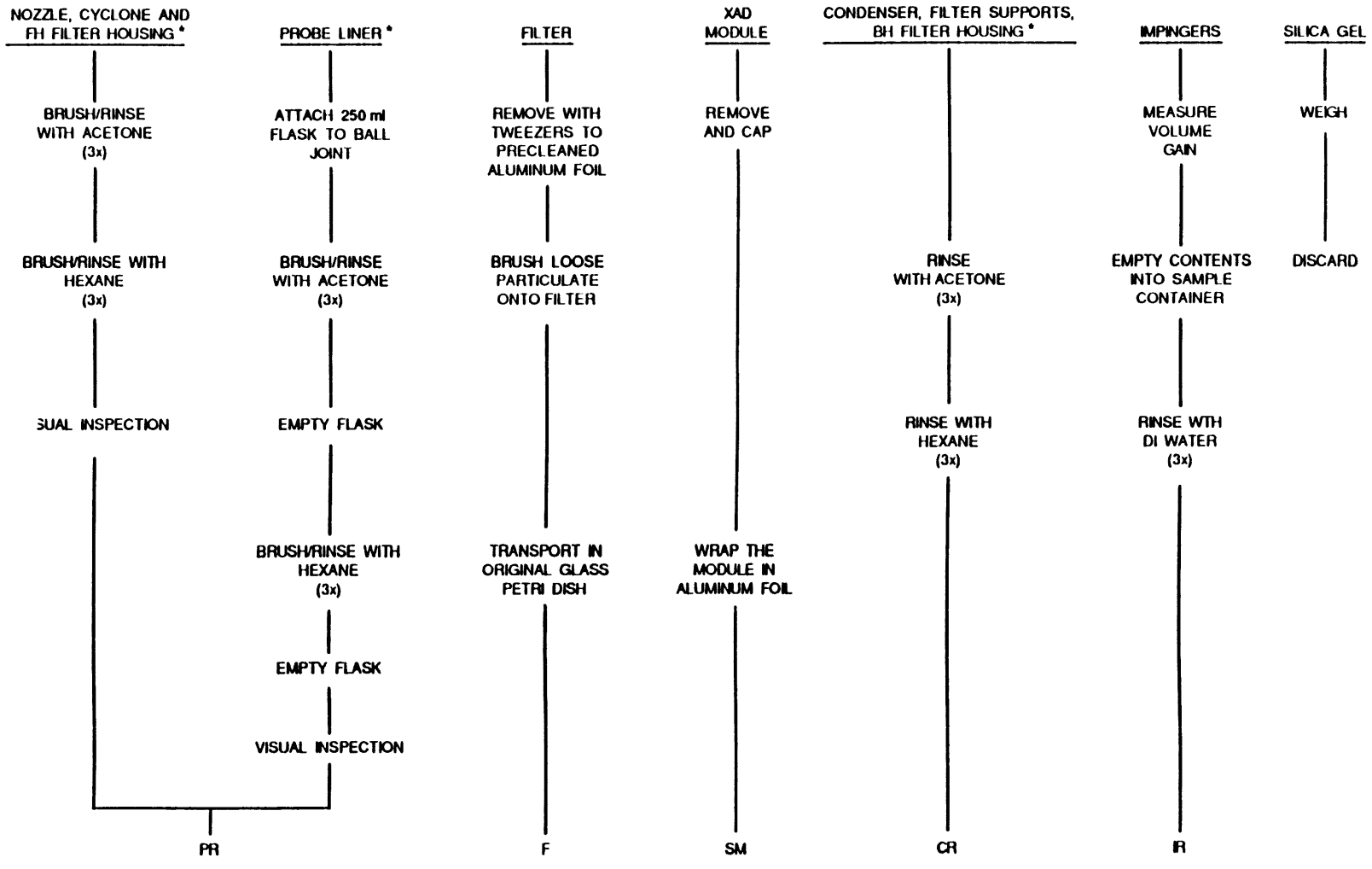


Figure 10. Schematic of the MM5 train for semivolatile organics and PCDD/PCDF.



* Final toluene rinse (3x).

Figure 11. Semivolatile organic train sample recovery scheme.

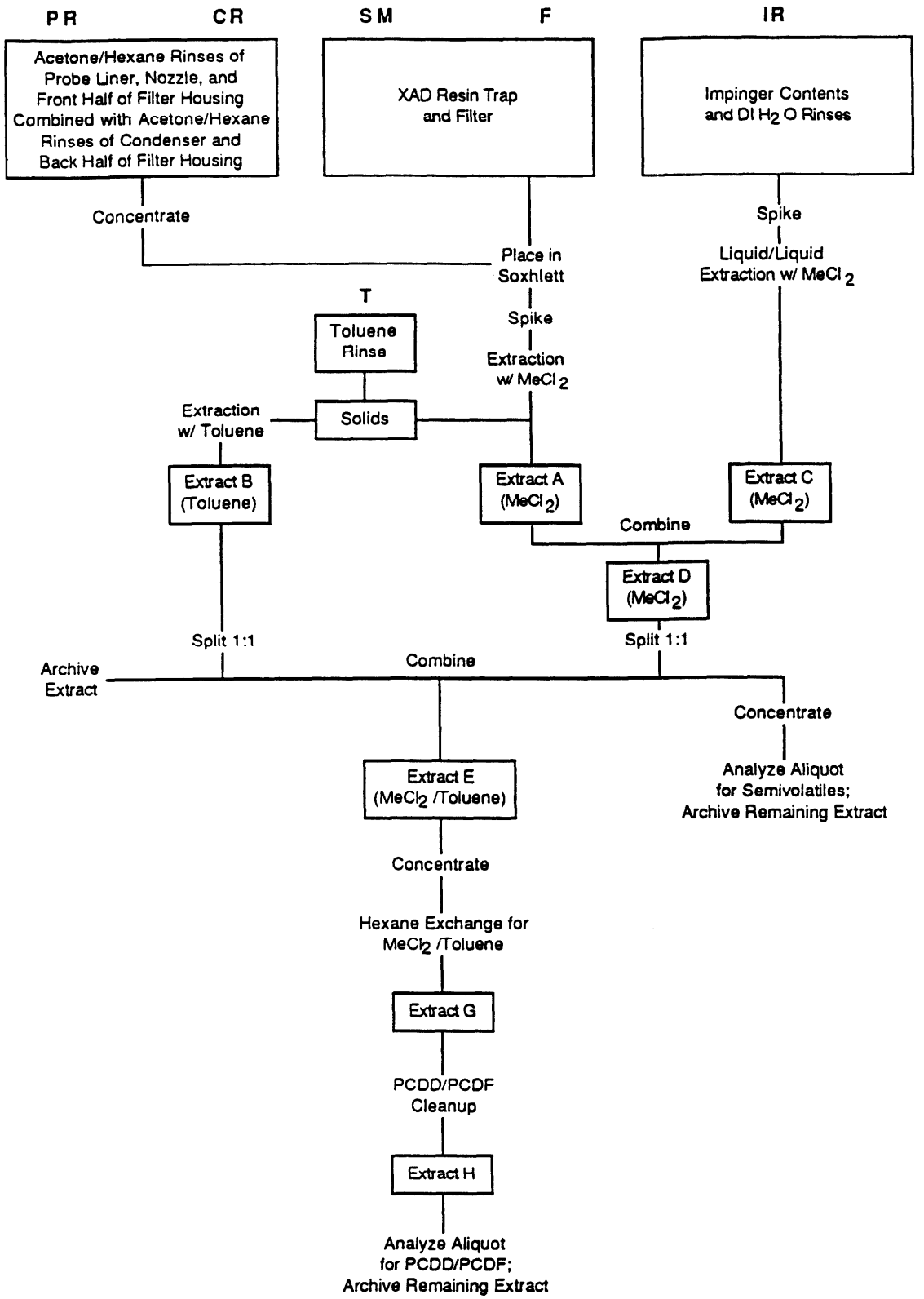


Figure 12. Extraction for semivolatile organic samples.

