PETE WILSON, Governor

STATE OF CALIFORNIA

AIR RESOURCES BOARD
2020 L STREET
P.O. BOX 2815
SACRAMENTO, CA 95812

February 8, 1994

Mr. Tim Naquin
Petrochem Environmental Services
3207 Antonino Avenue
Bakersfield, CA 93308

Dear Mr. Naquin:

Request for Conditional Approval of Multiple Metals Train for Previously Conducted Air Toxics "Hot Spots" Source Tests

In your February 1, 1994, telephone conversation with Steven Giorgi of my staff, you indicated that Petrochem has conducted a source test at Golden State Metals during October 1993 to measure the emissions of trace metals to meet the requirements of the Air Toxics "Hot Spots" Information and Assessment Act of 1987. You also indicated that you followed the procedures outlined in draft ARB Method 436 which has not yet been adopted by the Air Resources Board (ARB). As stated in Section 93336(c) of the Emission Inventory Criteria and Guidelines Regulation (EIGR), equivalent sampling and analysis methods may be approved only if the Executive Officer of the ARB determines that the alternative method is substantially equivalent to the ARB-adopted method for that facility for the purposes of complying with this regulation. Our records show neither Petrochem nor Golden State Metals applied for approval of an alternative test method prior to conducting the source test as required by the EIGR. Therefore, Petrochem would have been required to conduct separate source tests for each metal in accordance with the adopted ARB methods including ARB Method 12 (lead), ARB Method 101 (mercury), ARB Method 104 (beryllium), ARB Method 423 (arsenic), ARB Method 424 (cadmium), ARB Method 425 (hexavalent and total chromium), and ARB Method 433 (nickel).

Our records did indicate that Petrochem has previously applied for alternate approval and participated in this quality assurance program for source tests at other facilities. If Petrochem had applied for alternative approval, they would have been allowed to use the March 24, 1992, version of draft ARB Method 436 which allows for the determination of multiple metals using three runs of a single train. They also would have been required to participate in the quality assurance program which at the time of the October 1993 test would have consisted of the laboratory analysis of a set of spiked audit filters.

In light of the failure of Petrochem to obtain prior approval to use draft Method 436, you have requested that we consider the emission data from this source test to be valid and complete for the air toxics "Hot Spots" emission reports. We are willing to consider reviewing your draft source test report to evaluate if the requirements of the method have been satisfied. Additionally, Petrochem will be required to conduct additional quality control testing as part of the audit filter program if the source test appeared to have been conducted properly.

If this is agreeable to both Petrochem and to Golden State Metals, please submit a copy of either the complete draft source test report, or a complete data package for the metals testing only. The report must include a description of the facility, the procedures followed, and a complete set of field and laboratory data relating to the metals tests including information on stack gas parameters, source process conditions, sample blank results, details of laboratory analysis procedures and other associated data used in calculating the metals emissions. Upon receipt, we will evaluate the data submitted and we will provide comments on the completeness of the data. If the data appears to be sufficiently complete, we will request the analysis of a set of two spiked filters and a blank filter for 18 metals, which we will provide and/or we will request that you provide aliquots of the digested source test samples for analysis by ARB contracted laboratories. Upon receipt of the results of the filters or samples, we will provide comments on the validity of the results. Please be advised that the San Joaquin Valley Unified Air Pollution Control District must also approve the use of the source test results.

Please contact George Lew at (916) 445-0657 or Steven Giorgi at (916) 323-0668 if you need more information on this matter.

Sincerely,

William Loscutoff

William V. Loscutoff, Chief
Monitoring and Laboratory Division

cc: Takehisa Miyake, Golden State Metals
William Weese, SJVUAPCD
Luis Parades, Southern Region, SJVUAPCD

**PETRO
CHEM
ENVIRONMENTAL
SERVICES, INC.**

3207 Antonino Avenue
Bakersfield, California 93308
(805) 327-7300
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AB2588 SOURCE TEST REPORT – VOLUME 1

GOLDEN STATE METALS, INC.
2000 E. BRUNDAGE LANE
BAKERSFIELD, CALIFORNIA 93307

ATTENTION: TAKEHISH MIYAKE

UNIT TESTED:

AUTO SHREDDER RESIDUE SEPARATOR
APCD #5013003

DATE TESTED:

OCTOBER 18, 19, 21, 22, 25,
& NOVEMBER 8, 1993

DATE REPORTED:

JANUARY 12, 1994

DETERMINATIONS:

CONCENTRATION AND EMISSIONS OF VINYL CHLORIDE,
TOTAL AND HEXAVALENT CHROMIUM, ASBESTOS,
PCB, AND MULTIMETALS

PROJECT: #042-481

TESTED BY:
TIM NAQUIN

WRITTEN BY:
TIM NAQUIN & SHIRLEY BRUNNER

REVIEWED BY:

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SECTION 1.0

INTRODUCTION

INTRODUCTION

On October 18, 19, 21, 22, 25 and November 8, 1993, Petro Chem Environmental Services, Inc. (PCES) performed a series of AB2588 emission source tests for Golden State Metals, Inc. located in Bakersfield, California. The unit tested was the Auto Shredder Residue Separator. Concentrations and emissions of vinyl chloride, total and hexavalent chromium, asbestos, PCB, and multimetals were determined using the following procedures:

Parameters	Method	# Test Runs
% H_2O	Measured As A Part Of CARB 436, 425 and 427	3 runs per method
% O_2, CO_2, and N_2	Assumed Ambient Conditions	
Exhaust Rate	CARB Methods 1-4;	3 runs per method
Vinyl Chloride	CARB Method 106; Bag Sample, GC/FID Analysis Analytical Lab: Coast-to-Coast Analytical Services	3
Total & Hexavalent Chromium	CARB Method 425; Impingement, Ion Chromatography Analysis, High Detection Option Analytical Lab: Coast-to-Coast Analytical Services	3
Asbestos	CARB Method 427; In-stack polycarbonate filtration, Analysis by Transmission Electron Microscopy Analytical Lab: Forensic Analytical	3
PCB	CARB Method 428; XAD2 resin absorption Low Resolution GCMS Analysis Analytical Lab: Alta Laboratories	3
Multi Metals	CARB Method 436; Impingement, GFAA and ICP Analysis Analytical Lab: Coast-to-Coast Analytical	3

When pollutants (metals, PCB, asbestos) were not detected in a sample run, the results were asterisked and one-half the detection limit was used for emission calculations. When pollutants were partially detected (one or more of the fractions of a run were not detected) the fraction was noted and one-half the detection limit was used for the non-detected fractions.

All sampling was performed by Tim Naquin, John Hinkle, and Steve Lewis of Petro Chem Environmental Services, Inc. Luis Parroles of San Joaquin Valley Unified APCD was present and observed all testing.

This report is presented in 4 sections. Section 2 provides a brief description of the process being tested; Section 3 describes the sampling and analytical methodologies that were used to measure substances of concern, while Section 4 discusses test results and quality control.

SECTION 2.0

SOURCE PROCESS AND EQUIPMENT DESCRIPTIONS

SOURCE PROCESS AND EQUIPMENT DESCRIPTION

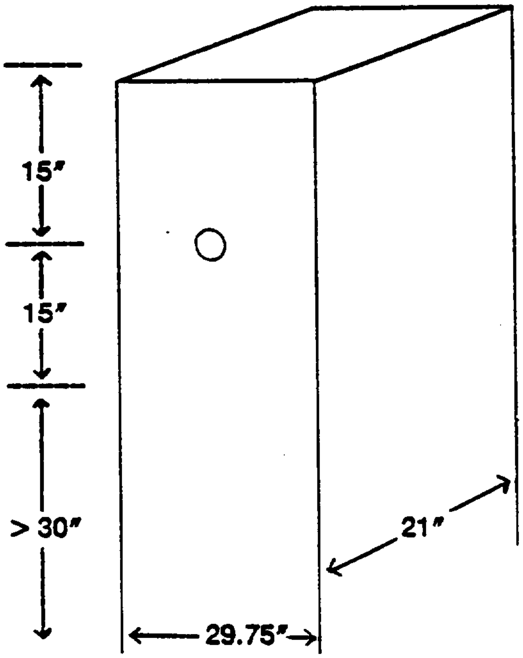
The facility receives scrap metals and processes them through a shredder. The ferrous material is separated and stored in a separate storage pile. The nonferrous material is air classified. Nonferrous metals are recovered and stored in separate storage piles. The remaining material is known as ASW. The small material is treated and will be disposed of off site.

The products from the facility include the recovered ferrous and nonferrous metals. The by-products from the facility include the large and small ASW.

The cyclone was constructed by Texas Shredder, Inc. It receives the air classified material from the "Z"-Box. The cyclone separates out over 99.7% of the particulate matter it receives. The separated material is transferred to the ASW treatment operation.

The only emission point from the cyclone is at the top and consists of the exhausted air containing entrained particulate matter. The exhaust is located on top of the cyclone. The exhaust flow rate is approximately 12,000 acfm. The stack is rectangular; the dimensions can be found in Figure 1.

