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THE FATE OF HEXAVALENT CHROMIUM IN THE ATMOSPHERE

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ABSTRACT

A three-phase study was conducted to determine the fate of hexavalent chromium [Cr(VI)] in the atmosphere. Components of the study included the following:

- Identification of the most suitable sampling and analytical methods for Cr(VI)
- Determination, through a series of laboratory reaction chamber tests, the most likely chemical pathways and rate of conversion of hexavalent chromium in ambient air to trivalent chromium [Cr(III)] under simulated atmospheric conditions
- A field test, conducted in California, to support those findings from the laboratory studies

Two general analytical methods were evaluated, a complexation/atomic absorption technique currently utilized by the California Air Resources Board (CARB) and an ion chromatographic method. The atomic absorption method was found to provide the required sensitivity for measurement of atmospheric Cr(VI) [3-10 percent coefficient of variation (C.V.)] and was reasonably precise in the determination of Cr(VI) corresponding to concentrations varying from 0.7 to 5.5 nanograms per cubic meter (ng/m^3).

The ion chromatographic technique was more precise, sensitive, and rapid. The detection limit was 0.1 ng/m^3 with a precision of better than five percent C.V. A modification of this method provided an even greater detection limit (0.1 ng/m^3 and lower) but was more time consuming and complex.

A sampling method currently employed by CARB utilizing polyvinylchloride (PVC) membranes was found to provide low estimates of the true Cr(VI) atmospheric concentrations. Air concentrations approximately ten times higher were measured using an impinger method that provided greater stability of the Cr(VI) species during sampling.

Laboratory reaction chamber tests were conducted that utilized PVC filters spiked with Cr(VI) compounds and exposed to atmospheric reactants typical of the Southern California region. The results indicated that under low atmospheric pH conditions (measurable atmospheric HNO_3, etc.)

greater than 50% of Cr(VI) species will be reduced in the presence of oxidizable species, such as unsaturated and oxygenated organic compounds, and mono and divalent vanadium [V(I,II)] species over a 24-hour period.

Finally, a two-phase field test conducted in the Los Angeles basin area indicated the following:

- Cr(VI) species exist at measurable levels at distances of up to 0.5 miles or greater from chromium emission sources.
- The rates of reduction of Cr(VI) under true ambient air conditions parallel those seen in the laboratory.

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DISCLAIMER

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1.0 SUMMARY AND CONCLUSIONS

1.1 MEASUREMENT STUDIES

The existing sampling/analytical method proposed by CARB (ADDL006) is flawed primarily in the sampling step. Reaction chamber tests and studies conducted in the field demonstrate that the hexavalent chromium species undergo reduction during sampling presumably due to reaction with oxidizable species such as Fe^{+2}, V^{+}, V^{+2}, organics, etc. under acidic conditions due to CO_2, HNO_3, or other atmospheric species. An ideal sampling device to address this problem has not been identified. Impinger solutions that maintain a neutral or higher pH represent one approach toward stabilizing the Cr(VI) species. These devices show some promise based on some field test data, but are inconvenient to handle and, due to high blank values provided by large volumes of impinger solution and surface problems associated with glassware, they are thus far unsuitable for total chromium determinations. Preliminary data suggest that the most suitable sampling scenario is a filter device that utilizes an alkaline or neutral buffered coating. While PVC or Teflon membranes do not provide suitable surfaces for coating, a material such as paper or glass fiber may hold some promise. Potential problems for these devices include potential sampling inefficiency and reactivity for paper devices and the need for filtering or centrifugation of the paper or glass fiber material following extraction procedures.

At this time, the sampling method of choice appears to be the buffered impinger. The device must provide for the control of the pH of the sampling medium in order to stabilize the oxidation state of the chromium species <u>during</u> sampling. As a consequence, impinger solutions of sodium carbonate (0.02-0.05 M) are currently in use and have provided a much closer approximation of the true Cr(VI) concentration than the previously used PVC membrane. A further improvement might involve the use of plastic impinger devices, if possible, to minimize surface and blank problems associated with glass and allow for Cr(III) quantitation, in addition to Cr(VI) quantitation. A more ideal approach would involve a buffered alkaline coating of a glass fiber or paper filter, but an evaluation of these devices has not been completed.

Of the analytical methods evaluated in the study, none were found suitable for the in-situ determination of any chromium species. However, at least two analytical methods appear suitable for measurement/speciation of hexavalent chromium in the laboratory--CARB Method ADDL006 and ion chromatography. Both methods appear suitable for the analysis of either impinger solutions or extracts of filter samples. In both cases, however, pH adjustment is essential for recovery of the Cr(VI) species. The CARB method is quite sensitive, capable of detecting atmospheric levels of Cr(VI) of 0.5 ng/m^3, assuming sampling rates of 10 Lpm over a 24-hour period. However, the method is somewhat labor-intensive. If the ion chromatographic (IC) method was used in conjunction with the extract of a suitable filter collection device, Cr(VI) levels of 0.3 ng/m^3 might be determined. The IC detection limit can be lowered to ~0.04 ng/m^3 using a preconcentration technique that is somewhat labor-intensive. This latter technique is also potentially suitable to impinger solution analysis, although the detection limit is then similar to the CARB method. The primary advantage of the IC method is that far fewer sample manipulations are performed during measurement, contamination is minimized, and the method, in general, appears more rugged. The pH adjustment of the sample only requires values greater than 6.8 prior to injection.

The most desirable measurement method at this point appears to be ion chromatography, although further laboratory work is necessary to properly evaluate this technique in conjunction with the sampling device proposed above. Further work refining the preconcentration IC method is required if an impinger approach is to be used in future work. The standard post-column reaction method appears suitable as is, but would require more extensive laboratory evaluation of recovery, accuracy, precision, interferences, etc. At this time, Method ADDL006 appears suitable until such an evaluation is performed, although it appears slightly prone to certain interferences.

1.2 REACTION CHAMBER STUDIES

The experimental design utilized in this phase of the study, namely, exposure of spiked filters to controlled artificial atmospheres of a wide variety of species considered ubiquitous to ambient air, was intended to provide an approximation of potential Cr(VI) atmospheric reactions. Semi-quantitative reaction rates have been obtained from individual tests. More quantitative rates would be difficult to obtain, due to the limited conditions/species employed in each test. Some "indicators" suggesting general conditions under which hexavalent chromium is likely to undergo atmospheric conversion are as follows:

1. In the presence of "acidic" species, e.g., HNO_3, Cr(VI) will react with "oxidizable" species such as aldehydes, unsaturated hydrocarbons, substituted aromatic compounds, and inorganic species such as V^+, V^{+2}, and Fe^{+2}.

2. "Ambient levels" of Cr(VI) (20-100 ng) demonstrated an average half life [50% conversion to Cr(III)] of 13 hours when exposed to simulated atmospheric reactants. Assuming wind speeds greater than one mile per hour, one might expect the vast majority of Cr(VI) collected within a few miles of a Cr(VI) source to remain in the hexavalent state.

3. Based on the series of chamber tests, no conclusion can be made regarding the humidity factor. For most of the tests, the relative humidity was fixed between 20 to 30 percent.

4. No chamber tests were run to isolate the photochemical input in the conversion of Cr(VI) species. However, later field reaction studies conducted in a manner similar to chamber tests show conversion rates at night were indistinguishable to those found in the daylight hours.

5. The reaction chamber tests tend to be consistent with Cr(VI) behavior in solution. One possible explanation may be in the formation of fine aerosols (droplets) that simulate solution chemistry.

6. Very limited tests in conjunction with literature findings indicate that conversion of trivalent chromium to the hexavalent form is not a likely chemical pathway.

7. The reaction chamber tests provided a field reaction study design that could be easily implemented to provide more realistic Cr(VI) conversion data.

1.3 FIELD STUDY

Samples obtained from the chrome plating facility contained measurable levels of Cr(VI), at distances of at least 0.5 km from the source. Measured Cr(VI) levels ranged from 26.3 ng/m^3 to 315 ng/m^3. These elevated levels are reflective of an improved impinger sampler that allows for some degree of stabilization of the Cr(VI) species during collection. This type of sampler was utilized as a result of the laboratory reactivity tests, which demonstrated significant reduction on filters during simulated sampling conditions. Previous sampling that had been performed by CARB had featured the use of PVC (or Teflon) membranes to collect Cr(VI), and therefore contained no provision for the fixation of the collected Cr(VI). It is expected that this approach provided estimates of the Cr(VI) atmospheric concentrations that were perhaps only five to ten percent of the true values. This is, in fact, dramatically seen in the results obtained from the CARB measurements performed October 6-9, 1987 at the same general chrome plating site utilized by Entropy Environmentalists during their field test. While levels of hexavalent chromium were measurable at 0.5 Km, most sites at greater distances did not provide sufficient levels to allow for quantitation of a relationship of Cr(VI) to total chromium. It was hoped that if this had been possible, some measure of Cr(VI) reduction with distance from the source could have been obtained. This was not the case, except with one ambient test run.

Levels of hexavalent chromium at the cooling tower site were generally at or near the detection limit. Exceptions are included in this report. Possible contributing factors to low levels at the cooling tower facility include high dilution rates and variable winds.