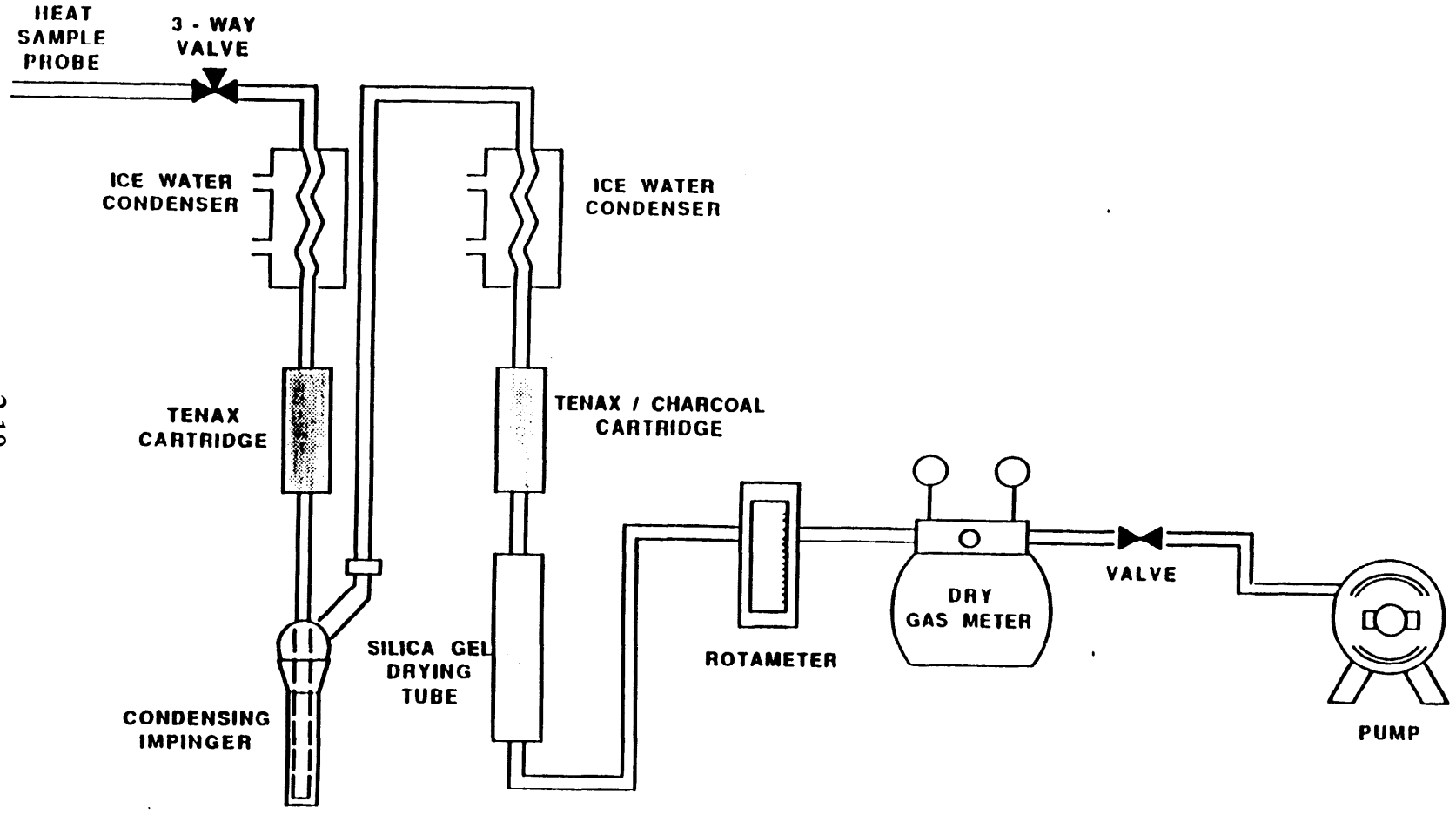


Figure 13. Schematic of volatile organic sampling train.

solution was analyzed by ICAP following the procedures described for the flue gas samples and archived for possible GFAAS analysis, however, GFAAS analyses were not required.

Portions of the scrubber water samples were analyzed for metals by acidifying with HNO_3 and then reducing to near dryness on a hot plate. Because the venturi scrubber discharge water samples had a high solids content, the solids were subjected to the microwave HNO_3/HF digestion described above. The digested solutions were analyzed by ICP for all the target metals except Hg following the procedures described for the flue gas samples. A portion of each solution was archived for possible graphite furnace atomic absorption spectroscopy (GFAAS) analysis, but the GFAAS analyses were not required.

After determination of the moisture content following ASTM D3174, incinerator bottom ash samples were analyzed for the target metals, including Hg, using the same procedures as described above for the sludge samples.

Incinerator and control system operating parameters were monitored during all manual test runs to characterize the system operations. The parameters typically monitored are presented in Table 3.

TABLE 3. TYPICAL PROCESS MONITORING DATA

Parameter	Frequency of Readings	Source of Readings
Incinerator Operating Data		
Wind Box Temperatures	60 minutes	Plant operating log
Bed Temperatures	60 minutes	Plant operating log
Freeboard Temperatures	60 minutes	Plant operating log
Heat Exchanger Inlet Temp	60 minutes	Plant operating log
Heat Exchanger Outlet Temp	60 minutes	Plant operating log
Incinerator Outlet O_2	Continuous	Entropy CEMSs
Auxiliary fuel usage	As used	Plant operating log
Sludge Feed Rate	60 Minutes	Plant operating log
Sludge Feed Characteristics		
Moisture (wt %)	Once per run	Entropy analysis
Volatiles (wt %)	Once per run	Entropy analysis
Heating Value	Once per run	Entropy analysis
Scrubber System Operating Data		
Differential Pressure (in. H_2O)	60 minutes	Plant operating log
Scrubber Inlet Temp (°F)	60 minutes	Plant operating log
Scrubber Outlet Temp (°F)	60 minutes	Plant operating log

3.0 RESULTS AND DISCUSSION

The primary objective of this study was to determine ratios of hexavalent-to-total chromium and nickel subsulfide-to-total nickel for a typical sewage sludge incinerator under normal combustion conditions (higher concentrations of carbon monoxide and total hydrocarbons) and improved combustion conditions (lower concentrations of carbon monoxide and total hydrocarbons). The two combustion conditions (normal and improved) were tested at Sites 6 and 9, which were multiple hearth furnaces. At Site 8, a fluidized bed furnace, only the normal combustion condition was investigated because furnace operating techniques are limited and these furnaces generally have good combustion.