FIG 1. CYCLONE EXHAUST STACK



SECTION 3.0

TEST PROCEDURES

SAMPLING AND ANALYTICAL PROCEDURES

A variety of specialized testing methods were required to quantify the emissions of substances of concern at Golden State Metals. Appropriate techniques based on methods promulgated by either the California Air Resources Board (CARB) or the Environmental Protection Agency (EPA) were used to collect and analyze emissions samples. Table 1-1 in Section 1 summarizes the test methods used, and the number of samples collected.

3.1 Stack Gas Exhaust Rate

Exhaust rates (dscfm) were measured as a part of each sampling method (in accordance with CARB Methods 1-4) with the exception of CARB Method 106 (vinyl chloride). Point-to-point exhaust rate measurements were used to calculate isokinetic sampling rates. The average exhaust rate measured during each run was thus used to calculate the emission rate for each substance of concern. The only method not requiring isokinetic sampling was CARB Method 106 (vinyl chloride). Because all three CARB Method 106 samples were collected during the third CARB Method 427 replication, the exhaust rate measured during that run was used to calculate the mass emission rate of vinyl chloride.

A brief description of CARB Methods 1-4 follows:

CARB Method 1: Sampling and Velocity Traverses for Stationary Sources

Prior to the source test a site assessment was performed in order to locate sample points for obtaining the best representative measurements. CARB Method 1 takes into account duct area, straight run, cyclonic or stratified flow patterns.

CARB Method 2: Velocity and Volumetric Flow Rates

A computer was used to select suitable sample/traverse points. A calibrated pitot tube was connected to a magnehelic gauge and leak checked. Temperature and velocity head measurements were made at each traverse point, and the duct static pressure was recorded.

At the end of each run, stack temperatures and velocity heads were averaged (stack temperature averaged arithmetically, root mean square average was used for velocity head) and used to calculate an average exhaust rate.

CARB Method 3: % CO_2, % O_2, Dry Molecular Weight

Because the exhaust gas was composed of ambient air, dry molecular weight was calculated using ambient oxygen (20.9 %) and carbon dioxide (0.1 %) concentrations.

CARB Method 4: Stack Gas Moisture Concentration

Stack gas moisture content was measured as a part of each isokinetic sampling method. Moisture content was determined gravimetrically by measuring impinger weight gain.

3.2 CARB Method 106 - Vinyl Chloride Emission

Vinyl chloride emissions were measured in accordance with CARB Method 106. Stack gas samples were withdrawn from the stack using a 1/4-inch Teflon sampling line and collected into a 20-liter Tedlar bag where it remained until analyzed. A vacuum pump was used to draw a negative pressure on a ridged opaque container enclosing the bag. The reduced pressure inside the drum caused the stack gas to flow from the stack and collect in the bag. The sampling rate was controlled using a needle valve (sampling rate did not exceed 500 ml/min) and monitored using a rotameter.

The sampling apparatus was transported to the sampling location where it was set up and leak tested. A leak-free system was verified by evacuating the Tedlar bag and observing the evacuation rate fall to "zero" using a rotameter. Following evacuation, the Tedlar bag and sampling system were purged twice with stack gas prior to collecting the actual sample. After sampling was completed a post-test leak check was performed by pressurizing each bag to 4 inches of water and observing no change in this pressure over a ten minute time frame. Pressure was measured using an inclined manometer.

A total of three samples and a field blank were collected. The field blank was collected via the same sampling apparatus by employing the same techniques that were used to collect stack gas samples, with the exception of drawing ultra-pure nitrogen through the system instead of stack gas.

Samples were contained in opaque containers to protect them from light during the 48 hour time interim between sample collection and sample analysis. During analysis, vinyl chloride was separated from other sample gas components via gas chromatography (GC) and quantified using a flame ionization detector (FID).

An analytical equipment and operating condition summary follows:

GC/FID: SRI 8610 with FID
Column: 1/-inch x 3m Waters and Associates GC Durapak N-Octane Porasil C 80/100
Temperature Program:
    Initial Temperature: 50C
    Rate: 3 C/min
    Final: 82 C
    Final Time: 8 min.
Flow Rate:
    Carrier Gas: He 50 ml/min
    Air: 190 ml/min
    H_2: 300 ml/min

Calibration Standard: 2.3 ppm vinyl chloride

To satisfy CARB and SJVUAPCD requirements, the following test activities were performed:

- Pre-test and post-test Tedlar bag leak checks were performed (described above);
- All samples were collected in new Tedlar bags;
- A field blank was collected and submitted for analysis (described above);
- A multi-point calibration was preformed prior to analysis (calibration gas data located in Appendix I); and
- Accuracy was indicated via a QC spike (discussed in Section 4).

3.3 CARB Method 425 - Hexavalent And Total Chromium Emissions

Hexavalent and total chromium emissions measurements were conducted in accordance with CARB Method 425 using the high range option (hexavalent and total chromium were detected in all three test replications).

TRAIN DESCRIPTION

The sampling apparatus consisted of a quartz nozzle, followed by a quartz probe and Teflon sample line leading to the first of four modified Greenberg-Smith impingers. The first two impingers (Impingers 1 and 2) contained 100 mls of a 0.1N solution of NaOH followed by an empty impinger (Impinger 3) and a fourth containing silica gel (Impinger 4) to remove any residual moisture. A Teflon coated filter was placed between Impingers 3 and 4 to trap any residual particulate matter.

TRAIN PREPARATION AND OPERATION

Prior to testing, all components that were to be exposed to the sample gas were cleaned with three successive rinses of hot soapy water, followed by several successive rinses with tap water. Train components were then soaked (overnight) in a 6N solution of nitric acid (HNO_3). The following day, train components were removed form the acid soak and rinsed repeatedly with distilled water until all traces of acid were removed. Train components were then conditioned with a 0.1 N solution of sodium hydroxide (NaOH) and sealed with Teflon tape to prevent contamination. All sample containers were also pre-cleaned using the same procedure that was used to clean train components.

TRAIN OPERATION

Prior to sampling, all equipment was assembled and leak tested at 10 inches of Hg. The probe was inserted into the stack and isokinetic sampling initiated as per CARB Method 425.

Upon test completion, the probe was withdrawn from the stack, and a post-test leak check was conducted at a vacuum equal to or greater than the maximum vacuum observed during the test.

The equipment was then disassembled, sealed with Teflon tape, and transported to the laboratory for sample recovery.

SAMPLE RECOVERY

Each test replication produced a total of three samples (low range option). These samples were labeled as follows: "Front Half" (consisting of the nozzle, probe and sample line); "First Impinger" (Impinger 1 contents and rinse) and "Second Impinger" (Impinger 2 contents, rinse and Teflon filter catch).

The "Front Half" was collected by titling the probe and brushing three successive times while rinsing with 0.1N NaOH. The rinse was collected in a 500 ml amber glass sample bottle and labeled, "Front Half".

The first, second and third impingers were disassembled and weighed for moisture determination.

The contents of the first impinger and its rinse were emptied into a 500 ml amber glass bottle which was labeled, "Impinger 1".

The contents of the second impinger and its rinse were likewise emptied into a third 500 ml amber glass bottle along with the Teflon filter. This bottle was labeled, "Impinger 2".

Following recovery, these samples were stored in the sample custody area prior to shipment to the analytical laboratory. The 0.1N solution of NaOH used as impinger solution and recovery reagent was also transported to the laboratory with the samples to be used during sample analysis.

SAMPLE ANALYSIS

The high detection option was inadvertently used during sample analysis. The contents of the first two sample containers were combined (Front Half and Impinger 1), while the contents of the third sample (Impinger 2) was analyzed separately. All three fractions were split prior to analysis. One of the splits was set aside for hexavalent chromium analysis by ion chromatography (IC), while the second split was digested and used to quantify total chrome via graphite furnace atomic adsorption spectroscopy (GFAAS).

AGENCY REQUIREMENTS

To satisfy CARB and SJVUAPCD requirements, the following activities were performed:

- Pre-test analyses of reagents (0.1N NaOH and 6N H_2SO_4) to demonstrate that they were free of contamination and reducing agents as per Section 4.3.9 of CARB Method 425;
- All three sampling probes were rinsed with 0.1 N NaOH and submitted for pre-test analysis so as to demonstrate that they were contamination free;
- Hexavalent chromium was quantified via ion chromatography (IC), while total chromium was analyzed by GFAAS (discussed above);
- The same solution of 0.1N NaOH was used for all sampling and analytical procedures (discussed above);
- Accuracy was indicated via QC and matrix spikes (discussed in Section 4); and
- Precision was indicated by performing QC and matrix spike duplicate analysis (discussed in Section 4).

3.4 CARB Method 427 - Asbestos Emissions

Asbestos emissions were measured in accordance with CARB Method 427. The sampling apparatus consisted of a stainless steel nozzle, a stainless steel filter holder, and a stainless steel probe. The probe was connected to a Teflon filter-to-impinger line. A series of impingers were connected in tandem (similar to Method 5) and immersed in an ice bath. The first two impingers contained 100 mls of deionized water, the third impinger was empty, while the fourth contained a known amount of silica gel to remove residual moisture.

The CARB Method 427 apparatus was assembled in the laboratory. The nozzle was brushed out and rinsed with distilled water and acetone, then the filter holder was loaded with a nucleopore polycarbonate filter (0.4 μ pore size). The sampling apparatus was sealed and transported to the sampling site where it was assembled and leak tested at 10 inches of mercury.