Field reaction studies that simulated in the field those reactivity tests performed in the laboratory were performed at both sites. Useful data were provided at both sampling sites. PVC filters loaded with 20-100 ng of Cr(VI) at the emission source were taken to an El Monte site (CARB facility) away from the source and exposed to ambient air at a sampling flow rate of 3 Lpm for 24 hours. Hexavalent chromium reduction was observed over this period that paralleled those reduction rates observed in the laboratory under simulated conditions. An average half life of approximately 16 hours was observed over seven field reaction tests conducted at both sites (with a range of 9 to 23 hours). These results corroborated those laboratory chamber tests that demonstrated an average experimental half life of 13 hours (6 to 20 hours).

2.0 RECOMMENDATIONS

A sampling method has been identified that provides a more accurate estimate of the atmospheric hexavalent chromium burden. The technique, an impinger, provides greater stability for Cr(VI) species during sampling than the currently used PVC membrane, but nevertheless does not provide the ideal conditions for fixing the Cr(VI) species. In addition, it is cumbersome to work with for personnel conducting the sampling. However, handling difficulties might be eased considerably if plastic impinger devices were used. This also would minimize blank problems associated with glass surfaces. If ultrapure or subboiled acids were used during sample preparation, these devices might also allow for Cr(III) quantitation. It is recommended that further work be performed to determine the feasibility of an alkaline- or neutral-buffered coating on a membrane filter. For example, glass (or quartz) fiber material could provide sites for a reagent coating, but would also pass an adequate air flow without sacrificing collection efficiency. In addition, the ease of removal of Cr(VI) species from the membrane must be evaluated. Any potential methods must be evaluated for stability over time; e.g., a 30-day storage period under a variety of conditions.

Further work is needed to evaluate the precision and accuracy of the ion chromatographic (IC) method. If an impinger sampling method is indicated as most suitable, the IC method involving the use of the preconcentration column must be subjected to a full-scale method evaluation as well. In addition to the above mentioned considerations, the technique should be carefully evaluated for potential interferences since the preconcentration column efficiency might be adversely effected by certain species commonly existing in the environment.

The reactivity of trivalent chromium was not closely examined in this study. While not a likely chemical pathway, the potential oxidation of Cr(III) should be studied due to the significance of any possible conversion scenarios. It is recommended that a few selected laboratory reactivity tests be conducted in the presence of manganese dioxide (MnO_2) under varying pH conditions. Subsequent to any findings indicating possible reactivity of Cr(III), additional laboratory tests might be conducted on available representative fly ash materials containing Cr(III), likewise in the presence of MnO_2, in order to simulate more realistic conditions.

Should results from these laboratory tests indicate potential Cr(III) reactivity, field tests should be conducted at Cr(III) emission sources [preferably low in Cr(III) emissions] to support these findings. Simultaneously, a field reactivity test might be conducted to parallel the laboratory test design.

3.0 INTRODUCTION

3.1 PURPOSE OF THE STUDY

The health hazards of certain substances have been found to be a function of the chemical forms of these substances. For example, arsenic (V) is carcinogenic, while arsenic (III) is only toxic. The same is true for chromium (VI) and chromium (III), respectively. Chromium (VI) has been identified by the California Air Resources Board (CARB) as an air contaminant and thus poses a potential health hazard. Of concern to CARB is the environmental fate of the chromium (VI) species. That is, airborne hexavalent chromium may be reduced to chromium (III), or it may settle out of the air as particulate matter or be washed out with precipitation. Of these possibilities, the primary concern and thus primary objective of this study, is the determination of the rates of reduction of Cr(VI) to Cr(III) in ambient air. The following three steps have been taken in meeting this objective:

- Identify, evaluate, and validate an accurate and precise methodology for sampling and analyzing the Cr(VI) species.
- Using this measurement methodology, expose Cr(VI)-containing particulate to a variety of potential reducing agents and/or reduction catalysts of the type expected in the ambient air and measure rates of any reduction observed.
- Perform a field measurement study for chromium species at three different sites in California near likely sources of Cr(VI) emissions, with the intent of determining the rate of conversion of Cr(VI) to Cr(III).

There have been a large number of techniques developed for the speciation of hexavalent and trivalent chromium. The most well established methods have been used primarily for samples collected at the chromium sources or in the industrial workplace (1-8). For both cases, chromium levels are much higher than those normally encountered in ambient air, and as a consequence, avoid certain problems frequently peculiar to ambient air analysis such as sensitivity, contamination, and sample (species) stability. However, a few techniques have been developed prior to this study that have shown promise in this particular application (4, 9, 10). CARB Method ADDL006 utilizes a complexation reaction with Cr(VI) followed by isolation and acid digestion of the complex. Measurement of the digest is by graphite furnace atomic absorption. An additional ion chromatographic method had been developed by an instrument manufacturer that shows promise.

The second phase of this study presented the greatest challenge. In order to conduct this phase of the study, an understanding of the physical and chemical properties of chromium aerosols was required. Individuals at RTI and elsewhere with atmospheric chemistry experience were consulted. Of primary concern initially was the selection of a suitable reaction chamber design in order to conduct simulated interactions of Cr(VI) and Cr(III) species with a variety of expected atmospheric reactants. RTI has a significant amount of experience with continuously stirred tank reactors (CSTRs) (11, 12). However, several investigators have observed problems with CSTRs when studying aerosols, including severe losses due to the static charge on the particle even when utilizing all metal (aluminized) chambers (13). An alternate configuration utilizes filters spiked with target species that are subsequently exposed to "interferent" atmospheres (14, 15). The degradation of the spiked species is measured over time to establish general reaction rate "trends" as a function of a particular reactant. This approach was utilized during the second phase of the study. Nevertheless, many unanticipated problems were encountered that required changes in design of this phase of the study.

The third phase of the study, the field test, was conducted with the goal of verifying the findings of the second phase in addition to conducting a limited ambient sampling program. CARB utilizes Method ADDL006, which involves sampling utilizing PVC membrane collection. RTI experience during the laboratory reactivity tests indicated that, under typical ambient sampling conditions, more than 50 percent of the Cr(VI) species may be expected to be reduced to trivalent chromium over a 24-hour period. An impinger sampler approach was utilized during the study in order to provide a closer estimate of the Cr(VI) concentrations in the atmosphere. In order to verify those results, a test configuration (similar to that conducted during the laboratory chamber tests) had to be utilized. As a consequence, filters were loaded with Cr(VI) from actual sources and exposed to environmental reactants in a manner analogous to the laboratory test configuration. On the basis of the laboratory reactivity tests, some adjustments were made immediately before, during, and after this field phase, which pertained mainly to the sampling approach.

3.2 COMPONENTS OF THE STUDY

The following components were included in the study:

- A thorough study of the literature, plus communication with experts to identify methods capable of providing the speciation (identification/measurement) of trivalent and hexavalent chromium in the ambient air samples. In addition, the literature was consulted to determine potential chemical pathways of both hexavalent and trivalent chromium species in atmospheres typical to those encountered in California.
- Testing those analytical methods selected for potential applicability and acceptability (appropriate recovery, precision, detection limit, etc.) by CARB for ambient air applications.
- Constructing an atmospheric test chamber that provides a means of predicting general trends in the atmospheric reactivity of hexavalent and trivalent chromium species, and conducting a series of reactivity tests that provide the general pathways expected in ambient air.
- Validation of the findings of reaction chamber tests through field tests conducted at ambient sites located in the Los Angeles area near two chromium emission sources, one a chrome plating facility and the other a cooling tower.

4.0 CHEMICAL REACTION SCENARIO BASED ON LITERATURE STUDIES

4.1 INTRODUCTION

A literature study and examination of the chemistry of Cr(VI) and Cr(III) has been performed in order to arrive at a scenario for the potential atmospheric reactions of these species in air. The approach taken has been first to study general inorganic texts and reports dealing with both the general chemistry and also the atmospheric chemistry of chromium. This has been followed by performance of a literature search and contact with experts regarding the atmospheric chemistry of chromium. Data collected includes proposed reactions along with corresponding equilibrium or thermodynamic data, atmospheric concentrations of potential reactants and estimated rates of reaction.

The texts reviewed presented some of the general chemistry of chromium including the acid/base equilibria and various complexation and precipitation reactions. Several major reports on chromium were acquired from the EPA, NTIS, etc. These deal principally with sources of atmospheric chromium (16) and the health effects of chromium (17, 18). They also present some basic inorganic chemistry of various chromium compounds and an overview of methods of analysis. A literature review on occurrence and methodology for determination of chromium species in air prepared by Battelle Columbus Laboratories in 1984 was acquired (19). The only selective analytical procedure for Cr(VI) identified in this study was the ASTM Method utilizing s-diphenylcarbazide as a selective complexing agent.

The most important report identified was that by Christian Seigneur of Systems Applications, Inc., entitled "A Theoretical Study of the Atmospheric Chemistry of Chromium" (20). This report presented a thorough review of the inorganic reactions of Cr(III) and Cr(VI), atmospheric concentrations of potential reactants, and conclusions about the potential reaction scenario for these two species. However, little information was presented about the reactions of these chromium species with organic compounds. Despite, this shortcoming, this report has served as the principal resource for preparation of this chapter.

The literature, though quite thorough, has not revealed any studies of the actual atmospheric chemistry of the chromium species. Several papers have indicated that Cr(VI) species would be expected to react with organic material and any reducing species such as Fe^{2+}.

Chromium ranks as the 21st element in the earth's crust in relative abundance and is more abundant than nickel, zinc, and copper. Chromium ion has oxidation states in compounds ranging from -2 to +6, but most commonly occurs as 0, +2, +3, and +6. Only +3 and +6 are found in stable form in natural materials. Cr(III) compounds are relatively stable in aqueous solution. The +3 ion is readily complexed to form octahedral, six-coordinate ions. The chemistry of the +6 oxidation state of chromium (especially CrO_4^{2-}) is very much like that of sulfate. However, free chromic oxide CrO_3 does not exist. In acid solutions, the dichromate ion ($Cr_2O_7^{2-}$) is favored and is a strong oxidizing agent.

