

4.3.3 Flue Gas Moisture Content. The moisture content was determined in conjunction with the appropriate pollutant emissions methods discussed in the following sections.

4.4 Emissions Determinations. Table 4-1 outlines the sampling parameters used for the test program.

TABLE 4-1
SAMPLING PARAMETERS

<u>Sampling Method</u>	-- Number Of -- <u>Axes</u>	<u>Points</u>	<u>Total</u> <u>Points</u>	<u>Minutes</u> <u>Per Point</u>	<u>Total</u> <u>Minutes</u>
<u>Main and Bypass Stacks</u>					
EPA 3A, 6C, 7E, 10, 25A	1	1	1	NA	180
EPA 5/0050	4	6	24	5	120
EPA MMTL	4	6	24	5	120
EPA M23	4	6	24	3.75	180
VOST	1	1	1	NA	160
EPA 8	4	6	24	2.5	60
Cr+6	4	6	24	5	120
<u>Clinker Stack</u>					
EPA 5	2	12	24	5	120
EPA MMTL	2	12	24	5	120

4.4.1 Carbon Monoxide, Nitrogen Oxides, Sulfur Dioxide, and Total Hydrocarbons. Continuous emissions monitoring (CEM) was conducted for carbon dioxide (CO₂) and oxygen (O₂) concentrations and sulfur dioxide (SO₂), nitrogen oxides (NO_x), carbon monoxide (CO), and total gaseous organic (TGO) emissions. The sampling and analytical procedures for CO₂/O₂, SO₂, NO_x, CO, and TGO were in accordance with EPA Methods 3A, 6C, 7E, 10, and 25A, respectively.

Valid
The extractive monitors require that the effluent gas sample be conditioned to eliminate any possible interference (i.e., water vapor and/or particulate matter) before being transported and injected into each analyzer. All components of the sampling system which contacted the sample were constructed of Type 316 stainless steel or Teflon. The outputs from the monitors were connected to a computerized data acquisition system (DAS). The DAS uses a portable computer with a 20MB hard disk and an internal 12-bit analog-to-digital converter with a 16 channel multiplexer. In addition to providing an instantaneous display of analyzer responses, the DAS compiles the analyzer data collected once each second and averages them, calculates emission rates, and documents analyzer calibrations. The DAS integrates the real-time measurements and provides printouts of 1-minute, 15-minute, and 60-minute averaged emissions.

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The CO₂/O₂, SO₂, NO_x, and CO sample collection system consisted of a heated probe with an in-stack glass wool particulate filter, heated sample lines, a moisture removal trap, an out-of-stack secondary particulate filter, and a pump. The TGO sample collection system was the same except no moisture removal trap or secondary particulate filter were used. All samples were routed through a distribution manifold board for delivery to the analyzers. The configuration of the sampling system allows for the injection of calibration gases directly to the analyzers or through the sampling system. A Thomas Model 2107CA 18-TFE pump was used to move the effluent sample through the system. All pretest and posttest calibration procedures were performed as outlined in the specific EPA methods. The operation of each analyzer and the DAS are described below.

ACS Fuji 3300 CO₂ Analyzer. This nondispersive infrared analyzer automatically and continuously monitors the CO₂ concentration. The theory of operation is based on the principle that CO₂ has a unique absorption line spectrum in the infrared region. The instrument consists of an infrared light source, a chopper, a measuring cell, and a two-chamber, sealed detector.

The infrared light beam emitted by the source passes through the measuring cell which is filled with a continuously flowing gas sample. Before reaching the front chamber of the detector, the light beam is partially absorbed or attenuated by the gas species of interest in the cell. Both the front and rear chambers of the detector are filled with a reference gas. The difference in the amount of light absorbed between the front and rear chambers is dependent on the concentration of the gas species of interest within the measuring cell and creates a pressure differential between the two chambers. The pressure differential is then observed as gas flow by the micro-flow sensor located in the channel communicating the two chambers. The resulting AC signal from the sensor is rectified, amplified, and linearized into DC voltage signal for output.