The nozzle was positioned into the gas flow and the vacuum pump was started immediately and adjusted to obtain an isokinetic sample rate.

Upon completion of sampling, the apparatus was leak tested at a vacuum greater than the highest observed vacuum. The leak was recorded and the apparatus was sealed and transported to the mobile laboratory.

The filter and any loose particulate were carefully removed from the filter holder with forceps and placed in a labeled petri dish. The nozzle, probe, and front half of the filter housing were rinsed and brushed six times with acetone. The sample fractions were combined, bottled, labeled, and fluid level marked. Aliquots of filter and acetone were similarly treated for blank analysis. Asbestos was quantified by transmission electron microscopy (TEM).

To satisfy CARB and SJVUAPCD requirements, a field blank was collected and analyzed for asbestos.

3.5 CARB Method 436 - Multiple Metals Emissions

Multiple metals emissions were measured in accordance with CARB Method 436. The metal constituents measured include: Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni), Selenium (Se), Silver (Ag), Thallium (Tl), Aluminum (Al), Aluminum Oxides, Iron (Fe), Manganese (Mn), Phosphorus (P) and Zinc (Zn).

TRAIN PREPARATION

The sampling apparatus was configured in the same manor as the CARB Method 5 train and therefore consisted of a quartz nozzle, a heat traced quartz probe, a heated borosilicate filter holder (with a Teflon-coated screen filter support), a Teflon sample line and six modified Greenburg Smith impingers containing the following solutions: 100 ml of 5% HNO_3 /10% H_2O_2 (Impinger 1), 100 ml of 5% HNO_3 /10% H_2O_2 (Impinger 2), an empty impinger (Impinger 3), 100 ml of acidified $KMnO_4$ (Impinger 4), 100 ml of acidified $KMnO_4$ (Impinger 5), and an impinger filled with a known amount of silica gel so as to remove any residual moisture (Impinger 6).

Prior to testing, all train components that were to come into contact with the sample gas were cleaned with successive rinses of hot soapy water, followed by several rinses with tap water. Following the tap water rinse, train components were soaked overnight in a 6N HNO_3 solution. The following day, these train components were rinsed several times with distilled H_2O to remove all traces of acid and then sealed with Teflon tape to prevent contamination. All sample containers were prepared in like manor.

TRAIN OPERATION

Prior to testing, all sampling equipment was assembled and leak tested at 10 inches of Hg, followed by heating the probe and filter components to 250°F (± 25). The probe was then inserted into the stack and isokinetic sampling initiated as per CARB Method 436.

Upon test completion, the probe was withdrawn from the stack and leak tested at a vacuum equal to or greater than the maximum vacuum observed during sampling. The train was then disassembled, sealed with Teflon tape (to protect against contamination) and transported to the laboratory for subsequent recovery.

SAMPLE RECOVERY

During each replicate, a total of five samples were recovered. These fractions include: the "Front Half" (nozzle, probe and front half of filter housing), the "Filter Catch", the "Back Half" (Impingers 1, 2 and 3 contents and rinses), the "Potassium Permanganate Catch" (Impingers 4 and 5 contents and rinse) and the "Hydrochloric Acid Rinse" (rinse obtained by rinsing Impingers 4 and 5 with 8N HCl).

The filter and nozzle were separated from the probe. The probe was tilted and brushed three successive times while rinsing with a 0.1N solution of nitric acid and rotating. The probe rinse was caught in a 500 ml amber glass sample bottle. The nozzle and front half of the filter housing were likewise rinsed with 0.1N nitric acid and then combined with the probe wash. This sample was labeled, "Front Half".

The filter was removed from the filter holder with Teflon coated forceps, folded and placed into a petri dish. This sample was labeled, "Filter Catch".

The first, second and third impingers were disassembled, weighed, and their contents transferred to a 1000 ml amber glass bottle. The impingers and crossovers were then rinsed three times each with a solution of 0.1N HNO_3. The rinses were combined with the impingate sample. This sample was labeled, "Back half".

The fourth and fifth impingers were disassembled, weighed, and their contents transferred to a 500 ml amber glass sample bottle. The impingers were then rinsed three times with acidified $KMnO_4$ solution and combined with the impingate sample. This sample was labeled, " Potassium Permanganate Catch".

These same two impingers were then rinsed with a solution of 8N HCl and placed in a separate 250 ml amber glass bottle. This sample was labeled, "Hydrochloric Acid Rinse".

SAMPLE ANALYSIS

During each replicate, five samples were generated for analysis. The Method 436 protocol details the analysis of metals using cold vapor atomic adsorption (CVAAS), inductively coupled argon plasma emission spectroscopy (ICAP) and graphite furnace atomic adsorption spectroscopy (GFAAS). The analytical methodologies and the instrumentation used to quantify each metallic substance are summarized in Table 3-1.

AGENCY REQUIREMENTS

To satisfy CARB and SJVUAPCD requirements the following activities were performed:

- Analysis of the filter, impinger solutions and recovery reagents (discussed in Section 4);
- Collection and analysis of a field blank (discussed in Section 4);
- Analysis of a method blank (discussed in Section 4);
- Analysis of arsenic, lead, chromium and cadmium via GFAAS (see Table 3-1); and

TABLE 3-1. ANALYTICAL METHODS USED TO QUANTIFY METALS

SUBSTANCE OF INTEREST	ANALYTICAL METHOD	PRINCIPAL
Antimony (Sb)	EPA 6010	ICP
Arsenic (As)	EPA 7060	GFAAS
Barium (Ba)	EPA 6010	ICP
Beryllium (Be)	EPA 6010	ICP
Cadmium (Cd)	EPA 7131	GFAAS
Chromium (Cr)	EPA 7191	GFAAS
Copper (Cu)	EPA 6010	ICP
Lead (Pb)	EPA 7421	GFAAS
Mercury (Hg)	EPA 7470	CVAAS
Nickel (Ni)	EPA 6010	ICP
Selenium (Se)	EPA 6010	ICP
Silver (Ag)	EPA 6010	ICP
Thallium (Ti)	EPA 6010	ICP
Aluminum (Al)	EPA 6010	ICP
Iron (Fe)	EPA 6010	ICP
Manganeese (Mn)	EPA 6010	ICP
Phosphorus (P)	EPA 6010	ICP
Zinc (Zn)	EPA 6010	ICP

- Accuracy was indicated by the analysis of a QC spike (discussed in Section 4), while Precision was indicated via a duplicate analysis of a QC spike.

3.6 CARB Method 428 - Measurement Of PCB Emissions

Polychlorinated biphenyl (mono through deca) emissions were measured in accordance with CARB Method 428.

TRAIN DESCRIPTION

The sampling apparatus was configured similarly to CARB Method 5 and consisted of a quartz nozzle, a heat traced quartz probe, a heated borosilicate filter holder (with a Teflon-coated screen filter support), a Teflon sample line, a condenser, an XAD-2 resin trap, and four modified Greenburg Smith impingers. The impingers were arranged as follows: an empty impinger (Impinger 1), 100 ml DI H_2O (Impinger 2), an empty impinger (Impinger 3), and a fourth containing silica gel to remove any residual moisture (Impinger 4).

Prior to sampling, all train components that were to be exposed to the sample gas were cleaned with successive rinses of hot soapy water, followed by several rinses with tap water to remove all traces of soap. Grease was then removed with chromic acid. All traces of chromic acid were then removed with distilled water. All train components were then rinsed three times with methanol, toluene (substituted for benzene, see CARB approval in Appendix VI), and methylene chloride. All sample containers were likewise prepared.

Prior to testing, all sampling equipment was leak tested at 10 inches of Hg, followed by heating the probe and filter housing to 250°F (± 25). The probe was then inserted into the stack and isokinetic sampling initiated as per CARB Method 428.

Upon test completion, the probe was withdrawn from the stack and the sampling system leak tested at a vacuum equal to or greater than the maximum vacuum observed during sample collection. The equipment was then disassembled and the components sealed with hexane rinsed aluminum foil and transported to the laboratory for sample recovery.

SAMPLE RECOVERY

Each CARB Method 428 replication resulted in six samples which include: the "Front Half" (nozzle, probe, front half of filter housing), the "Filter Catch", the "Back Half" (back half of filter housing, sample line and condenser), the "XAD Resin Module", "Impinger 1 Catch", and "Impingers 2 and 3".

The filter and nozzle were separated from the probe. The probe was tilted and brushed three successive times while rinsing three times with methanol, toluene and methylene chloride. All rinses were contained in a 500 ml amber glass sample bottle. The nozzle, and front half of the filter housing were likewise recovered and were thus combined with the probe wash. This sample was labeled, "Front Half".

The filter was removed from the filter housing with Teflon coated forceps, folded, wrapped in hexane rinsed aluminum foil, placed into a glass petri dish and sealed with Teflon tape. This sample was labeled, "Filter Catch".

The back half of the filter housing, the Teflon sample line and the condenser were likewise rinsed three times with methanol, toluene and methylene chloride and placed into a 500 ml amber glass sample bottle. This sample was labeled, "Back half".

The XAD resin module was removed and sealed with hexane rinsed aluminum foil. This sample was labeled, "XAD Resin Module".