The chemistry of the chromium species is quite complex. The type of reactions which can occur include the following:

- Adsorption
- Acid/base equilibria
- Complexation reaction
- Precipitation reactions
- Reduction/oxidation reactions

Each of these will be considered separately with regard to inorganic and organic reactants.

4.2 ADSORPTION

Natural highly oxygenated and/or ion exchange materials such as silicates can adsorb chromium species. A general reaction is as follows:

$$CrO_4^{2-}/Cr_2O_7^{2-} + \begin{matrix}\text{siliceous}\\ \text{particulate}\end{matrix} \text{------>} CrO_4^{2-}/Cr_2O_7^{2-}\text{:} \begin{matrix}\text{siliceous}\\ \text{particulate}\end{matrix}$$

Quantitative values for the extent of this reaction are not available.

4.3 ACID/BASE EQUILIBRIA

4.3.1 Cr(III)

The Cr(III) may be present in the form of its oxide, Cr_2O_3, or as soluble salts. Cr(III) in water and in the absence of ligands will exist as a complex molecule with six waters of hydration. Unlike the chromate and dichromate species which act as bases, the Cr(III) species is not basic in nature. It does undergo hydrolysis, however, which is described in a subsequent section.

4.3.2 Cr(VI)

The principal acid/base equilbria for Cr(VI) are as follows:

	k
H_2CrO_4 <------> $HCrO_4^-$ + H^+	1.21
$HCrO_4^-$ <------> CrO_4^{2-} + H^+	3.0×10^{-7}
$2CrO_4^{2-}$ + $2H^+$ <------> $Cr_2O_7^{-2}$ + H_2O	4.2×10^{14}
$H_2Cr_2O_7$ <------> H^+ + $HCr_2O_7^-$	large
$HCr_2O_7^-$ <------> H^+ + $Cr_2O_7^{2-}$	0.85
$2HCrO_4^-$ <------> $Cr_2O_7^{2-}$ + H_2O	35.5

At pH less than 0, dihydrogen chromate, H_2CrO_4 , becomes the predominant species. Between pH 1 and 5, which is the principal pH range for atmospheric aerosols, hydrogen chromate and chromate, $HCrO_4^-$ and CrO_4^{2-} , will be the dominant species. At high $HCrO_4^-$ concentration and low pH, dichromate, $Cr_2O_7^{2-}$, will be a major species.

Acidic species in the aerosols may exchange both protons and ligands with the chromium species. Possible reactions are:

	k
HSO_4^- + $HCrO_4^-$ <------> $CrSO_7^{2-}$ + H_2O	4.1 M^{-1}
HSO_3^- + $HCrO_4^-$ <------> $CrSO_7^{2-}$ + H_2O	36 M^{-1}
H^+ + Cl^- + $HCrO_4^-$ <------> CrO_3Cl^- + H_2O	11 M^{-2}
$HCrO_4^-$ + $H_2PO_4^-$ <------> $HCrPO_7^{2-}$ + H_2O	2.9 M^{-1}
$HCrO_4^-$ + H_3PO_4 <------> $H_2CrPO_7^-$ + H_2O	9.4 M^{-1}

4.4 COMPLEXATION AND LIGAND EXCHANGE REACTIONS

4.4.1 Cr(III)

A major reaction pathway for the Cr(III) species is hydrolysis. Possible reactions are as follows:

	k
$Cr(H_2O)_6^{3+} + H_2O \longrightarrow CrOH^{2+} + H_3O^+$	10^{-4} M
$Cr(H_2O)_5(OH)^{2+} + H_2O \longrightarrow Cr(H_2O)_4(OH)_2^+ + H_3O^+$	2.8×10^{-6} M
$Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3$ (s)	10^{30} M^4
$Cr(OH)_3$ (s) $+ OH^- \longrightarrow Cr(OH)_4^-$	0.40
$2CrOH^{2+} \longrightarrow Cr_2(OH)_2^{4+}$	10^4 M^{-1}

Additional possible reactions with other species likely to be present in the aerosols, including nitrate, sulfate, chloride and fluoride, are as follows:

	k
$Cr^{3+} + 3NO_3^- \longrightarrow Cr(NO_3)_3$ (s)	2.6 M^{-4}
$Cr^{3+} + SO_4^{2-} \longrightarrow CrSO_4^+$	1.38 M^{-1}
$2Cr^{3+} + 3SO_4^{2-} \longrightarrow Cr(SO_4)_3$ (s)	$7.7 \times 10^{+6}$ M^{-5}
$Cr^{3+} + Cl^- \longrightarrow CrCl^{2+}$	2.2×10^{-1} M^{-1}
$CrCl^{2+} + Cl^- \longrightarrow CrCl_2^+$	2.9×10^{-2} M^{-1}
$CrCl_2^+ + Cl^- \longrightarrow CrCl_3$ (s)	1.5×10^{-3} M^2
$CrCl_2^+ + Cr(OH)_2^+ \longrightarrow 2CrClOH^+$	2.5
$CrCl_2^+ + H_2O \longrightarrow CrCl_2OH + H^+$	10^{-6} M^1
$Cr^{3+} + F^- \longrightarrow CrF^{2+}$	2.6×10^4 M^{-1}
$CrF^{2+} + F^- \longrightarrow CrF_2^+$	2.5×10^3 M^{-1}
$CrF_2^+ + F^- \longrightarrow CrF_3$	3.0×10^2 M^{-1}

4.4.2 Cr(VI)

Reactions that involve ligand exchange are presented in Section 4.3.2 since they also involve proton transfer. Complexation reactions which lead to precipitation are presented separately in the following section.

4.5 PRECIPITATION REACTIONS

4.5.1 Cr(III)

Except for chromium oxide, Cr_2O_3, most Cr(III) species are quite soluble. Three possible, though not likely precipitation equilibrium reactions are as follows:

	k_{sp}
$Cr(NO_3)_3$ (s) <---> $Cr^{3+} + 3NO_3^-$	0.4 M^4
$Cr_2(SO_4)_3$ (s) <--> $2Cr^{3+} + 3SO_4^{2-}$	1.3×10^{-7} M^5
$CrCl_3$ (s) <------> $CrCl_2^+ + Cl^-$	1.5×10^{-3} M^2

4.5.2 Cr(VI)

Cr(VI), as compared to Cr(III), forms many relatively insoluble compounds. Possible precipitation equilibrium reactions are as follows:

	k_{sp}
$PbCrO_4$ <------> $Pb^{2+} + CrO_4^{2-}$	1.8×10^{-14}
Ag_2CrO_4 <------> $2Ag^+ + CrO_4^{2-}$	9.0×10^{-12}
$BaCrO_4$ <------> $Ba^{2+} + CrO_4^{2-}$	3.0×10^{-10}
$ZnCrO_4$:$4Zn(OH)_2$ <------> $Zn^{2+} + CrO_4^{2-} + 4Zn(OH)_2$	5×10^{-17}
$ZnCrO_4$ <------> $Zn^{2+} + CrO_4^{2-}$	1.1×10^{-5} M^2
$SrCrO_4$ <------> $Sr^{2+} + CrO_4^{2-}$	3.0×10^{-5}
$CuCrO_4$ <------> $Cu^{2+} + CrO_4^{2-}$	3.6×10^{-6} M^2
$CaCrO_4$ <------> $Ca^{2+} + CrO_4^{2-}$	2.3×10^{-2}
$K_2Cr_2O_7$ <------> $2K^+ + Cr_2O_7^{2-}$	4.9×10^{-3} M^3
K_2CrO_4 <------> $2K^+ + CrO_4^{2-}$	0.23 M^3
Na_2CrO_4 <------> $2Na^+ + CrO_4^{2-}$	3.65 M^3
$(NH_4)_2Cr_2O_7$ <------> $2NH_4^+ + Cr_2O_7^{2-}$	4.0 M^3
CrO_3 (s) <------> CrO_3 (aq)	6.2 M
$(NH_4)_2CrO_4$ <------> $2NH_4^+ + CrO_4^{2-}$	20 M^3
$Na_2Cr_2O_7$ <------> $2Na^+ + Cr_2O_7^{2-}$	5.1×10^2 M^3

4.6 REDUCTION/OXIDATION REACTIONS

4.6.1 Oxidation of Cr(III)

A number of airborne species can react with Cr(III) to form Cr(VI) species, though Cr(III) is not a strong reducing agent. Possible reactions are as follows:

$5H_2O + 2Cr^{+3} + 3O_3 \longrightarrow 2CrO_4^{2-} + 10H^+ + 3O_2$

$2H_2O + 2Cr^{+3} + 3H_2O_2 \xrightarrow{\text{(basic)}} 2CrO_4^{2-} + 10\ H^+$

$3H_2O + 2Cr^{+3} + 2MnO_4^- \xrightarrow{\text{(basic)}} Cr_2O_7^{2-} + 2MnO_2 + 6H^+$

$H_2O + 2Cr^{+3} + 3PbO_2 \longrightarrow Cr_2O_7^{2-} + 3Pb^{+2} + 2H^+$

$2Cr^{3+} + 6Mn^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 6Mn^{2+} + 14H^+$