3.1 Metals and Particulate

Metals and sludge feed rates to the incinerators are shown in Table 4 for both normal and low CO (improved combustion) conditions. Chromium, lead, and nickel consistently had the highest metals feed rate to the incinerators. At Site 6, chromium had the highest feed rate (48-58 g/hr) due to the contamination in the ferric chloride used to condition the sludge at this site. At Site 6, lead had the second highest feed rate (11 g/hr). At Site 8 and Site 9, lead had the highest feed rates (39 g/hr and 189-228 g/hr, respectively). Chromium had the second highest feed rate (30 g/hr) at Site 8, followed by nickel (19 g/hr). At Site 9, nickel had the second highest feed rate (120-152 g/hr), followed by chromium (76-85 g/hr).

In Table 5, particulate matter and metals emissions factors from the control device outlet are shown for normal and low CO conditions. The particulate matter emission factor represents the mass of particulate emitted per mass of dry sludge fed.

TABLE 4. FEED RATES FOR METALS IN THE SLUDGE (g/hr).

	Site 6 Normal	Site 6 Low CO	Site 8 Normal	Site 9 Normal	Site 9 Low CO
METALS					
Arsenic	ND	ND	ND	<100	<100
Beryllium	0.05	0.05	0.27	<0.8	<0.8
Cadmium	0.82	0.78	2.20	8.60	8.75
Chromium	57.9	48.0	30.0	75.7	85.3
Lead	11.4	11.6	39.0	189	228
Nickel	4.41	3.42	19.0	120	152
Total Sludge Feed Rate (lbs/hr)	3733	3460		7482	7460
Dry Solids Feed Rate (metric ton/hr)	971	934		1571	1641

TABLE 5. PARTICULATE AND METALS STACK EMISSION FACTORS FOR STEADY STATE (LOW CO) AND NORMAL OPERATION.

	EMISSION FACTORS (g metal emitted/g metal fed)				
Pollutant	SITE 6 NORMAL	SITE 6 LOW CO	SITE 8 NORMAL	SITE 9 NORMAL	SITE 9 LOW CO
PM (g/kg dry sludge feed)	0.37	0.45	Need sludge feed rate 4.59	0.36	0.04
Arsenic	ND	ND	ND	<0.011	<0.013
Beryllium	<0.069	0.059	<0.0001	ND	ND
Cadmium	0.917	0.908	0.0003	0.336	<0.008
Chromium	0.011	0.005	0.0001	0.036	0.001
Lead	0.123	0.136	<0.0001	0.101	0.006
Nickel	0.030	0.013	<0.0001	0.004	0.0004

ND - Not detected, all sample measurements were below the analytical detection limit.
< - Outlet samples were below analytical detection limit, calculated ratio is less than value shown.

The metals emission factors represent the mass of metals emitted per gram of metal fed to the incinerator in the sludge. For particulate matter, the emission factors were 0.37 g/kg and 0.45 g/kg for Site 6 at normal and low CO conditions, respectively, and 0.040 g/kg without the wet ESP and 0.0055 with the wet ESP for Site 8. For Site 9, the particulate emission factors for normal combustion without the wet ESP was 0.36 g/kg and for low CO combustion and with the wet ESP was 0.04 g/kg. Cadmium had the highest emission factor of all the metals for each of the sites, ranging from 0.003 g/g for Site 8 to 0.917 g/g for Site 6 with normal combustion. At Site 6, the lead emission factor increased from 0.123 to 0.136 with improved combustion (higher hearth temperatures). At Site 9, the addition of the wet ESP lowered the cadmium emission rate from 0.101 to 0.006 g/g even with improved combustion and higher hearth temperatures. Due to the high collection efficiency of the venturi scrubber/impingement tray scrubber, metal emission factors were considerably lower for the fluidized bed incinerator at Site 8 compared to the multiple hearth incinerators at Site 6 and at Site 9 without the wet ESP. With the wet ESP, the emission factors from Site 9 were comparable to both Site 8 and Site 3, a fluidized bed incinerator in this study and tested by Radian, respectively, the latter during the preliminary studies on sludge incineration. The lower emission factors seen for the fluidized bed incinerators may have been due to less volatilization and/or better removal in the venturi/scrubber system. The large amounts of inert material discharged from a fluidized bed incinerator to the pollution control device may provide condensation sites for the volatile metals allowing their removal with larger particles.

At Sites 6, 8, and 9, the metals were measured at the venturi/scrubber inlet and outlet and at the outlet of the wet ESP for Sites 8 and 9. The removal efficiencies were calculated and are summarized in Table 6 (Arsenic and beryllium were essentially not detectable at all three sites). For Sites 6 and 9 with multiple hearth furnaces and venturi/scrubbers, only chromium and nickel had removal efficiencies within 10 % of the particulate matter removal efficiency. At Site 6, cadmium and lead had removal efficiencies of about 71% at normal combustion conditions and about 77% at low CO conditions compared to about 98% particulate matter removal efficiency. For Site 9,

TABLE 6. METALS AND PARTICULATE REMOVAL EFFICIENCY ACROSS THE VARIOUS CONTROL DEVICES

Metal	Site 6 Normal Scrubber (%)	Site 6 Low CO Scrubber (%)	Site 8 Normal Scrubber (%)	Site 8 Normal Wet ESP (%)	Site 9 Normal Scrubber (%)	Site 9 Normal Wet ESP (%)	Site 9 Low CO Scrubber (%)	Site 9 Low CO Wet ESP
Arsenic	NA	NA	>99.5	NA	NA	NA	NA	NA
Beryllium	>85.5	>86.7	>99.95	NA	--	--	--	--
Cadmium	71.9	77.3	99.82	71.0	0.0	NA	45.0	>98.0
Chromium	99.3	99.4	99.92	62.0	0.0	NA	89.0	88.0
Lead	71.3	78.1	99.91	>96.0	5.0	NA	54.0	96.0
Nickel	93.4	94.5	99.89	81.0	89.0	NA	96.0	90.0
Particulate Matter	98.5	97.6	99.99	78.0	85.0	NA	95.0	87.0

NA - Not Applicable

cadmium and lead had even lower removal efficiencies of 45% and 54%, respectively at low CO conditions compared to 95% particulate matter removal efficiency. For Site 8 with a fluidized bed and venturi/scrubber, cadmium, chromium, lead, nickel, and particulate matter had similar removal efficiencies of >99%. The pilot-scale wet ESP at Site 8 removed an additional 62-96% of the metals and particulate matter emitted from the venturi/scrubber. At Site 9, the full-scale ESP removed an additional 87-98% of the metals and particulate matter emitted from the venturi/scrubber.