The first, second and third impingers were then disassembled and weighed. The contents of the first impinger were emptied into a 500 ml amber sample bottle. The first impinger was then rinsed three times each with methanol, toluene and methylene chloride. This rinse was placed into the same 500 ml container as the contents. This container was labeled, " Impinger 1".

The contents of the second and third impingers were emptied into a 500 ml amber glass sample container and rinsed three times each with methanol, toluene and methylene chloride. This sample was labeled, "Impingers 2 and 3". All samples were stored at 4°C until they were analyzed.

SAMPLE ANALYSIS

The sample train was recovered as six fractions, however, the analysis was ultimately performed on a single composite of these six fractions. Each fraction was extracted with methylene chloride, concentrated and combined with the others to form a single composite sample. This sample was analyzed by low resolution mass spectrometry (LRGCMS) for polychlorinated biphenyls (mono through deca) relative to both an external and internal standard.

EQUIPMENT OPERATING PARAMETERS

PCB components were separated from one another using a DB-5 MS column purchased from J and W Scientific. The column was 60 meters long, having a 0.25 mm internal diameter and a 0.25 micron film.

The overall run time was 37.5 minutes. The maximum oven temperature was 320°C with a 0.20 minute equilibration time. The GC operating conditions were programmed as follows:

Run Time: 37.5 minutes,
    Temp 1: 100 C,
    Time 1: 2.00 minutes,
    Rate 1: 15.0 (C/min),
    Temp 2: 190 C,
    Time 2: 0.10 min,
    Rate 2: 50.0 C/min,
    Temp 3: 317 C,
    Time 3: 26.90 min,
    Rate 3: 0.0,
    Temp 4: 0.0,
    Time 4: 0.00.

AGENCY REQUIREMENTS

To satisfy CARB and SJVUAPCD requirements, the following test activities were performed:

- Pre-test contamination check of XAD-2 resin and filter (discussed in Section 4);
- Collection and analysis of a blank train (discussed in Section 4);
- No sealant greases were used to seal train components;
- Internal standards were added prior to extraction (discussed in Section 4);
- Analysis of a laboratory method blank (discussed in Section 4); and
- Analysis of a laboratory control sample (discussed in Section 4).

SECTION 4.0

RESULTS DISCUSSION

DISCUSSION OF RESULTS

On October 18, 19, 21, 22, 25 and November 8, 1993, a series of source tests were performed at Golden State Metals to measure emissions of several substances of concern in accordance with AB 2588 "Toxic Hot Spots" requirements. The substances of concern and test methodologies are summarized in Table 1-1, and discussed in Section 3. The results of those tests, as well as all pertinent quality assurance and quality control (QA/QC) data are discussed below for each method.

4.1 CARB Method 106 - Vinyl Chloride Emissions

Samples (three replications and a field blank) were collected to measure vinyl chloride emissions on October 19, 1993, during the third CARB Method 427 test replication. Samples were collected in Tedlar bags and analyzed via GC/FID. The concentrations (ppm) and emission rates (lb/hr) for vinyl chloride are summarized in Table 4-1. Vinyl chloride was not detected (detection limit = 1 ppm) during any of the three runs.

The conventions used to calculate and report vinyl chloride emissions are as follows:

- Vinyl chloride was reported as "not detected" and half the detection limit (0.5 ppm) was used to calculate the emission rate (lb/hr) for each run; and
- Emission rates were calculated for each replication using the exhaust flow rate measured during the third CARB Method 427 replication.

DATA QUALITY INDICATORS

Data quality indicators for accuracy were calculated from data obtained from the analysis of a QC spike. The QC spike analysis was performed on a gas sample (other than that used for calibration) containing a known concentration of vinyl chloride. Accuracy was indicated by comparing the measured concentration to the known concentration (spike recovery). The spike recovery was 105 percent.

TABLE 4.1
CARB METHOD 106
VINYL CHLORIDE EMISSIONS

CARB METHOD 1-4		
Sampled October 19, 1993 0600-0800		
CARB Method 106 samples taken during Run 3 of CARB Method 427		
Parameter	Units	Value (CARB 427 Run 3 Only)
Stack Gas Flowrate	dscf/min	11169

SOURCE TEST RESULTS

Vinyl Chloride	Lab Results ppmv *		Emissions lb/hr
Bag Sample 1	0.5		0.055
Bag Sample 2	0.5		0.055
Bag Sample 3	0.5		0.055
AVERAGE	**0.5**		**0.055**

* Results listed on analytical data as "ND" for vinyl chloride, used ½ detection limit.

Tedlar Bag Field Blank results were "ND" for vinyl chloride

Other quality assurance activities included:

- * Collection and analysis of a field blank;
- * GC/FID calibration; and
- * Performance of a pre-test instrument blank.

The field blank was obtained by collecting a sample of ultra-pure nitrogen using the same apparatus and techniques that were used to collect the actual samples. The purpose of the field blank was to demonstrate a contamination-free sampling apparatus. Vinyl chloride was not detected in this sample.

Prior to sample analysis the GC/FID was calibrated. The calibration data used to determine vinyl chloride concentrations and the calibration gas data are included in Appendix I.

An instrument blank was also performed prior to sample analysis. During the instrument blank, a sample of ultra-pure nitrogen was analyzed using the same procedures that were used to analyze the actual samples. Vinyl chloride was not detected and therefore demonstrated a contamination-free system.

4.2 CARB Method 425 - Hexavalent And Total Chromium Emissions

Samples were collected to measure hexavalent and total chromium emissions in accordance with CARB Method 425. Hexavalent chromium was quantified by ion chromatography (IC), while total chromium was measured via graphite furnace atomic adsorption spectroscopy (GFAAS). Three test replications were performed over a two day period. The first two replications were completed on October 21, 1993, while the third was performed on October 22, 1993.

The CARB Method 425 results (concentrations and emission rates) are presented (for all three runs) in Tables 4-2 and 4-3 for total and hexavalent chromium respectively. Hexavalent and total chromium were detected during each run. The conventions used to calculate and report emissions data are as follows:

- * Compound concentrations (ug/dscf, ug/dscm) and emission rates (lb/hr) were reported for each run separately;

TABLE 4.2
CARB METHOD 425
TOTAL CHROMIUM RESULTS

CARB METHOD 1-4		
Sampled October 21, 1993 Run 1 0600-0800, Run 2 0830-1030 October 22, 1993 Run 3 0815-1015		
Parameter	Units	Value (Average of 3 Runs)
Stack Gas Flowrate	dscf/min	10538

SOURCE TEST RESULTS

Pollutant: Total Chromium	Lab Results Total ug	Concentration ug/dscf	Concentration ug/dscm	Sample Gas Volume dscf	Emissions lb/hr
Run 1	5.3	0.098	3.46	54.04	.00014
Run 2	4.3	0.089	3.16	48.11	.00012
Run 3	4.9	0.103	3.63	47.70	.00014
AVERAGE		**0.0967**	**3.42**	**49.95**	**.00013**

TABLE 4.3
CARB METHOD 425
HEXAVALENT CHROMIUM RESULTS

SOURCE TEST RESULTS

Pollutant: Hexavalent Chromium	Lab Results Total ug	Concentration ug/dscf	Concentration ug/dscm	Sample Gas Volume dscf	Emissions lb/hr
Run 1	0.25	0.005	0.163	54.04	.0000065
Run 2	0.27	0.005	0.176	48.11	.0000070
Run 3	0.28	0.005	0.183	47.70	.0000073
AVERAGE		**0.005**	**0.174**	**49.95**	**.0000074**

- Emission rates reported for any given run were calculated using the flow rate measured during that specific run. For example, the emission rates reported for Run-1 were calculated using the flow rate measured for Run-1 (not the average flow rate); and

- Average concentration and emission rates were reported. The average emission rate reported is the mean emission rate (averages of Runs 1 through 3) and not the product of the average concentration and exhaust rate.

DATA QUALITY INDICATORS

Data quality indicators for accuracy and precision are presented in Table 4-4 along with probe proof, field blank and method blank results.

Accuracy Indicators

Accuracy was indicated through the use of matrix and QC spikes. The QC spike was prepared by adding a known amount of chromium to the sample matrix prior to sample preparation (digestion in the case of chromium). The purpose of the QC spike was to quantify any bias resulting from the digestion process. Because total chromium analysis was the only one that required digestion, a QC spike was not prepared for hexavalent chromium.

The matrix spike was prepared by adding known amounts of hexavalent and total chromium to the sample matrix immediately prior to sample analysis (after digestion if quantifying total chromium). The purpose of the matrix spike was to measure any bias resulting from the sample matrix itself so that an appropriate method of quantitation (MOQ) could be selected. Depending upon these results, samples would either be analyzed through the use of a calibration curve or by the method of standard additions.

A matrix spike was prepared both during the pre-test and analytical phase. During the pre-test phase (probe proof analysis), the method blank (0.1N NaOH and 6N sulfuric acid) was spiked with a known concentration of hexavalent chromium and then analyzed. The spike recovery was 121 percent.