4.6.2 Reduction of Cr(VI)

The Cr(VI) species are strong oxidizing agents and thus there are many possible reactions for this oxidation state of chromium. Several of the more likely atmospheric reactions are as follows:

$3V^{2+} + Cr(VI) \longrightarrow 3V^{3+} + Cr^{3+}$

$Cr(VI) + Fe(II) \longrightarrow Cr(III) + Fe(III)$

$2HCrO_4^- + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 5\ H_2O$

$2HCrO_4^- + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 8H_2O$

$2HCrO_4^- + 9I^- + 14H^+ + 4\ H_2O \longrightarrow 2Cr(H_2O)_6^{3+} + 3I_3^-$

$2HCrO_4^- + 4HSO_3^- + 6\ H^+ \longrightarrow 2Cr^{3+} + 2SO_4^{2-} + S_2O_6^{2-} + 6H_2O$

$2H_2AsO_3^- + 3Cr(VI) \longrightarrow 2Cr^{3+} + 3H_2AsO_4^-$

$2HCrO_4^- + 3H_2O_2 + 8H^+ \longrightarrow 2Cr^{3+} + 3O_2 + 8H_2O$

Though not given major significance by Seigneur, the reduction of the Cr(VI) species by organic compounds is, in fact, a major concern. Two reactions presented by Seigneur are:

$2Cr(VI) + 3HCOOH \longrightarrow 2Cr(III) + 3CO_2$

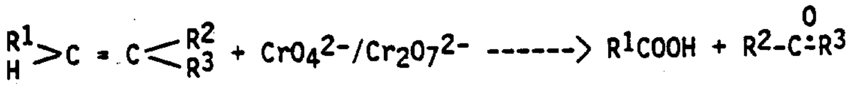
$2C_2H_5OH + 3Cr(VI) \longrightarrow 2CH_3COOH + 3Cr(III)$

Other reactions with organic species identified in the literature (21) are as follows:

$$R_3CH + CrO_4^{2-}/Cr_2O_7^{2-} \text{------}\!> R_3COH + Cr^{+3}$$

$$CH_3 + CrO_4^{2-}/Cr_2O_7^{2-} \text{------}\!> RCOOH$$

$$RCHO + CrO_4^{2-}/Cr_2O_7^{2-} \text{------}\!> RCOOH$$



$$\begin{matrix} R^1 \\ H \end{matrix}\!\!>C = C<\!\!\begin{matrix} R^2 \\ R^3 \end{matrix} + CrO_4^{2-}/Cr_2O_7^{2-} \text{------}\!> R^1COOH + R^2\text{-}\overset{O}{C}\text{-}R^3$$

$$PAH's + CrO_4^{2-}/Cr_2O_7^{2-} \text{------}\!> \text{quinones}$$

4.7 AVAILABILITY OF REACTANTS

The possibility of the reactions given above occurring depends upon the availability of reactants and reaction conditions, as each reaction is thermodynamically favored under conditions of unit activity. Doug Lawson of CARB and Tom Cahill of U.C.-Davis were contacted and air analysis data from a large study conducted in 1986 in the Los Angeles area were acquired. These data are presented in Table 4-1. As noted, metals that form "insoluble" precipitates with chromate, acid, ozone, hydrogen peroxide, and reactive organics are all present. A more comprehensive list found in the Seigneur report is presented in Table 4-2. The extent of reaction will depend both upon the "available" amount of these reactants and the aerosol matrix. The "available" or "reactable" amounts of each of these species is not known. To determine these amounts requires speciation of the inorganics, e.g., lead, and determination of whether the organic molecules are "free," adsorped on (or in) carbonaceous or siliceous material and/or complexed with a metal. The particle or aerosol matrix is also crucial. The two most important factors are the amount of water present and the acidity of this water, as the proposed reactions will occur only in solution. Experts have been contacted, and it appears that no one has determined the "solution" character of an aerosol or "wet" particle.

Despite these severe limitations, speculation about the most likely reactions based on thermodynamics, concentrations and kinetics measured in the laboratory can be made. This has been done by Seigneur and serves as the basis for the following sections.

TABLE 4-1
POTENTIAL REACTANTS IN LOS ANGELES BASIN AIR

Inorganics	Concentrations
Pb	0.1 - 0.4 $\mu g/m^3$
Ca	0.2 $\mu g/m^3$
Mn	0.03 $\mu g/m^3$
Zn	0.015 - 0.385 $\mu g/m^3$
SO_4^{2-}	3.6 - 11.8 $\mu g/m^3$
O_3	~ 200 ppb
H_2O_2	0.1 - 2.5 ppb
HNO_3	1 - 23 ppb

Organics	Concentrations
formaldehyde	4 - 22 ppb
acetaldehyde	2 - 15 ppb
TNMHC*	60% alkanes propane 67.8 ppbC n-pentane 43.5 ppbC isopentane 108 ppbC 15% alkenes ethylene 63.4 ppbC 25% aromatics toluene 116 ppbC benzene 42 ppbC p-xylene 69.6 ppbC
Organic carbon	5 - 9 $\mu g/m^3$
Elemental carbon	3 - 5 $\mu g/m^3$

*1218 ppb C on August 20, 1986

TABLE 4-2
TYPICAL RANGE OF ATMOSPHERIC CONCENTRATIONS OF CHEMICAL SPECIES INVOLVED IN CHROMIUM CHEMISTRY
(Seigneur)

AEROSOL SPECIES*		GASEOUS SOLUBLE SPECIES	
Chemical Species	Typical Concentrations	Chemical Species	Typical Concentrations
V	0.0013 to 0.022 $\mu g/m^3$	SO_2	10^{-3} to 10^{-2} ppm
Fe	0.026 to 0.59 $\mu g/m^3$	HCOOH	10^{-5} to 10^{-3} ppm
Mn	0.002 to 0.03 $\mu g/m^3$	C_2H_5OH	10^{-6} ppm
Ce	0.00002 to 0.0005 $\mu g/m^3$	H_2S	0 to 0.01 ppm
F	0.001 to 0.01 $\mu g/m^3$	HNO_2	10^{-6} to 10^{-5} ppm
Cl	0.01 to 0.09 $\mu g/m^3$		
Br	0.07 to 0.15 $\mu g/m^3$		
I	0.0004 to 0.003 $\mu g/^3$		
K	0.01 to 0.15 $\mu g/m^3$		
Na	0.05 to 0.35 $\mu g/m^3$		
Pb	0.045 to 0.72 $\mu g/m^3$		
Cu	0.003 to 0.028 $\mu g/m^3$		
Zn	0.007 to 0.10 $\mu g/m^3$		
As	0.0003 to 0.026 $\mu g/m^3$		
SO_4^{2-}	1.0 to 70 $\mu g/m^3$		
NO_3^-	0.0 to 4 $\mu g/m^3$		
NH_4^+	0.2 to 8 $\mu g/m^3$		
Ca^{2+}	0.01 to 0.25 $\mu g/m^3$		

*Concentrations reported are for fine aerosols (less than 2 μm in diameter).

4.8 REACTIONS BASED ON AVAILABLE THERMODYNAMIC, CONCENTRATION AND KINETIC DATA

4.8.1 Equilibrium Reactions

The report of Seigneur was reviewed and potentially significant reactions identified assuming a maximum upper limit for Cr(III) of 10 $\mu g/m^3$ and 10^{-4} g H_2O/m^3. These equilibrium reactions of Cr(III) are:

Reactant	Concentration	Potential Product	Product Formed?
OH^-	$10^{-10}M$	$Cr(OH)_3$	No
SO_4^{2-}	1 - 70 $\mu g/m^3$	$Cr_2(SO_4)_3$	No
NO_3^-	0 - 4 $\mu g/m^3$	$Cr(NO_3)_3$	No
F^-	0.001 - 0.01 $\mu g/m^3$	CrF^{x3-x}	99+% of Cr^{3+}
Cl^-	0.01 - 0.09 $\mu g/m^3$	$CrCl_3$	No
		$CrCl^{2+}$	30% of Cr^{3+}

Next to be considered are the Cr(VI) equilibrium reactions that are likely to occur based on concentrations available, including Cr(VI) at 10 $\mu g/m^3$ and H_2O at 10^{-4} g/m^3. Again the report of Seigneur was reviewed to identify such reactions; these reactions are:

Reactant	Concentration	Potential Product	Product Formed?
K^+	0.01 - 0.15 $\mu g/m^3$	K_2CrO_4	No
		$KCrO_4^-$	14% of CrO_4^-
		$K_2Cr_2O_7$	No
Na^+	0.05 - 0.35 $\mu g/m^3$	Na_2CrO_4	No
		$Na_2Cr_2O_7$	No
NH_4^+	0.2 - 8 $\mu g/m^3$	$(NH_4)_2CrO_4$	No
		$(NH_4)_2Cr_2O_7$	Only at high Cr(VI))/NH_4^+
Pb^{2+}	0.045 - 0.72 $\mu g/m^3$	$PbCrO_4$	Yes
Cu^{2+}	0.003 - 0.03 $\mu g/m^3$	$CuCrO_4$	No

Reactant	Concentration	Potential Product	Product Formed?
Zn^{2+}	0.007 - 0.10 $\mu g/m^3$	$ZnCrO_4$	No
		$ZnCrO_4{:}Zn(OH)_2$	Yes
Ca^{2+}	0.01 - 0.25 $\mu g/m^3$	$CaCrO_4$	No
SO_4^{2-}	1 - 70 $\mu g/m^3$	$CrSO_7^{2-}$	Only at high SO_4^{2-}
SO_2	10^{-3} - 10^{-1} ppm	$CrSO_6^{2-}$	Negligible