The ratios of individual metals to particulate matter are summarized in Table 7 for Sites 6, 8, and 9 for normal and low CO conditions. For Sites 6 (normal and low CO conditions) and 9 (normal conditions only), lead, at 28-32 mg/g and 12 mg/g , respectively, followed by cadmium, at 1.6-2.0 mg/g and 2.0 mg/g, respectively, had the highest metals to particulate matter ratios. In contrast the metals to particulate matter for chromium was 1.1 mg/g and for cadmium was 0.4 mg/g at Site 8. Generally the ratio of metals to particulate matter was lower for the fluidized bed incinerator at Site 8 than for the multiple hearth incinerators at Sites 6 and 9. At Site 6, the ratio of metal to particulate matter for cadmium, chromium, and nickel decreased and increased for lead from the normal

TABLE 7. RATIO OF METALS TO PARTICULATE MATTER EMISSIONS UNDER STEADY STATE (LOW CO) AND NORMAL OPERATION

Metal	SITE 6 Normal	SITE 6 Low CO	SITE 8 Normal	SITE 9 Normal	SITE 9 Low CO
	(μg metal/g particulate)				
Arsenic	<870	<622	ND	<1027	<6383
Beryllium	<3.78	<2.71	ND	--	--
Cadmium	2056	1645	417	1964	<553
Chromium	161	68	1094	1626	596
Lead	28173	31689	<179	12552	9191
Nickel	132	61	<1006	336	468

ND - Not detected, all sample measurements were below the analytical detection limit.

condition to the low CO condition. At Site 9, the wet ESP at the low CO condition had lower ratios for cadmium, chromium, and lead and a higher ratio for nickel compared to the normal condition without the wet ESP. The ratio of lead to particulate matter was lower at Site 8 compared to Site 6 even though the feed rate of lead at Site 8 was 15-20 times higher than Site 6 (see Table 4).

3.2 Hexavalent Chromium

A major accomplishment of this test program was the sampling of hexavalent chromium without artifact formation and the analyzing of the resulting samples specifically for hexavalent chromium at low concentrations. Sampling activities conducted at Site 5 were dedicated to developing a suitable measurement method for hexavalent chromium in emissions from incineration of municipal wastewater sludge. Hexavalent chromium sampling at the venturi/scrubber outlets at Site 6, 8, and 9 followed the same procedures of the draft EPA method. A new sampling technique was developed for this program where the impinger reagent is constantly recirculated to the inlet end of the sampling probe. A key element in sampling technique utilized for this program was the use of a hexavalent chromium radioactive isotope, $^{51}Cr^{+6}$, incorporated

into each sampling train. With the recirculating train design, the surrogate added to the impinger solution at the start of the test was exposed to the same conditions within the train as the native hexavalent chromium. The $^{51}Cr^{+6}$ surrogate measured the degree of conversion of hexavalent chromium to trivalent chromium occurring during the sampling and the handling of samples prior to analysis. The surrogate recoveries for Sites 6, 8, and 9 at both midpoint and wet ESP outlets and the ratio of hexavalent to total chromium measured with the recirculating train are shown in Table 8.

TABLE 8. HEXAVALENT CHROMIUM SAMPLING RESULTS

	SITE 6 Normal	SITE 6 Low CO	SITE 8 Normal	SITE 9 Normal	SITE 9 Low CO
Venturi/Scrubber Outlet					
Surrogate recovery,%	90.5	95.6	66.8	84.3	90.5
Hexavalent to total Cr ratio,%	1.9	4.4	<1.8	11.9	29.9
Wet ESP Outlet					
Surrogate recovery,%	NA	NA	81.5	90.1	93.1
Hexavalent to total Cr ratio,%	NA	NA	<1.4	29.9	42.5

NA = Not applicable, testing was not conducted.

Surrogate recoveries ranged from 67-96% during sampling at the venturi/scrubber outlet at Sites 6, 8, and 9. For the sampling at the wet ESP outlets at Site 8 and 9, surrogate recoveries ranged from 82-91%. The ratio of hexavalent chromium to total chromium measured by the recirculating train at the venturi/scrubber outlets ranged from < 1.8 - 11.9%, and at the wet ESP outlets, the ratio ranged from < 1.4 - 42.5%. (The hexavalent to total chromium ratios were not corrected for surrogate recovery).

At Site 6, the hexavalent to total chromium ratio increased from 1.9% to 8.3% between the normal combustion conditions and the low CO (improved combustion) conditions. An explanation for this observation, shown graphically in Figure 14, is that the higher hearth temperatures and excess oxygen levels recorded during the improved

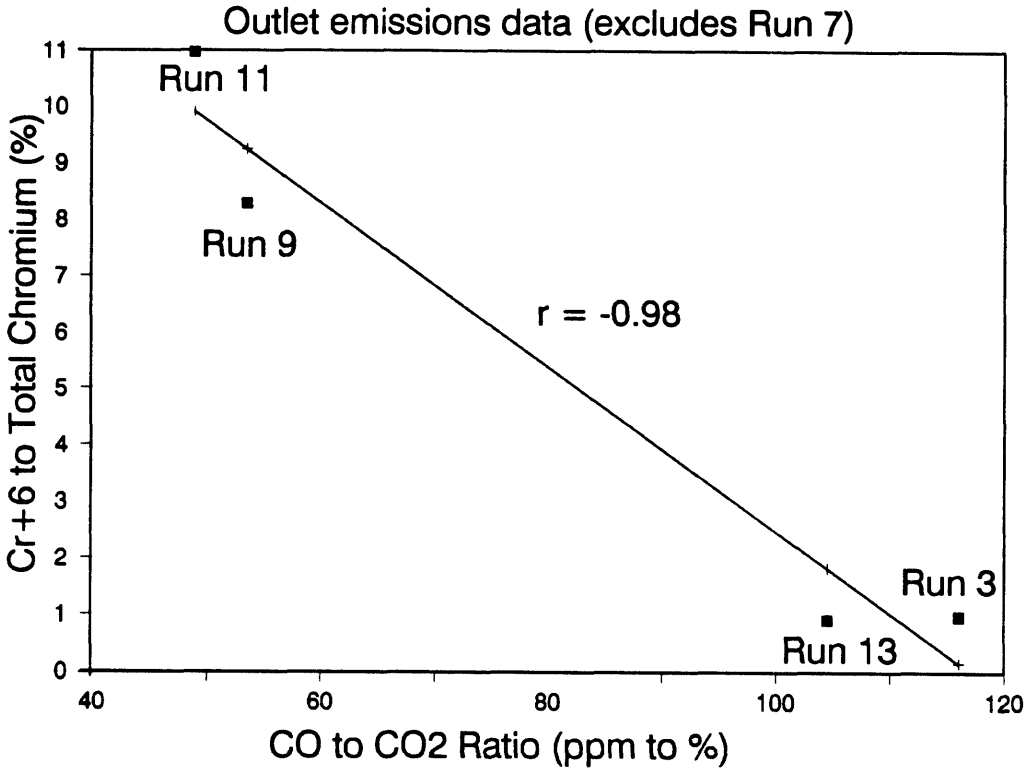


Figure 14. Correlation of combustion efficiency and hexavalent to total chromium ratio.

combustion condition favors the formation of hexavalent chromium. This effect was not seen at Site 9. The fluidized bed incinerator at Site 8 had the lowest ratio of hexavalent to total chromium in the venturi/scrubber emissions. A possible explanation for this low ratio at Site 8 is the lower residence time that occurs in the fluidized bed incinerator (seconds) compared to the higher residence time that occurs in multiple hearth incinerators (hours). (It should be noted that the multiple hearth design was originally used to roast ores such as chromium).