TABLE 4.4
CARB METHOD 425
QA/QC DATA

BLANK SAMPLES		
Sample	Total Chrome ug/ml	Hexavalent Chrome ug/ml
Probe Proof-1 (Run-1)	< 0.0052	0.000166
Probe Proof-2 (Run-2)	< 0.0046	< .00009
Probe Proof-3 (Run-3)	< 0.00549	< 0.00011
Field Blank	0.000366	0.0141
Method Blank (Reagent Blank) (0.1 N NaOH, 6 N H_2SO_4)		
Probe Proof	ND	ND
Samples	ND	ND

ACCURACY INDICATORS			
DQI	Substance	Recovery (Probe Proof)	Recovery (Sample)
Matrix Spike	Chromium	--	107 %
	Hex Chrome	121 %	--
QC Spike	Chromium	80 %	96 %

PRECISION INDICATORS					
DQI	Sample Batch	Substance	Rep1	Rep2	% Diff
Duplicate Matrix Spike	Sample	Chromium	62	54	14 %
Duplicate Matrix Spike	Probe Proof	Hex Chrome	0.17	0.17	0 %
Duplicate QC Spike	Probe Proof	Chromium	16	16	0 %
Duplicate QC Spike	Sample	Hex Chrome	9.6	12	22 %

During sample analysis (analysis of Runs 1 through 3), the field blank was spiked with a known concentration of chromium immediately following sample digestion and then analyzed. The spike recovery was 107 percent.

Because the measured matrix effects (121% for hexavalent chromium and 107% for chromium) did not warrant the use of standard additions, a calibration curve was used to quantify these compounds during both analytical phases. These calibration curves are presented in Appendix II.

Because probe proofs and field samples were analyzed on two separate occasions, two QC spikes were prepared and analyzed as well (one representing each batch analyzed). During both the pre-test (analysis of the probe proofs) and sample (analytical) phases, the method blank (0.1N NaOH solution) was spiked with a known amount of chromium prior to digestion and then analyzed. Accuracy was indicated by comparing the amount of chromium measured to the known value and was expressed as a percentage (known as a spike recovery). The spike recoveries measured during the pre-test and sample analysis phases were 80 and 96 percent respectively. QC spikes were prepared and analyzed for chromium only because no preparation was performed prior to hexavalent chromium analysis (in the case of hexavalent chromium, a QC spike would be equivalent to a matrix spike).

Precision Indicators

Precision was indicated via duplicate QC and matrix spike analysis. Precision was quantified by comparing one replicate analysis to a second and expressing the difference as a percentage. These results are presented in Table 4-4.

<u>Blank Analysis</u>

Prior to testing, three probe proofs and a reagent blank were submitted for analysis. The probe proofs were prepared by rinsing each probe with 0.1N NaOH. Probe proofs were collected to demonstrate that each probe was contamination free. Due to the plating nature of chromium, probes used to collect samples were not to be re-used until another probe proof was performed. Chromium was not detected in any of the probe proof samples. Hexavalent chromium was detected (0.000166 ug/ml) in the probe that was used during Run-1. The detection limit for this sample was 0.000105 ug/ml. The hexavalent chromium contamination found in the Run-1 probe represents 17.2 percent of that found during Run-1. The impact that this has on Run-1 data quality cannot be adequately determined due to the instability of hexavalent chromium.

Reagent Blank

Reagent blanks consisting of 0.1N NaOH and 6N sulfuric acid were analyzed for total and hexavalent chromium during both the pre-test (probe proof analysis) and analytical (sample analysis) phases. The purpose of the reagent blanks were to determine background levels of hexavalent and total chromium so that they could be used to correct stack gas samples. Neither compound was detected in the reagent blanks and therefore no corrections were performed.

Field Blank

Field blanks were prepared following the third test replication. A field blank was prepared by recovering a train that had been assembled, transported to the stack, leak checked and returned to the recovery area without having any stack gas drawn through it. The purpose of the field blank was to indicate the amount of residual hexavalent and total chromium that remained after recovery. As can be seen in Table 4-4, both hexavalent (0.0141 ug/ml) and total chromium (0.000366 ug/ml) were detected in the field blank.

4.3 CARB Method 427 - Asbestos Emissions Measurements

Samples were collected to measure asbestos emissions in accordance with CARB Method 427 over a two day period. Runs 1 and 2 were completed on October 18, 1993, while Run-3 was completed on October 19, 1993. A field blank was collected after the third run. Asbestos levels were quantified via transmission electron microscopy (TEM). Asbestos data is presented in Table 4-5.

Asbestos levels were detected in all three runs and were reported in units of fibers/dscf and fibers/dscm. Asbestos was not detected in the field blank thus indicating no pre-test contamination.

TABLE 4.5
CARB METHOD 427
ASBESTOS - CHRYSOTILE

SOURCE TEST RESULTS

ASBESTOS VARIETY: Chrysotile

SAMPLE ID	RUN 1	RUN 2	RUN 3	AVERAGE
FILTER				
Total Concentration (F/F)*	980000	2000000	1400000	1460000
SAMPLE GAS VOLUME				
Vm(std), dscf	52.37	55.28	56.72	54.79
Vm(std), dscm	1.483	1.565	1.606	1.551
CONCENTRATION				
Fibers/dscf	18713	36179	24683	26525
Fibers/dscm	660840	1277658	871655	936718

* (F/F) = Fibers / Filter

Fibers/dscf = Fibers/filter * filter/train * train/Vm(std), dscf

ASBESTOS VARIETY: Chrysotile

SAMPLE ID	RUN 1	RUN 2	RUN 3	AVERAGE
PROBE & NOZZLE RINSE			**	
Total Concentration (MFL)*	103	5.1	0.26	36.1
Total Sample Volume, ml	75	53	105	
SAMPLE GAS VOLUME				
Vm(std), dscf	52.37	55.28	56.72	54.79
Vm(std), dscm	1.483	1.565	1.606	1.551
CONCENTRATION				
Million Fibers/dscf	0.148	0.099	0.191	0.146
Million Fibers/dscm	5.21	3.49	6.73	5.14
Fibers / dscf	147508	98752	190673	145644
Fibers / dscm	5209172	3487368	6733534	5143358
TOTAL CONCENTRATION				
FILTER + P/N RINSE				
Fibers / dscf	166221	134931	215356	172170
Fibers / dscm	5870012	4765027	7605189	6080076

* (MFL) = Million Fibers/Liter

** Results listed on analytical data as 'ND' for this run, used ½ detection limit.

Million Fibers / dscf = MF/L * 1 L / 1000 ml * Total Sample Volume, ml / train * train / Vm(std), dscf

4.4 CARB Method 428 - PCB Emissions Measurements

Samples were collected to measure polychlorinated biphenyls (mono through deca) in accordance with CARB Method 428. Polychlorinated biphenyls (PCB) were quantified via LRGCMS. Three test replications were performed over a two day period. Run-1 was completed on October 25, 1993, while the final two runs were performed on November 8, 1993.

PCB concentrations (ng/dscf, ng/dscm) and emission rates (lb/hr) are presented in Tables 4-6 through 4-8 for Runs 1 through 3 respectively. Overall program averages are presented in Table 4-9. Monochloro- through pentachlobiphenyls were detected during each of the three test runs. All hexachloro- through decachlorobiphenyls were not detected during any of the three test runs. The detection limit for each PCB specie was 1.37 ng/dscf(Run-1), 1.63 ng/dscf (Run-2) and 1.30 ng/dscf (Run-3). The slight deviation in detection limits was due to varying sample gas volumes.

The conventions used to calculate and report PCB emissions data were as follows:

- PCB concentrations were quantified relative to a set of internal standards (isotopically labeled) that were introduced to the sample matrix prior to methylene chloride extraction;
- Compound concentrations (ng/dscf, ng/dscm) and emission rates (lb/hr) were reported for each run separately;
- The emission rate reported for any given run was calculated using the flow rate measured during that specific run. For example, the emission rate reported for Run-1 was calculated using the flow rate measured for Run-1 (not the average flow rate);
- During runs in which a particular PCB compound was not detected, the concentration was reported as "nd" and half the detection limit was used to calculate the emission rate; and
- Mass emission rates for undetected PCBs were included when calculating the the program average for that PCB.

TABLE 4.6
CARB METHOD 428
POLYCHLORINATED BIPHENYLS
(PCB'S)

RUN-1 RESULTS

COMPOUND	Units Given ng/sample	ng/dscf	ng/dscm	lb/hr
Monochlorobiphenyl	6200	84.9	2999	1.1E-04
Dichlorobiphenyl	30000	411.0	14513	5.5E-04
Trichlorobiphenyl	15000	205.5	7256	2.7E-04
Tetrachlorobiphenyl	5100	69.9	2467	9.3E-05
Pentachlorobiphenyl	520	7.1	252	9.5E-06
Hexachlorobiphenyl *	50	0.7	24	9.1E-07
Heptachlorobiphenyl *	50	0.7	24	9.1E-07
Octachlorobiphenyl *	50	0.7	24	9.1E-07
Nonachlorobiphenyl *	50	0.7	24	9.1E-07
Decachlorobiphenyl *	50	0.7	24	9.1E-07
		TOTAL		*lb/hr* ***1.0E-03***

SAMPLE VOLUMES	VOLUMETRIC FLOW RATE
Vm (std) = 73.00 dscf	DSCFM = 10108
Vm (std) = 2.07 dscm	

CALCULATIONS

ng/dscf = (ng/sample) / (Vm(std), dscf)

ng/dscm = (ng/sample) / (Vm(std), dscm)

lb/hr = ng/dscf * dscfm * g/10e9 ng * lb/454 g * 60 min/hr

* Results listed on analytical data as 'ND' for these compounds, used ½ detection limit.