4.8.2 Reduction/Oxidation Reactions

The second major type of reaction to consider based on concentration of available reactants and laboratory-determined kinetics are the reduction/oxidation reactions. Potential reactions of Cr(III) to Cr(VI) are as follows:

Reactant	Concentration	Potential Product	Product Formed?
O_3	200 ppb	Cr(VI)	No
H_2O_2	0.1 - 2.5 ppb	Cr(VI)	No
MnO_2	0.03 $\mu g/m^3$	Cr(VI)	Significant if MnO_2 2+% of total Mn

Finally, we consider the oxidation reactions of Cr(VI). The predominant species in the pH 1 - 5 range found in the aerosols will be $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^-$. Seigneur calculated reaction rates based on kinetic data taken from the literature; reactions which could occur at significant rates at Cr(VI) concentration of 10 $\mu g/m^3$, H_2O at 10^{-4} g/m^3 and the reductant at its maximum concentration as presented in Table 4-2 are as follows:

Reactant	Concentration	Potential Product	Reaction Rate
V^{2+}	0.022 $\mu g/m^3$	Cr(III)	Rapid, 100+% per hour
V^{3+}	0.022 $\mu g/m^3$	Cr(III)	Moderate
VO^{2+}	0.022 $\mu g/m^3$	Cr(III)	Moderate
Fe^{2+}	0.59 $\mu g/m^3$	Cr(III)	Rapid

Reactant	Concentration	Potential Product	Reaction Rate
HSO_3^-	0.1 μg/m³	Cr(III)	Low
As^{3+}	0.026 μg/m³	Cr(III)	Low

4.9 CONCLUSION

Upon review of this data, it appears that several conclusions can be drawn. The first is that the Cr(III) species will consist principally as the soluble F^- and Cl^- complexes. Second, Cr(VI) will be precipitated as $PbCrO_4$ and probably as $ZnCrO_4{:}Zn(OH)_2$.

Oxidation of Cr(III) to Cr(VI) by MnO_2 is possible if the MnO_2 concentration is high enough. It is not likely that the MnO_2 concentration is high as it also acts as an oxidizing agent with NO_2, SO_2 and other reducing agents likely to be present. Therefore oxidation of Cr(III) to Cr(VI) is not expected to occur to any significant degree.

The reduction of Cr(VI) to Cr(III) does seem more probable. The reactions with V^{2+}, V^{3+} and VO^{2+} are rapid if such species exist in the aerosols. This is not likely since the HVO_4^- species is apparently the major environmental species (22). The reaction with Fe^{2+} is rapid, but again, this is a species not likely to exist in high concentration in the aerosols. One reaction likely to occur is the reaction with HSO_3^-. Finally there is the question of reactions with organic species. The concentrations reported for formic acid and ethanol by Seigneur are low and the reaction rates for these species are about 10^{-9} to 10^{-12} of those for the vanadium species and 10^{-7} to 10^{-8} of those for the HSO_3^- species; however, the concentration for total organic carbon is approximately 10^4 to 10^6 times the levels of these two organic species and 10^2 times the HSO_3^- species. (Table 4-1) This would indicate that the reaction of Cr(VI) with organic species is still slow relative to its reaction with HSO_3^- unless the HSO_3^- were lower than expected and the rates of reaction of the Cr(VI) with organic species other than formic acid and ethanol were much more rapid than those with these two species. In order to answer this question, more fundamental reaction kinetic studies will need to be performed and speciation of other substances which potentially react with Cr(VI) are necessary.

5.0 LABORATORY MEASUREMENT STUDIES

5.1 INTRODUCTION

The initial phase of this study involved the selection of an analytical technique capable of the speciation and measurement of the hexavalent chromium compounds in ambient air. Initially, a literature search was conducted to identify any potential techniques that would conform to the following criteria:

1. The method must provide adequate sensitivity for ambient air levels. Specifically, the method should be capable of detecting Cr(VI) at the approximately 5 ng level for a 15 m^3 air sample (or ~0.3 ng/m^3).
2. The method must be specific for Cr(VI). Cr(III) must not interfere with the method.
3. The method should be free of other interferents (i.e., free of those interferences found in ambient air under all expected conditions).
4. The method should be precise; the precision (C_V) should be ten percent or better at typical low ambient air levels; i.e., ~1 ng/m^3 or a total Cr(VI) sample loading of 10 to 15 ng.
5. The method should be reasonably rapid, and utilize instrumentation that is accessible to the typical small analytical laboratory.
6. The method should be fairly rapid and simple. Considerable care and expertise should not be required by the method.
7. If possible, the method should allow for the "simultaneous" measurement of both Cr(III) and Cr(VI) from the same sample.
8. If possible, the method should allow for the <u>in-situ</u> measurement of Cr(VI).
9. The method must be compatible with a sampling technique capable of collecting <u>and</u> preserving the Cr(VI) species.

Such a Cr(VI) sampling technique must have the following characteristics:

1. The device must be efficient; >95 percent.
2. Filters or impingers should be capable of passing air volumes of up to 15 m^3 in 24 hours or less.

3. The device must be capable of preserving the chromium oxidation state during the sampling period.
4. The chromium species should be efficiently removed from the sampling device with a minimum of simple manipulation.
5. The sampling material should be readily available and of minimal cost.

The sampling method ideally should be established prior to selection of the analytical/measurement methods. A wide variety of filters have been utilized for collection of ambient air particulate matter. These have included glass and quartz fiber filters, and polyvinylchloride (PVC) and Teflon membranes (23). Also, combinations of the above have been employed, such as Teflon-coated glass fiber (23). In addition, various paper filters have been utilized for the collection of ambient species.

Glass fiber filters generally exhibit excellent efficiency (>99 percent) for particles as small as 0.3 μM (24). However, glass fibers are generally not desirable for the determination of ambient levels of Cr(III) because of the difficulty in obtaining low blank values. In addition, extraction procedures invariably result in solutions that must be centrifuged prior to sample introduction into instrumentation. Cellulose paper filters (such as Scheicher and Schnell Fast Flow papers) tend to leave residues upon extraction, yet they are efficient and exhibit low pressure drops. Such devices have been used even for collection of gaseous species such as SO_2, NH_3, and HNO_3 when a coating has been applied (25-28). Even though such materials are potentially more reactive toward Cr(VI), they can readily accept various coatings that could be useful in Cr(VI) collection.

5.2 SAMPLING

Only two sampling devices were considered early in the study, PVC (5 μM) and Teflon (0.8 μM) membranes. The reasons for this included:

- Both devices were already in use by CARB; PVC for Cr(VI) and Teflon for total chromium sampling.
- Both devices have low background values for species to be collected (<3 ng Cr(VI) for PVC, <2 ng total Cr for Teflon).

- They do not impart any residue to the resultant extraction solution.
- Impinger solutions are considered relatively inconvenient to manipulate during both sampling and shipping.

PVC membranes were used throughout both the measurement study and the reaction chamber tests. While Teflon membranes are suitable for both species, they are somewhat less convenient to use for Cr(VI) analysis due primarily to the fact that they are not "wet" as easily as PVC by the Cr(VI) extraction solution.

However, it became clear from the results of the chamber tests that membranes (PVC or Teflon) may not be the ideal collection medium for Cr(VI). Throughout the chamber tests, it was consistently apparent that after 24 hours of exposure to a wide variety of typical atmospheric pollutants, Cr(VI) was decaying to Cr(III) at significant rates ranging from 50 percent to more than 90 percent. In addition, the flow rates used during the chamber tests ranged from 3 to 5 liters per minute instead of the 10 to 15 liters per minute used customarily by CARB during 24-hour sampling. Therefore, one might assume that during a typical 24-hour sampling period, one would obtain a very low estimate of the true Cr(VI) content, perhaps as low as ten percent. Since this conclusion was reached during the planning stages for the field study, it was felt that some reference device must be used in conjunction with the PVC filters to provide a comparison. It was felt that such a device must be able to stabilize the Cr(VI) species during collection. Since the scenario for conversion appeared to be low pH conditions in the presence of trace organics, it appeared that the need for some buffering action at neutral or higher pH was necessary. Also, the sample extract or resultant impinger solution should be compatible with both the CARB atomic absorption and the Dionex ion chromatographic measurement methods.

A pH 7 impinger solution appeared to be the most expedient approach to this problem. As a result, three such solutions were evaluated:

- Potassium acetate (0.01 M; pH ~7)
- Sodium acetate (0.01 M; pH ~7; ultra pure)
- CARB Method ADDL006 Buffer with the APDC Cr(VI) complexation reagent

The CARB reagent was prepared in the same manner as would be done during typical sample extractions. Smith-Greenberg impinger trains typically used for stationary source sampling (U.S. EPA Method 5) were employed in these experiments. One hundred milliliters of the test solution were placed in each of three impingers in series. One hundred nanograms of Cr(VI) (as $K_2Cr_2O_7$) was placed in the first impinger. The impinger assembly was placed outside the RTI laboratory and air was drawn through at flow rates of 30 to 40 Lpm for six hours. In parallel to the impinger train containing Cr(VI) was a second impinger train containing no Cr(VI), to serve as a control. Subsequent to sampling, the test solutions were carried through the CARB complexation/atomic absorption analytical method; i.e., pH adjustment to 4.8 followed by extraction, absorption on the Sep-Pak material, desorption, and graphite furnace atomic absorption analysis. The first test compared potassium acetate and Method ADDL006 solutions. After correcting the resultant Cr(VI) levels for the control sample Cr(VI) values, a recovery of 56 percent was obtained for the Method ADDL006 solution, whereas 108 percent of the Cr(VI) was recovered from the potassium acetate solution. An additional test was run under the same conditions. A similar trend was observed--109 percent recovery for the acetate solution and only 24 percent recovery for the CARB buffer. One drawback to the acetate solution was the somewhat high Cr(VI) blank level--approximately twice that of the Method ADDL006 reagent. As a consequence, an ultra pure reagent from Spex Industries, 99.999 percent pure sodium acetate, was purchased. This reagent yielded blank values that were one-third that of the potassium salt. A third test conducted under the same conditions as the first two tests yielded 102.5 percent recovery in the acetate buffer (0.01M) and <20 percent recovery for the CARB buffer. As a consequence, it was felt that an impinger sampler would provide a useful reference value for comparison with the PVC filters, or even be relied upon to provide the bulk of the Cr(VI) data from the subsequent field tests.