TECO Model 48/GFC CO Analyzer. The analyzer utilizes the gas filter correlation (GFC) technique to determine CO concentrations. The GFC technique involves the use of a high CO concentration filter which, when inserted into the infrared light beam, produces a reference beam, i.e., no further infrared radiation can be attenuated by the CO in the effluent sample. The CO filter is located on a modulated copper wheel which allows the use of a single infrared source and detector. A multiple pass optical bench/sample chamber of the white cell design provides improved sensitivity with a smaller chamber length.

TECO Model 10 NO/NO_x Analyzer. This analyzer automatically and continuously determines the concentration of the nitric oxide (NO) or nitrogen oxides (NO_x) in

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the effluent. The analytical technique is chemiluminescence. The sample is routed through a converter where the NO₂ is dissociated to form NO. The sample is then passed through a reaction chamber where the NO is quantitatively converted to NO₂ by gas phase oxidation with molecular ozone produced within the analyzer. In this reaction, the NO₂ molecules are elevated to an electronically excited state and immediately reverted to a nonexcited ground state. This reversion is accompanied by the emission of photons, which impinge on a photomultiplier detector and generate a low level DC current. The current is -- then amplified and used to drive a front panel meter and a data recorder. The NO_x concentration seen by the instrument includes the contributions of both the NO in the sample and the NO resulting from the dissociation of the NO₂ in the sample.

Maihak UNOR SO₂ Analyzer. This nondispersive infrared analyzer automatically and continuously monitors the SO₂ concentrations. The theory of operation is based on the principle that SO₂ has a unique absorption line spectrum in the infrared region. The instrument consists of an infrared light source, a chopper, a reference and measurement cell, two absorption chambers, and a two-chamber, sealed detector. The infrared light beam passes alternately through the reference cell and the measurement cell, which is filled with a continuously flowing gas sample. In the measurement cell, the light beam is partially absorbed or attenuated by the gas species of interest before reaching the front chamber of the detector. Both the front and rear chambers of the detector are filled with a reference gas. The greater depth of the rear chamber allows absorption of the weaker edges of the spectra, which increases the instrument's sensitivity. The difference in the amount of light absorbed between the front and rear chamber⁵ is dependent on the concentration of the gas species of interest within the measurement cell; a pressure differential is thus created between the two chambers. This pressure differential is detected by a differential-type diaphragm capacitor located in a channel connecting the two chambers. The variations in capacitance are amplified and converted into a concentration-proportional DC voltage signal for output.

Ratfisch Model RS-55 TGO Analyzer. This analyzer automatically and continuously monitors the TGO concentrations in a flowing gas mixture. The theory of operation is based on the principle of flame ionization detection. In the flame ionization detector, hydrogen is mixed with the sample gas and is burned in a small jet. The ionization current in the hydrogen flame is measured. In a pure hydrogen flame, very few ions are produced, but if an organic component or hydrocarbon is burned in the flame, the ion current is greatly increased. The

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current provide5 a quantitative measure of the amount of hydrocarbons in the flame. The current is converted to a voltage output. The hydrogen flame ionization detector is extremely sensitive and is capable of detecting hydrocarbon level8 in the low part8 per million range and is insensitive to inorganic gases such a8 nitrogen, carbon dioxide, and water vapor.

Teledvne Model 320P-4 O2 Analyzer. This analyzer was designed specifically to measure O2 in flue gas streams. It utilizes a patented micro-fuel cell that consumes O2 from the atmosphere surrounding the measuring probe. The consumption of O2 generate5 a proportional electric current, which is amplified and used to drive a built-in front panel meter with a **scale** of 0 to 25%. The analyzer incorporates its own integral pump and power system.