TABLE 4.7
CARB METHOD 428
POLYCHLORINATED BIPHENYLS
(PCB'S)

RUN-2 RESULTS

COMPOUND	Units Given ng/sample	ng/dscf	ng/dscm	lb/hr
Monochlorobiphenyl	1600	26.0	919	3.4E-05
Dichlorobiphenyl	12000	195.1	6890	2.5E-04
Trichlorobiphenyl	4000	65.0	2297	8.4E-05
Tetrachlorobiphenyl	2200	35.8	1263	4.6E-05
Pentachlorobiphenyl	140	2.3	80	2.9E-06
Hexachlorobiphenyl *	50	0.8	29	1.1E-06
Heptachlorobiphenyl *	50	0.8	29	1.1E-06
Octachlorobiphenyl *	50	0.8	29	1.1E-06
Nonachlorobiphenyl *	50	0.8	29	1.1E-06
Decachlorobiphenyl *	50	0.8	29	1.1E-06
		TOTAL		***lb/hr*** ***4.2E-04***

SAMPLE VOLUMES			VOLUMETRIC FLOW RATE
Vm (std) =	61.51	dscf	DSCFM = 9789
Vm (std) =	1.74	dscm	

CALCULATIONS

ng/dscf = (ng/sample) / (Vm(std), dscf)

ng/dscm = (ng/sample) / (Vm(std), dscm)

lb/hr = ng/dscf * dscfm * g/10e9 ng * lb/454 g * 60 min/hr

* Results listed on analytical data as 'ND' for these compounds, used ½ detection limit.

TABLE 4.8
CARB METHOD 428
POLYCHLORINATED BIPHENYLS
(PCB'S)

RUN-3 RESULTS

COMPOUND	Units Given ng/sample	ng/dscf	ng/dscm	lb/hr
Monochlorobiphenyl	3100	40.3	1424	5.4E-05
Dichlorobiphenyl	17000	221.1	7808	3.0E-04
Trichlorobiphenyl	5700	74.1	2618	9.9E-05
Tetrachlorobiphenyl	3500	45.5	1607	6.1E-05
Pentachlorobiphenyl	280	3.6	129	4.9E-06
Hexachlorobiphenyl *	50	0.7	23	8.7E-07
Heptachlorobiphenyl *	50	0.7	23	8.7E-07
Octachlorobiphenyl *	50	0.7	23	8.7E-07
Nonachlorobiphenyl *	50	0.7	23	8.7E-07
Decachlorobiphenyl *	50	0.7	23	8.7E-07
TOTAL				*lb/hr* *5.2E-04*

SAMPLE VOLUMES			VOLUMETRIC FLOW RATE
Vm (std) =	76.89	dscf	DSCFM = 10131
Vm (std) =	2.18	dscm	

CALCULATIONS

ng/dscf = (ng/sample) / (Vm(std), dscf)

ng/dscm = (ng/sample) / (Vm(std), dscm)

lb/hr = ng/dscf * dscfm * g/10e9 ng * lb/454 g * 60 min/hr

* Results listed on analytical data as 'ND' for these compounds, used ½ detection limit.

TABLE 4.9
CARB METHOD 428
POLYCHLORINATED BIPHENYLS
(PCB's)

AVERAGE CONCENTRATION AND EMISSION RATES

CARB METHOD 1-4		
Sampled October 25, 1993 Run 1 0710-1010, November 8, 1993 Run 2 0755-1055 Run 3 1125-1425		
Parameter	Units	Value (Average of 3 Runs)
Sample Gas Volume, $V_{m(std)}$	dscf	70.47
Sample Gas Volume, $V_{m(std)}$	dscm	2.00
Stack Gas Flowrate	dscf/min	10009

AVERAGE SOURCE TEST RESULTS

Pollutant: PCB's Values are average of 3 runs per compound	Concentration ng/sample	Concentration ng/dscf	Emissions lb/hr
Monochlorobiphenyl	3633	50.4	.000066
Dichlorobiphenyl	19667	275.7	.00037
Trichlorobiphenyl	8233	115	.000151
Tetrachlorobiphenyl	3600	50.4	.000067
Pentachlorobiphenyl	313	4.3	.0000058
Hexachlorobiphenyl *	50	0.73	.00000096
Octachlorobiphenyl *	50	0.73	.00000096
Nonachlorobiphenyl *	50	0.73	.00000096
Decachlorobiphenyl *	50	0.73	.00000096
TOTAL PCB's			**0.00065**

* Results listed on analytical data as "ND" for these compounds on all 3 runs, used ½ detection limit

Field Blank results were "ND" for all compounds

DATA QUALITY INDICATORS

Data quality indicators for accuracy and precision are presented in Tables 4-10 through 4-11.

Accuracy Indicators

Accuracy was indicated through the use of laboratory control samples (LCS) as well as the measurement of internal standard recoveries. Laboratory control samples were prepared by adding known amounts of native PCB compounds to the method blank (method blank is defined below). Accuracy was indicated for each PCB specie by comparing the amount measured during analysis to the known value. During this program, duplicate laboratory control samples were prepared and analyzed. To meet CARB acceptance criterion, the LCS recoveries for each PCB specie had to be between 60 and 140 percent. As can be seen from Table 4-10, all LCS recoveries met this criterion.

Isotopically labeled internal standards were added to samples prior to extraction and were thus used to quantify PCB concentrations in all samples. PCB concentrations were quantified based upon internal standard recoveries. Internal standard recoveries were determined based upon the response of recovery standards that were added immediately prior to sample injection.

Internal standard recoveries are presented in Table 4-11 for all runs. To meet CARB acceptance criteria, internal standard recoveries had to be between 40 and 120 percent or the signal to noise ratio had to exceed 10. As can be seen on Table 4-11, at least one of these two criteria were met for all PCB species during all analyses.

Precision Indicators

Precision was indicated via duplicate LCS analysis. Precision was quantified by comparing one LCS replication to a second and calculating a relative percent difference (RPD) for each PCB specie. All RPD results were less than 10 percent and thus met CARB acceptance criteria.

TABLE 4.10
CARB METHOD 428
LCS RECOVERIES

LABORATORY CONTROL SAMPLES			
Compound	LCSI (%)	LCS2 (%)	RPD (%)
Monochlorobiphenyl	98	100	2.0
Dichlorobiphenyl	86	92	6.7
Trichlorobiphenyl	94	93	1.1
Tetrachlorobiphenyl	99	97	2.0
Pentachlorobiphenyl	101	103	2.0
Hexachlorobiphenyl	102	101	1.0
Heptachlorobiphenyl	99	100	1.0
Octachlorobiphenyl	97	108	11
Nonachlorobiphenyl	84	92	9.1
Decachlorobiphenyl	98	98	0

TABLE 4.11
CARB METHOD 428
INTERNAL STANDARD RECOVERIES

	INTERNAL STANDARD RECOVERIES (%)					
Compound	Run-1	Run-2	Run-3	Filter Check XAD-Check	Method Blank	Field Blank
^{13}C-Monochlorobiphenyl	47	60	56	64	58	47
^{13}C-Trichlorobiphenyl	58	66	65	61	54	54
^{13}C-Tetrachlorobiphenyl	65	84	79	76	57	58
^{13}C-Pentachlorobiphenyl	56	73	68	71	52	54
^{13}C-Hexachlorobiphenyl	53	70	66	74	48	53
^{13}C-Heptachlorobiphenyl	45	61	56	65	46	46
^{13}C-Octachlorobiphenyl	43	49	50	68	43	41
^{13}C-Nonachlorobiphenyl	52	65	65	62	57	52
^{13}C-Decachlorobiphenyl	36	52	48	72	47	42

Notes:

1. Acceptance Limit 40%<% Rec<120 % or S/N > 10.
2. In cases where % Rec. limits were exceeded, the S/N > 10.

Blank Analysis

The following blanks were submitted for analysis: XAD Resin and glass fiber filter, and a field blank. The laboratory also performed a method blank.

Prior to analysis, contamination checks were performed on the XAD resin and glass fiber filters that were to be used to collect samples. During this pre-test contamination check, the filter and XAD module were extracted and analyzed using the same procedure that was used to analyze field samples. PCBs were not detected in the XAD resin or on the glass fiber filter.

Prior to analysis, the laboratory performed a method blank to demonstrate that all glassware and reagents used to collect samples, recover samples, and perform extractions were free from PCB contamination. These reagents included a glass fiber filter and XAD resin sample. PCBs were not detected in the method blank which demonstrates the cleanliness of the analytical equipment as well as confirming that the XAD resin and filters used to collect samples were free from contamination.

A field blank was collected by recovering a train that had been assembled, transported to stack, and returned to the recovery lab without having any stack gas drawn through it.

PCB compounds were not detected in the field blank, which provides further confirmation that both the glass fiber filter and the XAD Resin were free from contamination, as well as demonstrating the cleanliness of the train components and recovery solvents.

4.5 CARB Method 436 - Multiple Metals Emissions

Samples were collected to measure the concentration and emission rates of eighteen metallic substances of interest in accordance with CARB Method 436. Three test replications were performed over a two day period. Runs 1 and 2 were performed on October 22, 1993, while Run-3 was performed on October 25, 1993.