In the subsequent field test, personnel from both CARB and Entropy Environmentalists conducted ambient sampling at a chrome plating facility in the Los Angeles area. This field test is further described in the section entitled "Field Studies." Analysis by CARB personnel of the CARB field samples indicated that the RTI-type sampler provided levels of Cr(VI) that were from four to 27 times that obtained from the CARB PVC filters. These results are included in Appendix A.

5.3 MEASUREMENT

The analytical method developed at CARB involving complexation/extraction followed by graphite furnace atomic absorption (GFAA) was the first to be evaluated. Briefly, the method involves the complexation of Cr(VI) with ammonium pyrollidine dithiocarbamate (APDC) at a pH of 4.5. The complex is then absorbed on a resin and desorbed with acetone. The residue of the evaporated acetone extract is digested in nitric acid and analyzed by GFAA (Appendix B). Initial experiments entailed the spiking of laboratory pure water with chromium levels ranging from 10 to 50 ng (Table 5-1). Blanks showed Cr(VI) levels as high as 70 ng, higher than the highest spiking. Possible sources of contamination considered at this time included the Ultrex nitric acid and the acetone used to extract the chromium complex from the sorbent. Evaporating to dryness two grades of acetone (semiconductor grade and HPLC grade), dissolving the residue with Ultrex nitric acid (0.2 mL) and bringing to two (2) mL volume with laboratory pure water, no significant chromium levels were detected (<5 ng). Three additional sources of contamination were considered:

- Glassware
- APDC
- Buffer solution

When the buffer and APDC solutions used in the procedure were analyzed directly by GFAA, less than one nanogram per milliliter (1 ng/mL) was detected at this time. During a recovery study using spikes of 1 to 40 ng of Cr(VI), high blanks were still observed (>25 ng). Evaluating water as a source of contamination proved to be somewhat problematic. Fifty mL aliquots of water in scrupulously clean glass beakers were brought to near dryness, dissolved in 0.2 mL Baker Instra analyzed or Ultrex HNO_3 and diluted to 2 mL with laboratory pure water. One to eight nanograms of Cr(VI) were detected with no significant difference indicated between Ultrex and Baker Instra analyzed nitric acids. A comparison of several in-house

TABLE 5-1
SOLUTION SPIKING RECOVERY RESULTS

Cr(VI) Spike (ng)	Cr(VI) Spike Recovery (ng)	$\bar{X}$ (ng)
0	17.4, 19.0	18.2
10	19.2, 25.0	22.1
30	19.2, 43.0	31.1
50	49.2, 45.6	47.4

laboratory pure water systems showed no difference or significant water levels--approximately 2 ng per 50 mL of water. Laboratory pure water supplied by CARB contained about 7 ng Cr(VI) per 50 mL versus 6 ng Cr(VI) per 50 mL with RTI pure water.

At this point it was decided to reevaluate the possible contamination of the APDC reagent. One hundred mL of the APDC solution were extracted with 40 mL of chloroform. Subsequent analyses of three blanks yielded acceptably low Cr(VI) values--approximately 4 ng Cr(VI) per 50 mL of extraction solution. A brief recovery study of blanks and 40 ng spikes again showed blanks of 4 ng or less and recoveries of the spikes averaging 92 percent. It can only be speculated that there had been an indeterminate analytical error in the previous analysis of the APDC solution. A series of precision/recovery tests was then conducted using spiked solutions and PVC filters. Again, loadings were in the range of 10 to 50 ng. Results, which are shown in Table 5-2, indicate that recoveries exceeded 95 percent and the precision ranged from 3.0 to 9.8 percent C.V.

A technique based on the EPA Coprecipitation Method 218.5 (29) was evaluated next. This method, which is included in Appendix C, involved the precipitation of Cr(VI) species with lead nitrate at pH 3.5 ± 0.3, followed by centrifugation, dissolution of the precipitate in nitric acid, and measurement of the digest by GFAA. The initial recovery study performed on spiked solutions ranging from 10 to 80 ng showed poor recoveries below 40 ng (Table 5-3). Three deviations from the method were employed:

- The method was operated at Cr(VI) levels much lower than that for which it was originally designed.
- Plastic (instead of glass) centrifuge tubes were used.
- The final dissolution volume was much lower (2 mL) than the 50 to 100 mL called for in the method.

The use of glass tubes yielded similar recoveries in the 0 to 40 ng range--50 to 69 percent. It was observed from these tests that with normal centrifuging the precipitate was spread around the wall of the tubes instead of at the bottom. Therefore, when the supernatent liquid was decanted, it was proposed that much of the precipitate was carried away, resulting in low recoveries. It was decided to allow the solutions to sit

TABLE 5-2
RECOVERY STUDY
CARB METHOD ADDL006

Sample	ng Recovered	ng, Blank Corrected	Percent Recovery	
SOLUTIONS				
Blank #1	4.2			
Blank #2	5.4			
10 ng Spike #1	13.5	8.7	87.0	
#2	15.1	10.3	103	98.8 ± 9.5
#3	15.7	10.3	109	CV = 9.5%
#4	14.4	9.6	96.0	
25 ng Spike #1	32.9	28.1	112	
#2	28.0	23.2	92.8	104 ± 10.3
#3	29.5	24.7	98.8	CV = 9.8%
#4	33.2	28.4	114	
50 ng Spike #1	55.4	50.6	101	
#2	48.8	44.0	88.0	95.5 ± 5.6
#3	53.8	49.0	98.0	CV = 5.8%
#4	52.2	47.4	94.8	
FILTERS				
Blank #1	4.1			
50 ng Spike #1	51.3	46.6	93.2	
#2	57.5	52.8	106	99.1 ± 5.0
#3	55.0	50.3	101	CV = 5.0%
#4	55.2	50.5	101	
#5	52.3	47.6	95.2	
25 ng Spike #1	28.2	23.5	94.0	
#2	29.1	24.4	97.4	$\bar{x}$ = 96 ± 14
#3	30.8	26.1	104	CV = 14.7%
#4	23.1	18.4	73.6	
#5	32.4	27.7	111	w/o Result #4
				$\bar{x}$ = 102 ± 7.5
				CV = 7.4%

TABLE 5-3
RECOVERY STUDIES
EPA METHOD 218.5

Spiking Level (ng)	Mean Recovery (ng) N=2	Percent Recovery
0	<2	---
10	2.7	27
20	18.2	67
40	34.8	87
80	72.0	90

overnight following the precipitation step to localize the lead chromate precipitate. However, analysis of the resulting precipitate again yielded low recoveries (29 to 57 percent) over the 10 to 80 ng range. It is possible that the use of an ultracentrifuge may overcome the recovery problem at the 0-50 ng level. However, at this point, due to the lack of access to such instrumentation, it was decided to cancel further tests.