Data Acquisition System. The DAS **uses** a Compaq portable computer with a 20MB hard disk and an internal 12-bit analog-to-digital converter with a 16 channel multiplexer. In addition to providing an instantaneous display of analyzer responsee, the DAS compile8 the analyzer data collected once each second and average8 them, calculate8 emission rates, and document8 analyzer calibrations. The DAS integrates the real-time measurement8 and provides printout5 of 1-minute, 15-minute, and 60-minute averaged emissions.

4.4.2 Hexavalent Chromium. Samples were withdrawn **isokinetically** from the source using the sampling train outlined in the EPA draft hexavalent chromium (Cr⁺⁶) method.

Sample Collection. The sampling train consisted of a quartz nozzle, a pump/sprayer assembly for continuously recirculating the reagent to the nozzle, a Teflon probe with a Type S Pitot tube attached, five chilled impinger8 (four Teflon and one glass), and a metering console.

The first impinger contained 150 mL 0.1N potassium hydroxide (KOH), the second and third impinger8 each contained 75 mL of 0.1N KOH, the fourth impinger remained empty, and the fifth impinger contained 200 gram8 of silica gel.

A **posttest** nitrogen purge was **used** a8 a safeguard against conversion of hexavalent chromium to trivalent.

Sample Recovery. Following the nitrogen purge, the **KOH** reagent **was** returned to the original container, weighed, the weight recorded on the label, and the liquid level marked. The **silica** gel was returned to the original container, weighed, and the weight recorded on the label. The volume of water vapor condensed in the **impingers** and the volume of water vapor collected in the silica gel were summed and entered into moisture content calculations. All sample exposed portion8 of the **sample** train were first rinsed four times with DI water

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into the jar containing the KOH reagent followed by rinsing three times with 0.1N HNO₃ into a separate jar. The combined KOH reagent and DI water rinse were then pressure filtrated into a graduated cylinder to remove insoluble matter which could cause hexavalent conversion.

Sample Analveie. The combined KOH reagent/DI water rinse were analyzed for Cr⁺⁶ using ion chromatography coupled with a poet column reactor (IC/PCR).

4.4.3 **Metals.** Samplee were withdrawn ieokinetically from the source using an EPA Draft Multi-Metal sampling train.

Sample Collection. The sampling train coneieted of a glaee nozzle, a heated glass probe with a Type S Pitot tube attached, a filter, six chilled impingers, and a metering console. The particulate sample was collected on a Pallflex 2500QAT-UP quartz filter maintained at a temperature of 248° F ± 25° F. The first and second impingers each contained 100 mL of 5% nitric acid (HNO₃)/10% hydrogen peroxide (H₂O₂), the third remained empty, the fourth and fifth impingere each contained 100 mL of 4% potaeeium permanganate (KMnO₄)/10% sulfuric acid (H₂SO₄), and the eixth contained preweighed silica gel. Each run was a minimum of two hour in duration with a minimum sample volume of 60 dry atandard cubic feet.

Sample Recovery. A Teflon apatula and Teflon coated tweezers were used to remove the filter from the filter holder and place it in a 250 mL glass jar. The reagents were returned to the original bottlee, weighed, the weights recorded on the labels, and the liquid levels marked. The silica gel wae returned to the original container, weighed, and the weight recorded on the label. The volume of water vapor condensed in the impingers and the volume of water vapor collected in the silica gel were summed and entered into moieture content calculations.

The nozzle, probe, and fronthalf of the filter holder were rinsed with 100 mL of 0.1N HNO₃ into a 500 mL glass jar. A Teflon probe brush was used for cleaning the probe.

The backhalf of the filter holder and the first and second impingers were rinsed with 100 mL of 0.1N HNO₃ into the bottle containing the HNO₃/H₂O₂ reagent. The third impinger was rinsed with 100 mL of 0.1N HNO₃ into a 500 mL glass jar. The fourth and fifth impingers were rinsed with 100 mL of acidified KMnO₄ followed by a rinse with 100 mL of DI water into the 500 mL bottle containing the KMnO₄/H₂SO₄ reagent. To remove residual brown deposits, the fourth and fifth impingers were rinsed with 25 mL of 8N HCl into a 500 mL glass jar containing 200 mL of water.