3.3 Nickel Speciation

The major objective of the nickel speciation testing was to determine the percent of the nickel emissions in the form of nickel subsulfide. It was anticipated that the nickel subsulfide emissions from multiple hearth incinerators would constitute less than 1% of the total nickel emissions, because these incinerators typically operate with high excess air which is not favorable for the formation of nickel subsulfide. The results of the sequential leaching nickel analysis indicate that within the detection limit of the wet chemical method, no nickel subsulfide was present in the samples. Based on the detection limits, the nickel subsulfide to total nickel ratio at Sites 6 and 8 is less than 12% for the inlet emissions and less than 10% for the outlet emissions. Samples analyzed from the same runs by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) indicated that no nickel subsulfide was detected within the instrumental detection limit of 10% of the total nickel. For Site 9 the ratio of nickel subsulfide to total nickel in the inlet emissions is less than 2 % and in the midpoint emissions is less than 1%. (The reduction in the analytical detection limit was due to the higher amounts of total nickel present in the emissions).

3.4 PCDD/PCDFs and Semivolatile and Volatile Compounds

Sampling for polychlorinated dibenzodioxins and furans (PCDD/PCDFs) was performed at the venturi/scrubber outlet at Sites 8 and 9 and at the wet ESP outlet at

Site 9. Sampling at Site 9 was conducted at both normal and low CO conditions. The results for the PCDD/PCDF sampling are shown in Table 9. Total tetra-octa chlorinated dibenzodioxins and furans (CDD + CDFs) were the highest (102 ng/dscm) at the venturi/scrubber outlet at Site 9 during normal conditions. Improved combustion at Site 9 lowered the total tetra-octa CDD + CDF emissions from 102 ng/dscm to 8.7 ng/dscm. The wet ESP at Site 9 reduced the total tetra-octa CDD + CDF emissions from 102 ng/dscm to 15.6 ng/dscm under normal conditions and from 8.7 ng/dscm to 2.8 ng/dscm under the low CO condition. Total tetra-octa CDD + CDF emissions at the venturi/scrubber outlet at Site 8 were 2.1 ng/dscm compared to 102 and 8.7 ng/dscm for Site 9 at normal and low CO conditions, respectively.

At Site 9, sampling for semivolatile organic compounds was performed at the venturi/scrubber outlet and the wet ESP outlet under both normal and low CO conditions. The results for the semivolatile organic compound sampling are shown in Table 10. Several compounds were found above the minimum detection limit at both the midpoint and outlet locations under runs both normal and low CO incinerator operations. The concentrations and number of the semivolatile compounds detected were typically less under the low CO combustion conditions. For the normal combustion conditions, eleven semivolatile compounds were detected for both runs: 1,4-dichlorobenzene, benzyl alcohol, 1,2-dichlorobenzene, 2-nitrophenol, benzoic acid, 1,2,4-trichlorobenzene, naphthalene, 2-methylnaphthalene, dibenzofuran, phenanthrene, and bis(2-ethylhexyl)phthalate. For the low CO combustion conditions five semivolatile compounds were detected for both sample runs: phenol, benzyl alcohol, 4-methylphenol, benzoic acid, and 4-nitrophenol. Bis(2-ethylhexyl)phthalate was found in the sample blank and the emission results are likely due to contamination.

The concentration of the volatile organics in the flue gas are presented in Table 11. At Site 8 five of the target compounds were below the analytical detection limit during all three test runs: acrylonitrile, vinyl chloride, 1,2-dichloroethane, and chlorobenzene. The other eight target compounds were detected in all three test runs and averaged: methylene chloride - 110 ug/dscm, chloroform - 17 ug/dscm, 1,1,1-trichloroethane - 6.8

TABLE 9. PCDD/PCDF EMISSIONS SUMMARY

Isomer	Concentration (ng/DSCM[1])				
	SITE 8 Normal Outlet	SITE 9 Normal Outlet	SITE 9 Normal Mid-Pt	SITE 9 Low CO Outlet	SITE 9 Low CO Mid-Pt
2378-TCDD	0.007	ND	ND	ND	ND
Other TCDD	0.120	1.14	7.02	0.15	0.14
12378-PeCDD	0.061	ND	ND	ND	ND
Other PeCDD	0.053	0.05	0.22	ND	ND
123478-HxCDD	0.002	ND	ND	ND	ND
123678-HxCDD	0.005	ND	ND	ND	ND
123789-HxCDD	0.006	0.03	ND	ND	ND
Other HxCDD	0.036	0.13	0.48	ND	0.04
1234678-HpCDD	0.048	0.29	1.73	ND	ND
Other HpCDD	0.023	0.25	1.50	0.05	ND
OCDD	0.359	1.35	9.24	0.48	1.45
Total Tetra-Octa CDD	0.721	3.2	20.2	0.7	1.6
2378-TCDF	0.019	1.39	7.76	0.28	1.12
Other TCDF	0.507	4.55	28.9	0.10	3.19
12378-PeCDF	0.037	0.25	1.69	0.03	0.01
23478-PeCDF	0.024	1.17	7.25	0.12	0.44
Other PeCDF	0.361	3.62	27.1	0.58	1.87
123478-HxCDF	0.044	0.26	1.79	0.02	ND
123678-HxCDF	0.022	0.09	0.38	ND	0.04
234678-HxCDF	0.018	0.19	1.14	ND	0.06
123789-HxCDF	0.001	ND	ND	ND	ND
Other HxCDF	0.134	0.51	3.12	0.04	0.17
1234678-HpCDF	0.071	0.11	ND	0.03	0.06
1234789-HpCDF	0.010	0.01	ND	ND	ND
Other HpCDF	0.054	0.08	0.60	0.01	0.02
OCDF	0.108	0.06	1.67	ND	ND
Total Tetra-Octa CDF	1.41	12.4	81.9	2.1	7.1
Total Tetra-Octa CDD+CDF	2.13	15.6	102	2.8	8.7

1 = 68 Deg. F -- 29.92 inches Hg
[b]ND = Reported as not detected or estimated maximum possible concentration; both expressed as zero (0) in calculating totals and averages.
Note: PCDD/PCDF emissions testing not conducted at Site 6.