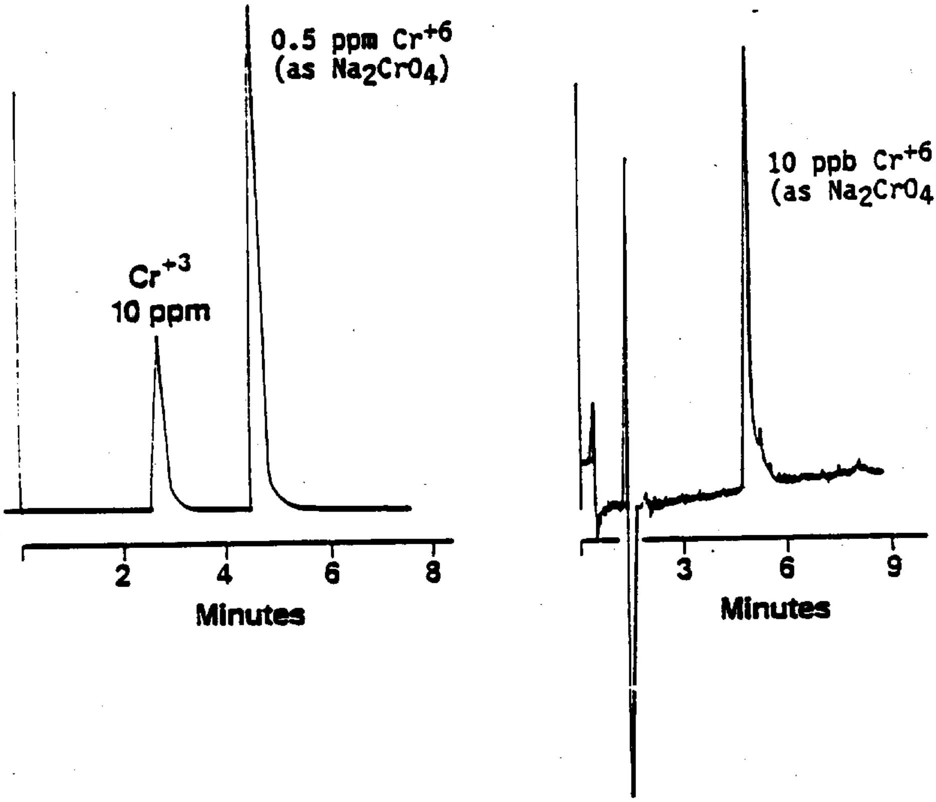
The other two analytical methods considered for Cr(VI) speciation involved ion chromatography (IC). Dionex Corporation provided the required equipment for these experiments, as well as the basic chromatography details. These methods are described in detail in Appendices D and E. In summary, hexavalent chromium ions are separated in an ion chromatographic transition metals column possessing both anionic and cationic character. The hexavalent chromium, once separated (by anion exchange), is complexed with the diphenyl carbazide (DPC) color reagent and the visible absorbance is measured photometrically at 520 nm. Although the system is capable of also detecting Cr(III), this latter determination is relatively insensitive for ambient applications. It was assumed that this method would only be suitable for the analysis of filter extracts due to the expected detection limit of 0.3 ng per liter of extract. The analysis of a series of standards in the laboratory yielded a detection limit at least as low as that advertised by Dionex Corporation. If Cr(VI) were collected on a membrane filter and desorbed (for example, in 5 mL of eluent), then the method would have more than adequate sensitivity. Three filters were spiked at the 10 ng level and desorbed in 5 mL of the eluent solution. This was accomplished by placing the filter in a culture tube, adding the solution, covering with parafilm, and manually shaking for one minute. The extract was then manually injected into the ion chromatograph (a Dionex Model 14) equipped with a 250 µL sample loop. Recoveries of 25-50 ng Cr(VI) for two filter types averaged better than 90 percent; the precision was better than seven percent (Table 5-4). It was concluded that the method was rapid [<five minutes elapsed time from sample preparation to measurement of Cr(VI)], sensitive, and precise. A typical chromatogram is shown in Figure 5-1. However, at this time, it was determined in separate experiments that the stability of Cr(VI) on membrane filters was not acceptable during ambient air sampling, and as a consequence, it was felt that a

TABLE 5-4
ION CHROMATOGRAPHY--FILTERS

Sample	ng Recovered	Percent Recovery	
PVC FILTERS			
50 ng Spike #1	50.0	100	
#2	51.7	103	102.2 ± 2.2
#3	52.5	105	CV = 2.1%
#4	50.0	100	
#5	51.7	103	
25 ng Spike #1	24.6	98.2	
#2	23.3	93.1	95.2 ± 3.7
#3	22.4	89.7	CV = 3.9%
#4	24.2	96.6	
#5	24.6	98.2	
1% NA_2CO_3 COATED WHATMAN 41 FILTERS			
50 ng Spike #1	49.1	98.2	
#2	48.2	96.4	99.8 ± 2.7
#3	50.0	100	CV = 2.7%
#4	51.8	104	
#5	50.5	101	
25 ng Spike #1	22.7	90.9	
#2	26.5	106	98.3 ± 6.7
#3	24.6	98.2	CV = 6.8
#4	26.0	104	
#5	23.2	92.7	

Summary of Conditions

Sample Size:	250 µL
Columns:	HPIC-CG5, Cation Guard Column HPIC-CS5, Cation Separator Column
Eluant Flow Rate:	1.0 mL/min
Post Column Reagent Flow Rate:	0.5 mL/min
Detection:	VIS at 520 nm



(A) Separations of Cr^{+3}, Cr^{+6}

(B) Typical Ambient Air Sample Extract

FIGURE 5-1
TYPICAL POST COLUMN REACTION CHROMATOGRAMS

buffered impinger solution (pH ≥7) that allows for the stabilization of the Cr(VI) species should be employed for sampling. Dionex Corporation recommended that a preconcentration technique be employed prior to injection onto the column to compensate for the larger volume associated with the impinger (30). A schematic of the IC system with and without a concentration column is shown in Figure 5-2. Instead of using a 250 μL injection loop, the Cr(VI) from solution samples of up to 50 mL might be concentrated onto a smaller column initially, then "injected" onto the separator column for separation and photometric detection. Theoretically, this could result in a Cr(VI) concentration factor of up 200X. A calibration curve was prepared in the one to five ng range. The calibration curve linearity was quite acceptable, yielding a correlation coefficient $\underline{r}$ of $>$0.999. The limit of detection was calculated to be approximately 0.1 ng corresponding to an air concentration of approximately 0.01 ng/m^3, assuming a 14 m^3 air sample drawn through a membrane filter (assuming a suitable one was developed). However, this level is somewhat unrealistic since the minimum detectable quantity will be related to the blank value of the analyte. One limit to the volume of sample extract used during preconcentration is the strength of buffer used in the extraction of a filter or in an impinger. A solution too high in ionic strength will result in the overloading of the preconcentrator column, or breakthrough of the Cr(VI) species prior to injection of the preconcentrator column contents onto the analytical column. Figure 5-3 depicts this breakthrough effect of Cr(VI) when dissolved in 0.05 M Na_2CO_3. After only two milliliters of solution are loaded onto the preconcentrator column, breakthrough begins to be evident. Based on these tests, it is evident that the weakest possible concentration of buffer required to stabilize Cr(VI) species during sampling must be utilized. Subsequent tests utilizing a 0.02 M Na_2CO_3 sample solution show that the Cr(VI) response is linear to approximately 10 mL.

A brief interference study was conducted utilizing interferent loadings up to 20 times that of typical environmental levels. Experimental parameters shown in Table 5-5 result in less than ten percent change in recovery over the control sample. Analysis of the same samples using CARB AA Method ADDL006 indicate a 20-24 percent loss in recovery compared to the