The concentrations (ug/dscf, ug/dscm) and emission rates (lb/hr) are presented in Tables 4-12 through 4-14 respectively. Overall program averages are presented in Table 4-15. The only

TABLE 4.12
CARB METHOD 436
MULTIMETALS

RUN-1 RESULTS

CONSTITUENT	Non-Detect Fractions **	Units Given Total ug **	ug/dscf	ug/dscm	lb/hr
Aluminum		1230	39.9	1409	0.05316
Antimony	Front & Back Half	2.5	0.081	2.86	0.00011
Arsenic	Back Half	1.9	0.062	2.18	0.00008
Barium		19.0	0.616	21.76	0.00082
Beryllium	Front & Back Half	0.25	0.008	0.29	0.00001
Cadmium		26.0	0.843	29.78	0.00112
Chromium		10.0	0.324	11.45	0.00043
Copper		7.0	0.227	8.02	0.00030
Iron		610	19.8	699	0.02637
Lead	Back Half	19.5	0.633	22.34	0.00084
Manganese	Back Half	15.0	0.487	17.18	0.00065
Mercury	Back Half	0.24	0.008	0.27	0.00001
Nickel	Back Half	8.5	0.276	9.74	0.00037
Phosphorus		119	3.86	136	0.00514
Selenium	Front & Back Half	2.5	0.081	2.86	0.00011
Silver	Front & Back Half	1.4	0.045	1.60	0.00006
Thallium	Front & Back Half	2.5	0.081	2.86	0.00011
Zinc		140	4.54	160	0.00605
	as Al	as Al2O3	ug/dscf	ug/dscm	lb/hr
Aluminum Oxide Front Half Only	1100	4155.56	134.8	4760	0.180
		TOTAL			***0.04259***

SAMPLE VOLUME			VOLUMETRIC FLOW RATE	
Vm (std) =	30.83	dscf	DSCFM =	10083
Vm (std) =	0.87	dscm		

CALCULATIONS

ug/dscf = Total ug / (Vm(std), dscf)
ug/dscm = Total ug / (Vm(std), dscm)
lb/hr = ug/dscf * dscfm * g/10e6 ug * lb/454 g * 60 min/hr

* Results listed on analytical data as 'ND' for these compounds, used ½ detection limit.

** Combined front half and back half fractions. If 'ND' on both fraction, used ½ detection limit. If 'ND' on only one fraction, used ½ detection limit plus result for other fraction.

*** Manganese blank corrected

Aluminum Oxide Calculations = Total ug * ug-mole / 27 ug * 102 ug/ug-mole
MW Al = 27
MW Al2O3 = 102

TABLE 4.13
CARB METHOD 436
MULTIMETALS

RUN-2 RESULTS

CONSTITUENT	Non-Detect Fractions **	Units Given Total ug **	ug/dscf	ug/dscm	lb/hr
Aluminum		1050	34.4	1214	0.04527
Antimony	Front & Back Half	2.5	0.082	2.89	0.00011
Arsenic		2.6	0.085	3.01	0.00011
Barium		20.0	0.655	23.13	0.00086
Beryllium	Front & Back Half	0.25	0.008	0.29	0.00001
Cadmium		15.0	0.491	17.35	0.00065
Chromium		14.0	0.458	16.19	0.00060
Copper		4.0	0.131	4.63	0.00017
Iron		520	17.0	601	0.02242
Lead	Back Half	6.0	0.196	6.94	0.00026
Manganese		15.3	0.501	17.69	0.00066
Mercury		0.50	0.016	0.58	0.00002
Nickel	Back Half	7.5	0.246	8.67	0.00032
Phosphorus		114	3.73	132	0.00491
Selenium	Front & Back Half	2.5	0.082	2.89	0.00011
Silver	Front & Back Half	1.4	0.046	1.62	0.00006
Thallium	Front & Back Half	2.5	0.082	2.89	0.00011
Zinc		150	4.91	173	0.00647
	as Al	as Al2O3	ug/dscf	ug/dscm	lb/hr
Aluminum Oxide Front Half Only	970	3664	120.0	4237	0.158
		TOTAL			***0.03786***

SAMPLE VOLUME			VOLUMETRIC FLOW RATE	
Vm (std) =	30.54	dscf	DSCFM =	9963
Vm (std) =	0.86	dscm		

CALCULATIONS

ug/dscf = Total ug / (Vm(std), dscf)
ug/dscm = Total ug / (Vm(std), dscm)
lb/hr = ug/dscf * dscfm * g/10e6 ug * lb/454 g * 60 min/hr

* Results listed on analytical data as 'ND' for these compounds, used ½ detection limit.

** Combined front half and back half fractions. If 'ND' on both fraction, used ½ detection limit. If 'ND' on only one fraction, used ½ detection limit plus result for other fraction.

*** Manganese blank corrected

Aluminum Oxide Calculations = Total ug * ug-mole / 27 ug * 102 ug/ug-mole
MW Al = 27
MW Al2O3 = 102

TABLE 4.14
CARB METHOD 436
MULTIMETALS

RUN-3 RESULTS

CONSTITUENT	Non-Detect Fractions **	Units Given Total ug **	ug/dscf	ug/dscm	lb/hr
Aluminum		1220	26.8	947	0.03484
Antimony	Front & Back Half	2.5	0.055	1.94	0.00007
Arsenic	Back Half	2.1	0.046	1.63	0.00006
Barium		21.0	0.461	16.30	0.00060
Beryllium	Front & Back Half	0.25	0.005	0.19	0.00001
Cadmium		1.3	0.029	1.01	0.00004
Chromium		12.2	0.268	9.47	0.00035
Copper		11.0	0.242	8.54	0.00031
Iron		580	12.7	450	0.01656
Lead		20.6	0.453	15.99	0.00059
Manganese	Back Half	6.1	0.134	4.73	0.00017
Mercury	Back Half	0.24	0.005	0.19	0.00001
Nickel	Back Half	9.5	0.209	7.37	0.00027
Phosphorus		131	2.88	102	0.00374
Selenium	Front & Back Half	2.5	0.055	1.94	0.00007
Silver	Front & Back Half	1.4	0.031	1.09	0.00004
Thallium	Front & Back Half	2.5	0.055	1.94	0.00007
Zinc		180	3.96	140	0.00514
	as Al	as Al2O3	ug/dscf	ug/dscm	lb/hr
Aluminum Oxide Front Half Only	1100	3664	80.5	2844	0.105
		TOTAL			***0.02810***

SAMPLE VOLUME			VOLUMETRIC FLOW RATE		
Vm (std) =	45.51	dscf	DSCFM =	9833	
Vm (std) =	1.29	dscm			

CALCULATIONS

ug/dscf = Total ug / (Vm(std), dscf)
ug/dscm = Total ug / (Vm(std), dscm)
lb/hr = ug/dscf * dscfm * g/10e6 ug * lb/454 g * 60 min/hr

* Results listed on analytical data as 'ND' for these compounds, used ½ detection limit.

** Combined front half and back half fractions. If 'ND' on both fraction, used ½ detection limit. If 'ND' on only one fraction, used ½ detection limit plus result for other fraction.

*** Chromium, Lead, and Manganese were blank corrected

Aluminum Oxide Calculations = Total ug * ug-mole / 27 ug * 102 ug/ug-mole
MW Al = 27
MW Al2O3 = 102

TABLE 4.15
CARB METHOD 436
MULTI METALS

AVERAGE CONCENTRATIONS AND EMISSION RATES

Pollutant: Multi Metals Values are average of 3 runs per compound	Concentration Total ug	Concentration ug/dscf	Emissions lb/hr
Aluminum	1167	33.7	.04442
Antimony*	2.5	.073	.0001
Arsenic	2.20	.064	.00008
Barium	20	.577	.00076
Beryllium*	.25	.007	.00001
Cadmium	15.5	.503	.00066
Chromium	13.3	.363	.00048
Copper	7.3	.200	.00026
Iron	570	16.5	.02178
Lead	26.7	.764	.00100
Manganese	12.1	.374	.00049
Mercury	.27	.0077	.00001
Nickel	8.5	.244	0.00032
Phosphorus	121	3.49	.00460
Selenium*	2.5	.0727	.0001
Silver*	1.4	.0407	.00005
Thallium*	2.5	.0727	.0001
Zinc	157	4.47	.00589
TOTAL			**.0811**
Aluminum Oxide	3828	111.77	**.148**

* Results listed on analytical data as "ND" for these compounds on all 3 runs, used ½ detection limit
Blank correction not applicable for this method.

metals not detected in all three runs include: antimony, beryllium, selenium, silver and thallium. The conventions used to calculate and report metals emissions data are as follows:

- The concentration and emission rate for each metals specie was reported for each run separately;
- The emission rate reported for any given run was calculated using the flow rate measured during that specific run. For example, the emission rates reported for Run-1 were calculated using the flow rate measured for Run-1 (not the average flow rate);
- When metals species were detected in some runs and not in others, half the detection limit was used to calculate the emission rate for the run in which the metal was not detected;
- Runs during which metals were not detected were included when calculating the program averages; and
- Program emission rates were calculated as the mean emission rate (averages of Runs 1 through 3) and not the product of the average concentration and exhaust rate.