Sample Analyses. The fronthalf HNO₃ rinse was evaporated to near dryness in a Teflon beaker. The filter, loose particulate, 3 mL of concentrated HNO₃, and 5

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mL of concentrated HF were added to the beaker. The sample was digested on a hotplate until brown fumes were evident, indicating the destruction of organic matter. After the addition of concentrated HNO_3 , the reagent and impinger rinses were evaporated to near dryness in a Teflon beaker on a hotplate. After cooling, 3 mL of concentrated HNO_3 and 5 mL of concentrated HF were added to the beaker and the sample was fumed on a hotplate to destroy organic residue. The prepared filter and $\text{HNO}_3/\text{H}_2\text{O}_2$ reagent samples were combined, brought to a final volume of 100 mL with 10% HNO_3 , and analyzed for all metals with a Perkin Elmer 3030 atomic absorption analyzer using the appropriate SW-846 methods. Cold vapor atomic absorption (CVAA) techniques were used to analyze the samples for mercury. The third impinger rinse, $\text{KMnO}_4/\text{H}_2\text{SO}_4$ reagent/rinse, and the HCl rinse were also analyzed for mercury by CVAA. Duplicate analyses were performed for approximately 10% of the emissions samples for all metals except mercury. For mercury, all samples were analyzed in duplicate.

4.4.4 Particulate and Hydrogen Chloride

4.4.4.1 Main and Bypass Stacks. Samples were withdrawn isokinetically from the source using a SW-846 Method 0050 sampling train.

Sample Collection. The sampling train consisted of a glass nozzle, a heated glass probe with a Type S Pitot tube attached, a filter, five chilled impingers, and a metering console. The particulate sample was collected on a Pallflex TX40HI75 Teflon filter maintained at a temperature of $248^\circ\text{F} \pm 25^\circ\text{F}$. The first two impingers each contained 100 mL of 0.1 N sulfuric acid (H_2SO_4), the third remained empty, the fourth contained 100 mL of 0.1 N sodium hydroxide (NaOH), and the fifth contained preweighed silica gel.

Sample Recovery. The filter was removed from the filter holder and placed in a 250 mL glass jar. The H_2SO_4 and NaOH reagents were returned to the original 1000 mL and 500 mL glass jars, weighed, the weight recorded on the labels, and the liquid levels marked. The silica gel was returned to the original tared container, weighed, and the weight recorded on the label. The volume of water vapor condensed in the impingers and the volume of water vapor collected in the silica gel were summed and entered into moisture content calculations.

The nozzle, probe, and fronthalf of the filter holder were rinsed with acetone into a 500 mL glass jar. The backhalf of the filter holder and the first, second, and third impingers along with the connecting glassware were rinsed with DI water into a 500 mL glass jar. The fourth impinger was rinsed with DI water into a separate 500 mL glass jar.

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Sample Analysis. EPA Method 5 analytical procedures were used to analyze the filter and fronthalf acetone rinse for particulate. The H_2SO_4 reagent and associated DI water rinse were analyzed for hydrogen chloride using ion chromatography as outlined in the method.

4.4.4.2 Clinker Stack. Samples were withdrawn isokinetically from the source using an EPA Method 5 sampling train.

Samole Collection. The sampling train consisted of a nozzle, a heated glass probe with a Type S Pitot tube attached, a filter, four chilled impingers, and a metering console. The particulate sample was collected on a Whatman EPM2000 glass fiber filter maintained at a temperature of $248^{\circ}F \pm 25^{\circ}F$. The first two impingers each contained 100 mL of deionized, distilled (DI) water, the third remained empty, and the fourth contained preweighed silica gel.