TABLE 10. SEMIVOLATILE EMISSIONS SUMMARY FOR OUTLET AND MIDPOINT AT SITE 9

Analyte	Concentration (μg/DSCM[1])			
	OUT-7A	MID-7A	OUT-7C	MID-7C
Phenol	ND	ND	176	162
bis(2-Chloroethyl)ether	ND	ND	ND	ND
2-Chlorophenol	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND
1,4-Dichlorobenzene	30.8	33.4	ND	ND
Benzyl alcohol	800	1120	4100	3930
1,2-Dichlorobenzene	25.6	26.7	ND	ND
2-Methylphenol	ND	ND	ND	ND
bis(2-Chloroisopropyl)ether	ND	ND	ND	ND
4-Methylphenol	ND	ND	21.2	20.6
N-Nitroso-di-n-propylamine	ND	ND	ND	ND
Hexachloroethane	ND	ND	ND	ND
Nitrobenzene	ND	ND	ND	ND
Isophorone	ND	ND	ND	ND
2-Nitrophenol	196	284	43.1	76.4
2,4-Dimethylphenol	ND	ND	ND	ND
Benzoic acid	2850	3220	5090	4240
bis(2-Chloroethoxy)methane	ND	ND	ND	ND
2,4-Dichlorophenol	ND	ND	ND	ND
1,2,4-Trichlorobenzene	699	768	ND	ND
Naphthalene	976	864	ND	ND
4-Chloroaniline	ND	ND	ND	ND
Hexachlorobutadiene	ND	ND	ND	ND
4-Chloro-3-methylphenol	ND	ND	ND	ND
2-Methylnaphthalene	43.4	45.5	ND	ND
Hexachlorocyclopentadiene	ND	ND	ND	ND
2,4,6-Trichlorophenol	ND	ND	ND	ND
2,4,5-Trichlorophenol	ND	ND	ND	ND
2-Chloronaphthalene	ND	ND	ND	ND
2-Nitroaniline	ND	ND	ND	ND
Dimethylphthalate	ND	ND	ND	ND
Acenaphthylene	ND	ND	ND	ND
3-Nitroaniline	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	ND
2,4-Dinitrophenol	ND	ND	ND	ND
4-Nitrophenol	ND	ND	97.4	1440
Dibenzofuran	45.2	44.7	ND	ND
2,4-Dinitrotoluene	ND	ND	ND	ND
2,6-Dinitrotoluene	ND	ND	ND	ND
Diethylphthalate	ND	ND	ND	ND
4-Chlorophenyl-phenylether	ND	ND	ND	ND

1 = 68 Deg. f -- 29.92 inches Hg.
ND = Not detected or EV catches; used as zero (0).

TABLE 10. (Continued)

Analyte	Concentration (μg/DSCM[1])			
	OUT-7A	MID-7A	OUT-7C	MID-7C
Fluorene	ND	ND	ND	ND
4-Nitroaniline	ND	ND	ND	ND
4,6-Dinitro-2-methylphenol	ND	ND	ND	ND
N-Nitrosodiphenylamine(1)	ND	ND	ND	ND
4-Bromophenyl-phenylether	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND
Pentachlorophenol	ND	ND	ND	ND
Phenanthrene	44.9	33.4	13.7	ND
Anthracene	ND	ND	ND	ND
Di-n-butylphthalate	ND	ND	ND	ND
Fluoranthene	ND	13.3	ND	ND
Pyrene	ND	ND	ND	ND
Butylbenzylphthalate	ND	ND	ND	ND
3,3'-Dichlorobenzidine	ND	ND	ND	ND
Benzo(a)anthracene	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND
bis(2-Ethylhexyl)phthalate	29.2	26.1	ND	71.6[2]
Di-n-octylphthalate	ND	ND	ND	ND
Benzo(b)fluoranthene	ND	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	ND	ND	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND	ND

[1] 68 Deg. f -- 29.92 inches Hg.
[2] Results are likely due to sample contamination.
ND = Not detected or EV catches; used as zero (0).

TABLE 11. VOLATILE ORGANICS EMISSIONS SUMMARY

VOC	SITE 8 VENTURI/SCRUBBER OUTLET	SITE 9 WET ESP OUTLET
	Concentration, ug/dscm [a]	
Acrylonitrile	ND	1060
Vinyl Chloride	ND	66.2
Methylene Chloride (m/z = 86)	108	38.3
Chloroform	16.8	24.1
1,2-Dichloroethane	ND	ND
1,1,1-Trichloroethane	6.8	17.5
Carbon Tetrachloride	ND	ND
Trichloroethene	5.2	24.6
Benzene	6.2	6390
Tetrachloroethene	9.4	29.0
Toluene	7.7	4080
Chlorobenzene	ND	55.5
Ethylbenzene	2.6	100

[a] = 68 Deg. F -- 29.92 inches Hg
[b]ND = Reported as not detected or estimated values; both expressed as zero (0) in calculating totals and averages.

ug/dscm, trichloroethene - 5.2 ug/dscm, benzene - 6.2 ug/dscm, tetrachloroethene - 9.4 ug/dscm, toluene - 7.7 ug/dscm, and ethylbenzene - 2.6 ug/dscm.

At Site 9, two of the target compounds were below the minimum detection limit during all three test runs: 1,2-dichloroethane and carbon tetrachloride. Vinyl chloride was measured in only two of the tube pairs. The other ten target compounds were detected for all three test runs and averaged: acrylonitrile - 1060 ug/dscm, methylene chloride - 38.3 ug/dscm, chloroform - 24.1 ug/dscm, 1,1,1-trichloroethane - 17.5 ug/dscm, trichloroethene - 24.6 ug/dscm, benzene - 6390 ug/dscm, tetrachloroethene - 29.0 ug/dscm, toluene - 4080 ug/dscm, chlorobenzene 55.5 ug/dscm, and ethylbenzene - 100 ug/dscm.

3.5 Carbon Monoxide and Total Hydrocarbon Monitoring

At Sites 6 and Site 9, a positive correlation between carbon monoxide emissions and total hydrocarbon (THC) emissions was observed. This relationship is shown graphically for Site 6 and Site 9 in Figures 15 and 16, respectively. At Site 8, both the CO and THC emissions were significantly low and a correlation could not be seen.

At Sites 6 and 9, the concentrations of THC and CO were reduced by about 75% during the improved combustion conditions.