Aluminum oxide concentration and emission rates were estimated by performing a mole ratio calculation using the mass of aluminum detected in the front half (probe rinse and filter catch) of the train. Although aluminum was detected in the back half (first three impingers), the amount detected in the front half was used because at stack conditions (ambient) aluminum oxide would exist as a particulate and not be able to penetrate the filter.

DATA QUALITY INDICATORS

Data quality indicators for accuracy and precision are presented in Table 4-16. Accuracy was indicated through the use of a QC spike, while precision was measured by performing a duplicate analysis on the QC spike.

TABLE 4.16
CARB METHOD 436
MULTI METALS

ACCURACY AND PRECISION INDICATORS

		Accuracy Indicator Spike Recovery	Precision Indicator % Difference Between Dup.
Antimony	Back Half	80 %	5.1 %
	Front Half	96 %	8 %
Arsenic	Back Half	105 %	33 %
	Front Half	125 %	13 %
Barium	Back Half	90 %	5.7 %
	Front Half	100 %	0 %
Beryllium	Back Half	88 %	2.3 %
	Front Half	100 %	0 %
Cadmium	Back Half	92 %	2.2 %
	Front Half	92 %	2.2 %
Chromium	Back Half	125 %	0 %
	Front Half	115 %	4.3 %
Copper	Back Half	92 %	0 %
	Front Half	96 %	0 %
Lead	Back Half	86 %	0 %
	Front Half	88 %	4.4 %
Mercury	Back Half	87 %	0 %
	Front Half	100 %	2.7 %

TABLE 4.16
CARB METHOD 436
MULTI METALS

ACCURACY AND PRECISION INDICATORS
(continued)

Substance Of Concern	Accuracy Indicator Spike Recovery	Precision Indicator % Difference Between Dup.
Nickel		
Back Half	94 %	4.3 %
Front Half	102 %	1.9 %
Selenium		
Back Half	90 %	0 %
Front Half	100 %	4.9 %
Thallium		
Back Half	95 %	5.4 %
Front Half	105 %	4.7 %
Aluminum		
Back Half	125 %	0 %
Front Half	115 %	4.3 %
Iron		
Back Half	140 %	19 %
Front Half	120 %	8 %
Manganese		
Back Half	94 %	2.2 %
Front Half	102 %	3.8 %
Zinc		
Back Half	108 %	3.6 %
Front Half	140 %	25 %

The QC spike was prepared by introducing known amounts of each metal specie to the method blank prior to digestion. The spiked sample was then digested and analyzed using the same techniques that were used to prepare and analyze all samples. Accuracy was measured for each metal by comparing the amount measured to the known concentration. This difference was expressed as a percentage and is presented in Table 4-16.

Precision was quantified by performing a duplicate analysis on the QC spike. Precision was measured by comparing one replicate analysis to the second and expressing this difference as a percentage. These results are presented in Table 4-16 for each metal.

BLANK ANALYSIS

Three blank samples were prepared to determine contamination levels in the analytical reagents, the sampling and recovery solutions and the sampling equipment itself. These blanks included: a method blank, a reagent blank and a field blank.

The method blank was prepared in the laboratory and was used to determine background contamination levels in the analytical reagents. The method blank was prepared and analyzed using the same methods that were used to prepare and analyze the actual field samples. None of the eighteen metals species were detected in the method blank.

The reagent blank consisted of the impinger and sample recovery solutions that were used during the sampling phase of the program. These solutions included: 0.1N nitric acid, 5% hydrogen peroxide/ 10% nitric acid, acidified potassium permanganate and 8N hydrochloric acid.

The purpose of the reagent blank was to determine background contamination levels of the impinger and recovery solutions as well as the filter. Because the same batch of solutions were used during each test, the results of the reagent blank could be used to correct the field data.

The results of the reagent blank are presented in Table 4-17. These results are reported for "Back Half" and "Front Half" samples. The front half results were obtained from the combined analysis of the filter and 0.1 N nitric acid used to recover the probe. The "Back Half" results

TABLE 4.17
CARB METHOD 436
MULTI METALS

RESULTS OF BLANK ANALYSIS

Substance Of Concern	Method Blank ug/ml	Reagent Blank ug/ml	Field Blank ug/ml
Antimony			
Back Half	ND	ND	ND
Front Half	ND	ND	ND
Arsenic			
Back Half	ND	ND	ND
Front Half	ND	ND	0.0087
Barium			
Back Half	ND	ND	0.0096
Front Half	ND	23	0.0679
Beryllium			
Back Half	ND	ND	ND
Front Half	ND	0.0140	ND
Cadmium			
Back Half	ND	ND	0.0020
Front Half	ND	0.0260	0.0043
Chromium			
Back Half	ND	ND	0.0071
Front Half	ND	0.0600	0.0494
Copper			
Back Half	ND	ND	ND
Front Half	ND	ND	0.0123
Lead			
Back Half	ND	ND	0.0471
Front Half	ND	0.0500	0.0432
Mercury			
Back Half	ND	ND	ND
Front Half	ND	ND	ND
Nickel			
Back Half	ND	ND	ND
Front Half	ND	ND	ND
Selenium			
Back Half	ND	ND	ND
Front Half	ND	ND	ND

TABLE 4.17
CARB METHOD 436
MULTI METALS

RESULTS OF BLANK ANALYSIS
(continued)

Substance Of Concern	Method Blank ug/ml	Reagent Blank ug/ml	Field Blank ug/ml
Silver			
Back Half	ND	ND	ND
Front Half	ND	ND	ND
Thallium			
Back Half	ND	ND	ND
Front Half	ND	ND	ND
Aluminum			
Back Half	ND	ND	0.305
Front Half	ND	25	4.383
Iron			
Back Half	ND	ND	0.423
Front Half	ND	ND	1.481
Manganese			
Back Half	ND	ND	0.0188
Front Half	ND	0.0300	0.0246
Zinc			
Back Half	ND	ND	0.1176
Front Half	ND	87	0.6172
Phosphorus			
Back Half	ND	0.3900	ND
Front Half	ND	ND	ND

represent the analysis of the 5% nitric acid / 10% hydrogen peroxide impinger solution. The "Back Half" results reported for mercury were obtained from the analysis of the potassium permanganate solution used in impingers 4 and 5.

The impact that blank and QA/QC data had on the test results are discussed below.

Antimony, Beryllium, Selenium, Silver and Thallium

Concentrations of antimony, selenium, silver and thallium were not detected during any of the three runs or in any of the blank samples. These metals were reported at half their detection limits. Beryllium was not detected in any of the three test runs or in the field blank, but was detected in trace amounts in the front half reagent blank (0.0140 ug/ml). Its absence in the field blank as well as in the gas samples suggests that it could have been due to trace amounts that could have been present on the filter.

Arsenic, Chromium, Copper, Lead, Mercury, Nickel, Iron and Manganese

Levels of arsenic, chromium, copper, lead, mercury, nickel, iron and manganese were detected during at least one test replication. Of these elements, levels of lead, chromium and manganese were detected in the reagent blank and were therefore used to correct field data. Levels of arsenic, copper, mercury, nickel and iron were not detected in the reagent blank and therefore no corrections were necessary for these compounds.

Levels of arsenic, chromium, copper, lead, iron and manganese were detected in the field blank at slightly higher levels than were detected in the reagent blank. This is reasonable due to the fact that this sample was collected after the third test run was completed.

Barium, Cadmium, Aluminum, Zinc and Phosphorus

Levels of barium, cadmium, aluminum, zinc and phosphorus were detected during at least one of three test replications. However, the following anomaly should be noted: all five elements were detected in the reagent blank at levels that were much higher than those determined in both the field blank and stack samples.

Due to the fact that all five of these elements were detected in the front half only (none were detected in the back half), at levels that far exceeded those of the field blanks (especially for barium, aluminum and zinc), it is reasonable to suspect that the filter (submitted as a part of the reagent blank) was contaminated with these compounds. Had the 0.1N nitric acid been contaminated, these levels would have also been detected in the field blank and field samples as well. Because filters are destroyed during the digestion phase, only one filter (selected at random to represent the batch being used) can be analyzed. The impact this has on data quality is therefore inconclusive.

APPENDIX I

CARB METHOD 106
VINYL CHLORIDE

CARB METHOD 106

CALCULATIONS

COMPANY : GOLDEN STATE METALS, INC.
UNIT : METAL SHREDDER
DATE : 10-19-93
PROJECT : 042-481

CARB Method 106

Vinyl Chloride

COMPOUND	BAG SAMPLE	Lab Results ppmv	FLOW RATE dscfm **	lb/hr
Vinyl Chloride *	1	0.5	11169	0.055
Vinyl Chloride *	2	0.5	11169	0.055
Vinyl Chloride *	3	0.5	11169	0.055
			AVERAGE	0.055

* Results listed on analytical data as 'ND' for these compounds, used ½ detection limit.

** Bag Samples were taken on 10-19-93 during Run #3 for CARB Method 427.
Volumetric flow rate for Run #3 of CARB Method 427 was used in calculating lb/hr.

CALCULATIONS:

lb/hr = ppmv sample/10e6 ppm * (lb mole/379.56 dscf) * 62.5 lb/lb mole * dscfm * 60 min/hr

CARB METHOD 106

REDUCED ANALYTICAL DATA