Sample Recovery. The filter was removed from the filter holder and placed in a 250 mL glass jar. The DI water reagent was returned to the original 1000 mL glass jar, weighed, the weight recorded on the label, and the liquid level marked. The silica gel was returned to the original tared container, weighed, and the weight recorded on the label. The volume of water vapor condensed in the impingers and the volume of water vapor collected in the silica gel were summed and entered into moisture content calculations.

All fronthalf components of the sampling train including the nozzle, probe, and filter holder were rinsed with acetone into a 500 mL glass jar.

Samole Analysis. EPA Method 5 analytical procedures were used to analyze the filter and fronthalf acetone rinse for particulate.

4.4.5 Plume Opacity. The procedures outlined in EPA Method 9 were used for the determination of the plume opacity. A certified, experienced visible emissions (VE) observer was on site to record plume opacity. Each run consisted of the VE obeerver reading the plume opacity every 15 seconds for 60 minutes.

4.4.6 Sulfur Dioxide. Samples were withdrawn isokinetically from the source using an EPA Method 8 sampling train.

Sample Collection. The sampling train consisted of a stainless steel nozzle, a heated glass probe with a Type S Pitot tube attached, a filter, four chilled impingers, and a metering console. An unheated Whatman EPM2000 glass fiber filter was used between the first and second impingers. The first impinger contained 100 mL of 80% isopropyl alcohol (IPA), the second and third impingers each contained 100 mL of 5% hydrogen peroxide (H_2O_2), and the fourth impinger contained preweighed silica gel. After sample collection, purging was conducted by drawing ambient air through the train for 15 minutes.

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Sample Recovery. The IPA reagent was returned to the original 500 mL glass jar, weighed, the weight recorded on the label, and the liquid level marked. The H₂O₂ reagent was returned to the original 1000 mL glass jar, weighed, the weight recorded on the label, and the liquid level marked. The silica gel was returned to the original container, weighed, and the weight recorded on the label. The volume of water vapor condensed in the impingers and the volume of water vapor collected in the silica gel were summed and entered into moisture content calculations.

The probe, first impinger, and fronthalf of the filter holder, and the filter were rinsed with DI water into the IPA reagent jar. The backhalf of the filter holder, second impinger, and third impinger were rinsed with DI water into the H₂O₂ reagent jar.

Sample Analveis. The H₂O₂ reagent and DI water rinses were analyzed for SO₂ using the barium-thorin titration method.

4.4.7 PCDD/PCDF and Semivolatiles. Samples for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) and semivolatiles were withdrawn isokinetically from the source using a promulgated EPA Method 23 sampling train.

Sample Collection. The sampling train consisted of a nickel-plated stainless steel nozzle, a heated borosilicate glass probe, a Whatman EPM2000 glass fiber filter maintained at a temperature of 248° F ± 25° F, a water-cooled condenser, a sorbent trap containing EAD-2 resin, five chilled impingers, and a metering console.

The water-cooled condenser and aorbent trap was arranged in a manner that allowed the condensate to drain vertically through the trap. Gas entering the trap was maintained at or below 68° F.

The first impinger (optional knockout) remained empty, the second and third impingers each contained 100 mL of DI water, the fourth remained empty, and the fifth contained preweighed silica gel. Sealing greases were not used on any portion of the sample train.

Sample Train Component Preparation.

Glassware. All glass parts of the sample train including the sorbent trap, were precleaned prior to **sampling** according to the following procedures.

1. Soaked in hot **soapy water** (Alconox) at 50° C or higher
2. Rinsed three times **with** tap H₂O
3. Rinsed three **times with** DI H₂O
4. Rinsed three times **with** pesticide grade acetone
5. Rinsed **three times with** pesticide grade methanol/methylene chloride
6. Baked at 450° F for 2 hours
7. Capped with **clean glass** plugs or methylene chloride rinsed aluminum foil

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