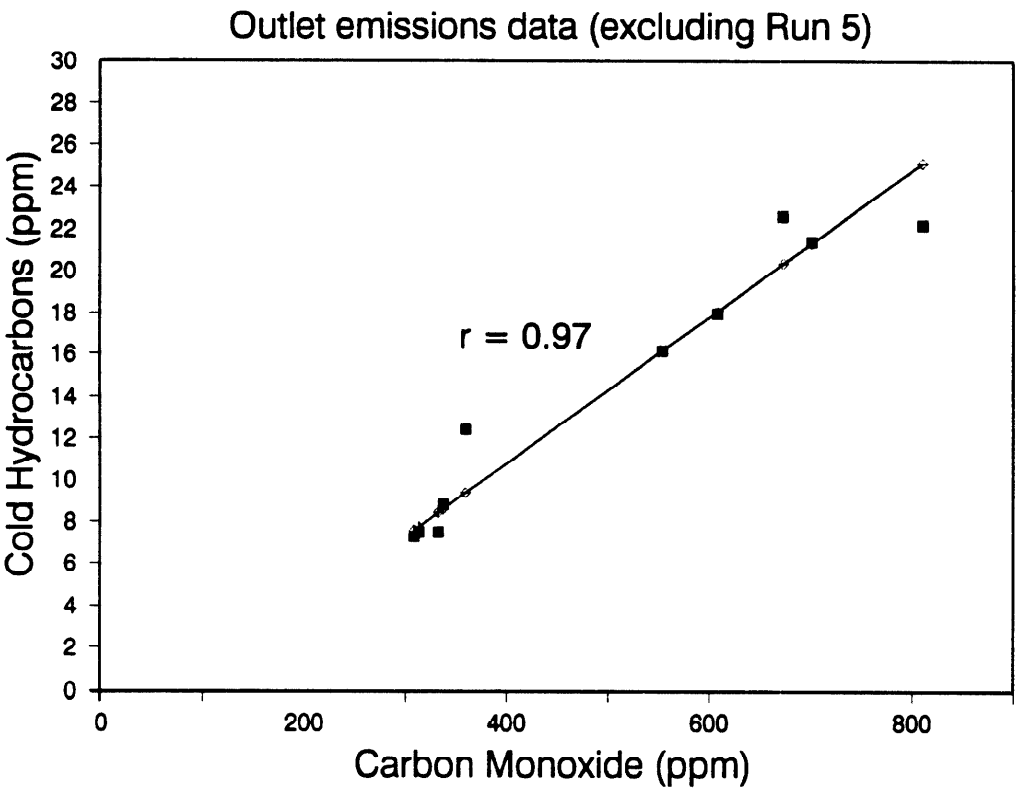


Figure 15. Total hydrocarbon emissions versus carbon monoxide emissions, Site 6.

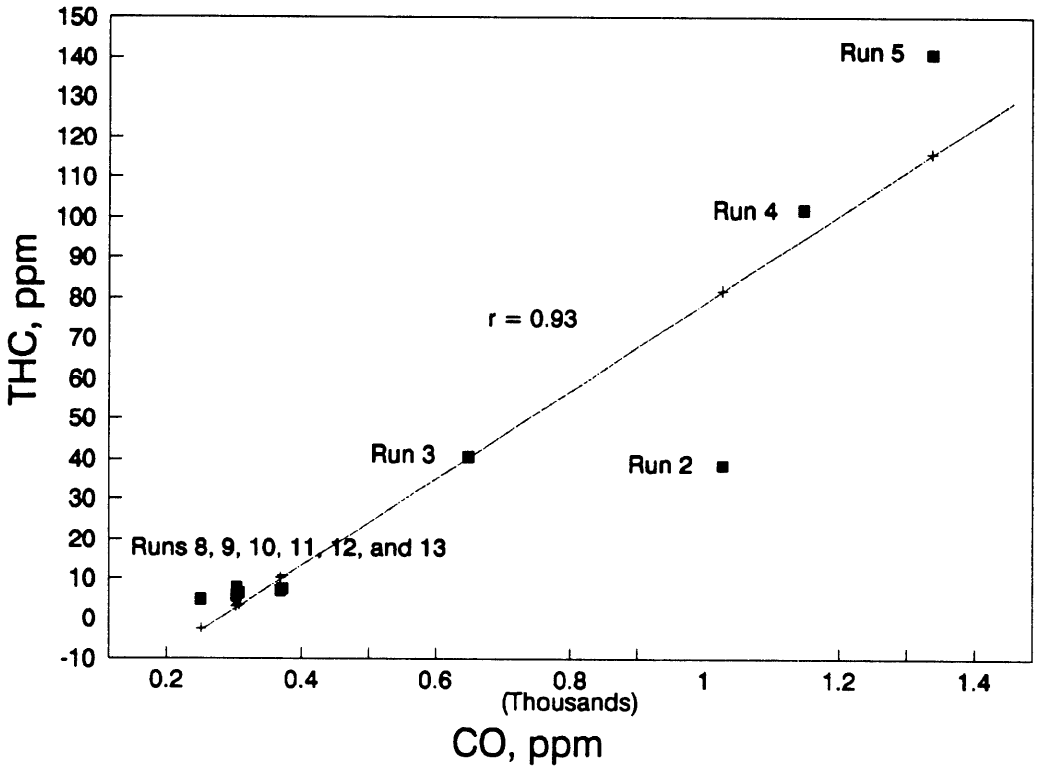


Figure 16. Total hydrocarbon emissions versus carbon monoxide emissions, Site 9.

4.0 CONCLUSIONS

4.1 Metals and Particulates

The total metals and particulate results from Sites 6, 8, and 9 added significantly to the OW data base especially with respect to the use of the addition of a Wet ESP as a retrofit to existing systems or as part of the overall control system at a new facility. Of the metals measured, chromium, lead, and nickel consistently had the highest feed rate to the incinerators. Cadmium and lead had the highest emission factors of the metals fed to the incinerators. The emission control devices at the multiple hearth incinerators had similar removal efficiencies for particulate matter, chromium, and nickel, with lead and cadmium removal efficiencies being less than particulate matter. At the fluidized bed incinerator, the venturi/scrubber had the highest removal efficiency without discriminating between metals and particulate matter. The wet ESPs were effective in further removal of the metals and particulate matter emitted form the venturi/scrubbers.

4.2 Hexavalent Chromium

At the beginning of this study, EPA did not have a published test method that gave acceptable results at combustion sources. Through the efforts in this study along with concurrent work with EPA's Quality Assurance Division, Atmospheric Research and Exposure Assessment Lab, the hexavalent chromium test method developed for this program provided acceptable results for the measurement of hexavalent chromium without artifact formation at the outlet locations. At Site 6, the ratio of hexavalent chromium to total chromium was high when lime was used for sludge conditioning, during good combustion conditions, and with the long residence times required for combustion of sludge in a multiple hearth incinerator. At Site 8, the ratio of hexavalent

chromium to total chromium in the emissions was very low from a fluidized bed incinerator (despite relatively high total chromium levels), probably due to the short sludge retention time in the incinerator and the absence of alkaline material in the sludge. At Site 9, the ratio of hexavalent chromium to total chromium was significantly higher than had been anticipated. The facility was selected because it does not use lime for sludge conditioning. The high hexavalent chromium to total chromium ratio was discussed with facility representatives and it was determined that some of the sludge that is transported to the facility contains lime. Also some lime is used at the facility. The archived sludge digested samples were analyzed for calcium. The sludge solids were determined to contain 2 to 3% lime by weight. This percentage of lime may be the reason for the higher than anticipated ratio of hexavalent chromium to total chromium.

4.3 Nickel Subsulfide

Prior to the program EPA did not have a published method for nickel speciation. Based on new instrumental techniques developed by Brigham Young University and the continued wet chemical techniques developed by Dr. Vladimar Zatka, it was demonstrated that nickel subsulfide is not emitted from sewage sludge incinerators above the level of detection for both analytical techniques. At Site 6, the ratio of nickel subsulfide to total nickel was extremely low under both normal combustion and improved combustion conditions. At Site 8, the ratio of nickel subsulfide to total nickel in the emissions was extremely low, with the nickel sulfide/subsulfide species measured at the inlet and midpoint being less than the detection limit. The ratio of sulfidic nickel to total nickel in the emissions from Site 9 is extremely low at Site 9, with the reduced nickel species being measured at less than detection limit (about 1 to 2% of the total nickel).

4.4 Continuous Emission Monitoring of CO and THC

The combustion efficiency at both multiple hearth incinerators was improved during the test programs. The improved combustion furnace operating conditions established for the second series of test runs at Site 6 and Site 9 reduced the concentrations of CO and THC emissions by about 75%. A good correlation between CO emissions and the THC emissions was seen at the sources that a wide range of CO and THC was measured.

4.5 Semivolatile Organics

Compared to Site 3, a fluidized bed incinerator where the only semi-volatile organic compound detected was bis(2-ethylhexyl)phthalate, several additional semivolatiles were found in the emissions at Site 8. These were 1,2-dichlorobenzene, 1,4-dichlorobenzene, benzyl alcohol, benzoic acid, and naphthalene.

Only two semivolatile organic compounds, benzyl alcohol and benzoic acid, were found under normal and improved combustion conditions at Site 9. This number was less than at Site 2, a multiple hearth incinerator where seven semi-volatile compounds, phenol, naphthalene, bis(2-ethylhexyl)phthalate, 1,2,-dichlorobenzene, 1,3,-dichlorobenzene, 1,4,-dichlorobenzene, and 2-nitrophenol were detected. Several additional compounds were found in the Site 9 emissions for the normal or improved combustion conditions; these compounds were 1,4-dichlorobenzene, 1,2-dichlorobenzene, 2-nitrophenol, 1,2,4-Trichlorobenzene, naphthalene, 2-methylnaphthalene, dibenzofuran, phenanthrene, bis(2-ethylhexyl)phthalate, phenol, 4-methylphenol, and 4-nitrophenol.

4.6 Volatile Organics

The volatile organic compound emission results for Site 8 were consistent with the results for Site 3 (another fluidized-bed incinerator). Carbon tetrachloride and

chlorobenzene, reported in the emissions at Site 3, were not found in the emissions from Site 8.

The volatile organic compounds detected in the Site 9 multiple hearth incinerator emissions were similar to the compounds reported for Sites 1, 2, and 4 (other multiple hearth incinerator tested). Carbon tetrachloride, reported in the emissions at the other three sites, was not found in the emissions from Site 9.

4.7 Overall Conclusions from the Study

The primary purpose of the test program at Site 6 was to determine the effect of lime conditioning and excess combustion air on the formation of hexavalent chromium emissions. The Entropy sampling and analytical method for hexavalent chromium worked extremely well in demonstrating the relationship of combustion conditions to the formation of hexavalent chromium during lime conditioning. A correlation was demonstrated between CO and THC emissions which was of interest to OW. The nickel subsulfide emissions were demonstrated to be extremely low. It was also demonstrated that the CO and THC concentrations could be reduced by about 75% with better combustion conditions. This reduction of the CO and THC concentrations was not an intent of the program but was a benefit to the OW data base.

An evaluation of CO and THC monitors was conducted at Site 7. The data showed that "cold" and "hot" THC monitors give the same results. The application of the monitors at Site 7 allowed the operators to adjust their incinerator conditions and significantly reduce the CO and THC concentrations. The trends between CO and THC concentration were very comparable.

The test program at Site 8 was designed to assess hexavalent chromium and nickel subsulfide emission from a fluidized bed incinerator. During the planning stages, it was decided that a pilot-scale wet ESP would be added to the control system at the site and sampling would be conducted at the inlet, midpoint, and outlet of the control system. Also sampling and analysis for dioxins/furans, semivolative organics, and volatile organics were added to the program. Levels of hexavalent chromium, nickel subsulfide,

CO, and THC were shown to be extremely low. The pilot-scale wet ESP demonstrated significant collection efficiency at extremely low concentrations of particulate and metals emissions. The organic emissions were found to be extremely low and were principally the same compounds previously measured for sewage sludge incinerators.

Entropy conducted the final test program at Site 9 which included a full-scale wet ESP. The pollutants measured at Site 9 parallelled those at Site 8. The Entropy recirculating train method for sampling and analysis of hexavalent chromium yielded consistent data and documented a higher level of chromium than had been anticipated. It was demonstrated that less than 0.5% of the nickel emissions were nickel subsulfide at the scrubber discharge. The correlation between CO and THC concentrations was demonstrated once again as well the reduction in these emissions by about 75% by using good combustion conditions. It was demonstrated that the full-scale wet ESP could reduce concentrations of particulates and metals by about 90%. Dioxins/furan were reduced by about 75% by using good combustion conditions and the wet ESP collected an additional 75% of the dioxins/furan emissions.

The accomplishments of the study were far greater than could have been anticipated at the outset of the program. Specifically, the following has been accomplished.

1. Documented hexavalent chromium emissions from sewage sludge incinerators.
2. Documented nickel subsulfide emissions from sewage sludge incinerators.
3. Developed a hexavalent chromium sampling and analytical method.
4. Developed a nickel speciation sampling and analytical method.
5. Provided additional metals data.
6. Provided additional trace organics data.
7. Documented a correlation between CO and THC.
8. Documented that CO and THC concentrations can be reduced when the plant has a CO and/or THC monitor to improve combustion conditions.
9. Demonstrated that the use of a wet ESP is a viable retrofit option for significantly reducing particulate and metals emissions.

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16. ABSTRACT

At Site 5 (continuing a numbering system initiated in a previous 4-site project) tests were only conducted for methods development purposes. At Site 6, emissions were measured at the inlet and outlet of the control device. At Site 7, an evaluation of CO and THC CEMSs was performed. At Sites 8 and 9, emissions were measured at the inlet of the venturi scrubber, at the midpoint located between the venturi scrubber and the wet ESP, and at the outlet of the wet ESP. For Sites 6, 8, and 9, midpoint and outlet air emission samples were collected and analyzed for particulate matter, metals, PCDD/PCDFs, volatile and semivolatile compounds (except Site 6), and hexavalent chromium and nickel subsulfide species. Continuous emission monitoring (CEM) for O_2, CO_2, CO, SO_2, and NO_x at the control system inlet and O_2 (except Site 6), CO_2 (except Sites 6 and 9), CO, SO_2 (except Sites 6 and 9), NO_x (except Sites 6 and 9), and THC was conducted at the control system outlet stack.

The metals found in the greatest concentration in the sludge were lead, chromium and nickel. The need for sampling of hexavalent chromium without artifact formation and analysis of the resulting samples specifically for hexavalent chromium at low concentrations was a major accomplishment of this test program. The results of the nickel sampling and analysis indicate that within the detection limit of the wet chemical method, no nickel subsulfide was present in the air emissions.

At Site 6 and Site 9, a positive correlation between carbon monoxide emissions and total hydrocarbon (THC) emissions was observed. At Site 7, a positive correlation was demonstrated between the "Hot" and "Cold" THC CEMs.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Wastewater, sludge disposal, incinerators, combustion products	Emissions chromium compounds nickel compounds total hydrocarbons dioxin/furans organic compounds	

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