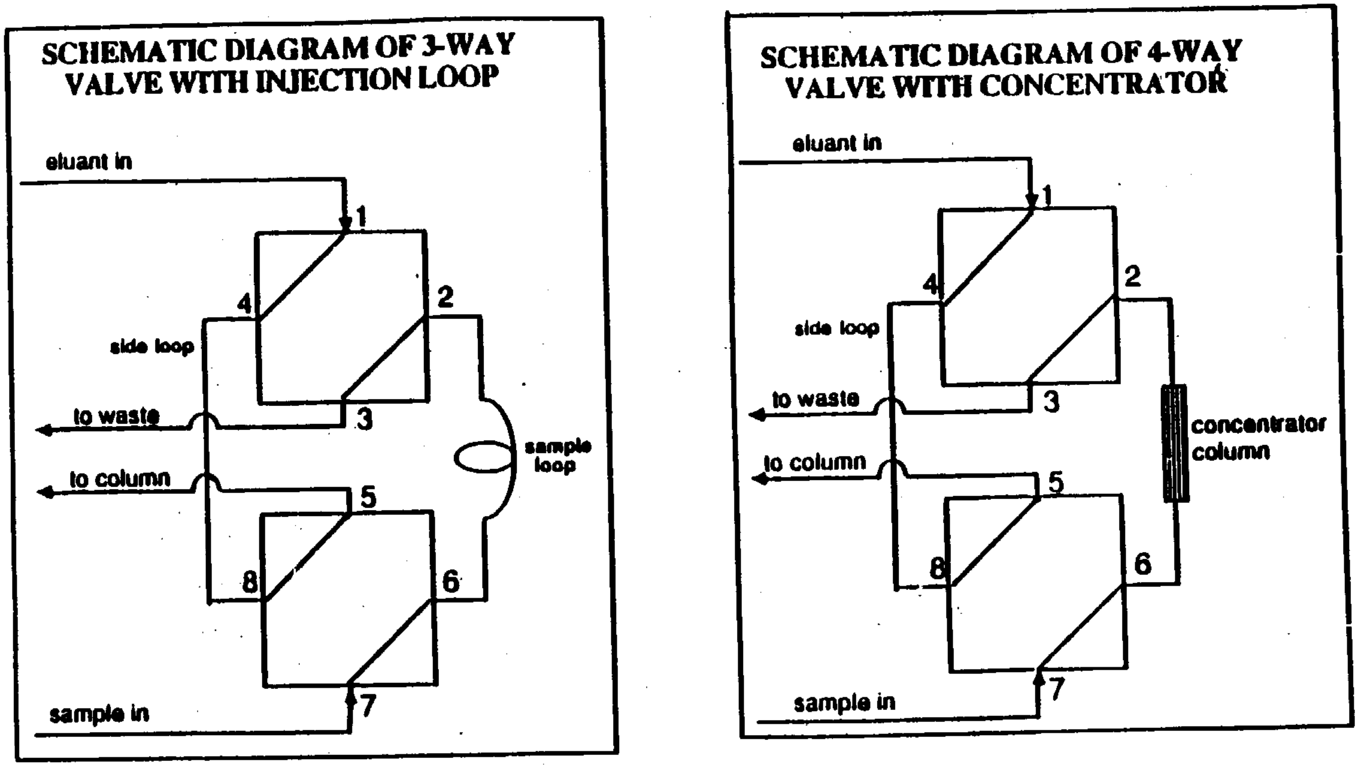


FIGURE 5-2
ION CHROMATOGRAPHIC SCHEMATICS
WITH AND WITHOUT PRECONCENTRATION SAMPLES

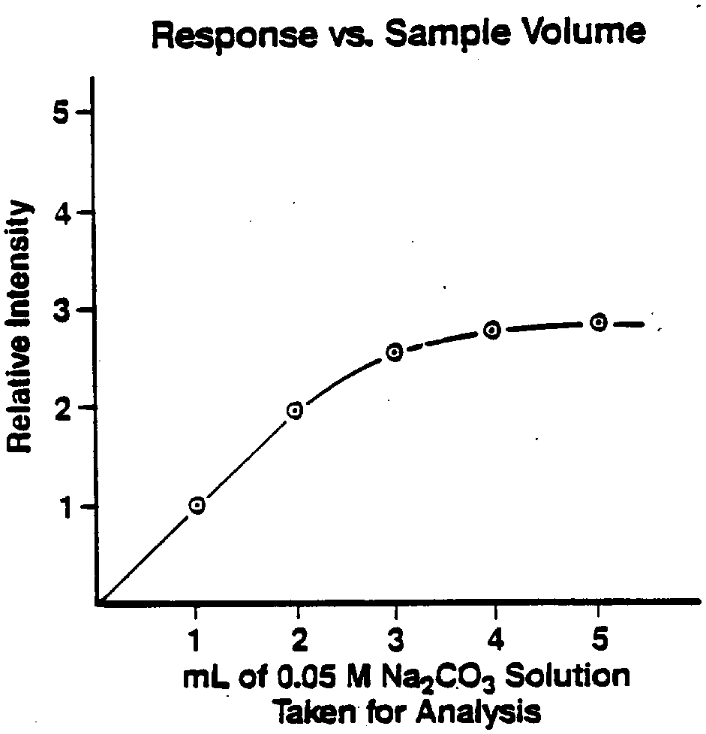


FIGURE 5-3
ION CHROMATOGRAPHY--PRECONCENTRATION METHOD

TABLE 5-5
INTERFERENCE STUDY PARAMETERS

Species	A (ng)	B (ng)
Cr(VI)	25	50
Pb	1,000	2,000
Ag	50	100
Ba	50	100
Ca	50,000	100,000
Mn	50	100
Fe	10,000	20,000
$SO_4^=$	25,000	50,000

control samples. A detailed procedure outlining the preconcentration ion chromatographic technique is shown in Appendix E.

A brief stability study was conducted for sample solutions collected using the acetate impinger sampling technique. The study was conducted over a thirty-day period. Two solution types were evaluated--one with Cr(VI) spiked into pure impinger solutions and the second spiked into actual field impinger solutions. Results obtained by ion chromatographic analysis indicated almost complete conversion.

Subsequent studies with 0.02 M Na_2CO_3 buffer solutions demonstrated excellent stability. The reanalyses of four field impinger samples after 60 days in storage demonstrated no measurable conversion (see Table 5-6).

Recently an additional technique has been evaluated by the Texas Air Control Board (31). This method involves collection of the hexavalent species employing a glass fiber high volume sample filter. Plugs are removed with a device such as a cork borer and are desorbed in a weakly alkaline solution containing ethylene diamine. The resulting extract is divided into two portions. To one portion is added an ion exchange resin to selectively remove Cr(VI). The total chromium content in each solution is then measured using inductively coupled plasma emission spectrometry (ICP). The Cr(VI) levels are then obtained by difference between the two values. The method is described as being labor-intensive and, in its present form, appears to lack the required sensitivity for ambient applications. A minimum detectable Cr(VI) air concentration of 5 ng/m^3 is quoted, as opposed to less than 0.5 ng/m^3 for the CARB method or either ion chromatographic technique. In addition, this detection limit is obtained using a 2000 m^3 sample instead of the 10-20 m^3 utilized in the other techniques described in this report. It may be possible to improve this detection limit by utilizing graphite furnace atomic absorption for chromium measurement. However, a major drawback involves the indirect measurement of the Cr(VI) species. If Cr(III) values are high (e.g., greater than 200 ng/m^3), low values of Cr(VI) (e.g., less than 20 ng/m^3) will be difficult to measure. A measurement precision of, e.g., five percent, represents 20 ng/m^3 of Cr(VI) at the 200 ng/m^3 level of total chromium! This latter drawback appears to be the greatest impediment to the method's applicability to ambient air measurements.

TABLE 5-6
FIELD SAMPLE STABILITY STUDY[a]

	Sample A	Sample B	Sample C
Sampling Date	2/11/88	2/11/88	2/23/88
1st Analysis Date	3/1/88	3/1/88	3/1/88
2nd Analysis Date[b]	4/10/88	4/10/88	4/10/88
1st Analysis (ng/mL)	6.0	8.2	2.7
2nd Analysis (ng/mL)	6.2	8.8	2.9

[a] Samples in 0.02 M Na_2CO_3 matrix, analyzed by ion chromatography, preconcentration method

[b] Samples stored at 4°C (refrigerated)

6.0 REACTION CHAMBER TESTS

6.1 INTRODUCTION

The chamber reaction studies, which were designed to simulate those ambient conditions to which Cr(VI) species would be exposed, were conducted in the following overall manner:

1. Eight or more 37 mm membrane filters (Teflon or PVC) were spiked with levels of Cr(VI) (ranging from 20 ng to 1,000 ng, depending on the test conditions). Initially, this was performed by pipetting known quantities of solutions onto the filter and then drying at room temperature in a vacuum dessicator. Later, the Cr(VI) spiking was performed by creating an aerosol with an inhaler device and allowing the aerosol to merely deposit without pumping onto the filter surface. The aerosol was created inside a plastic can with a fan inside to disperse the aerosol as much as possible, thereby optimizing the uniformity. Nevertheless, since some inhomogeneity was anticipated, CARB suggested the use of a lithium internal standard in the solution to be aspirated. In this way, the lithium content could be measured, in addition to the Cr(VI) species, in order to provide a means of monitoring the variability in the Cr(VI) loadings. A schematic of the aerosol generator is shown in Figure 6-1.
2. Six of these filters were placed in a sampling manifold containing 37 mm polystyrene filter holders with backup pads.
3. The sampling manifold was located in the environmental chamber. Initially, the chamber was one constructed of plexiglass or other plastic materials wherever possible. A schematic of the initial test chamber design is shown in Figure 6-2. Later, the design of the chamber was changed (for reasons to be explained in this section) to that of an all-aluminum design. An aluminum "suitcase" approximately 2 feet x 2 feet x 1 foot was fitted for a gas reactant inlet and for the sampling manifold (Figure 6-3).

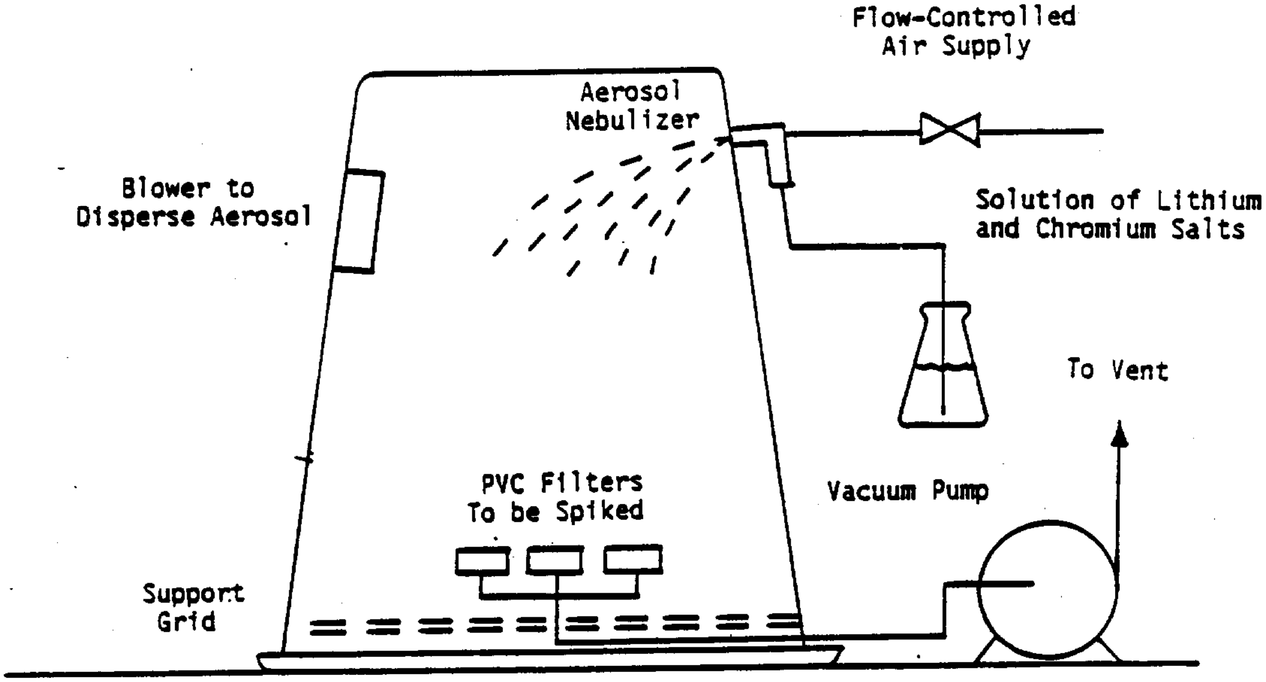


FIGURE 6-1
AEROSOL SPIKING SYSTEM

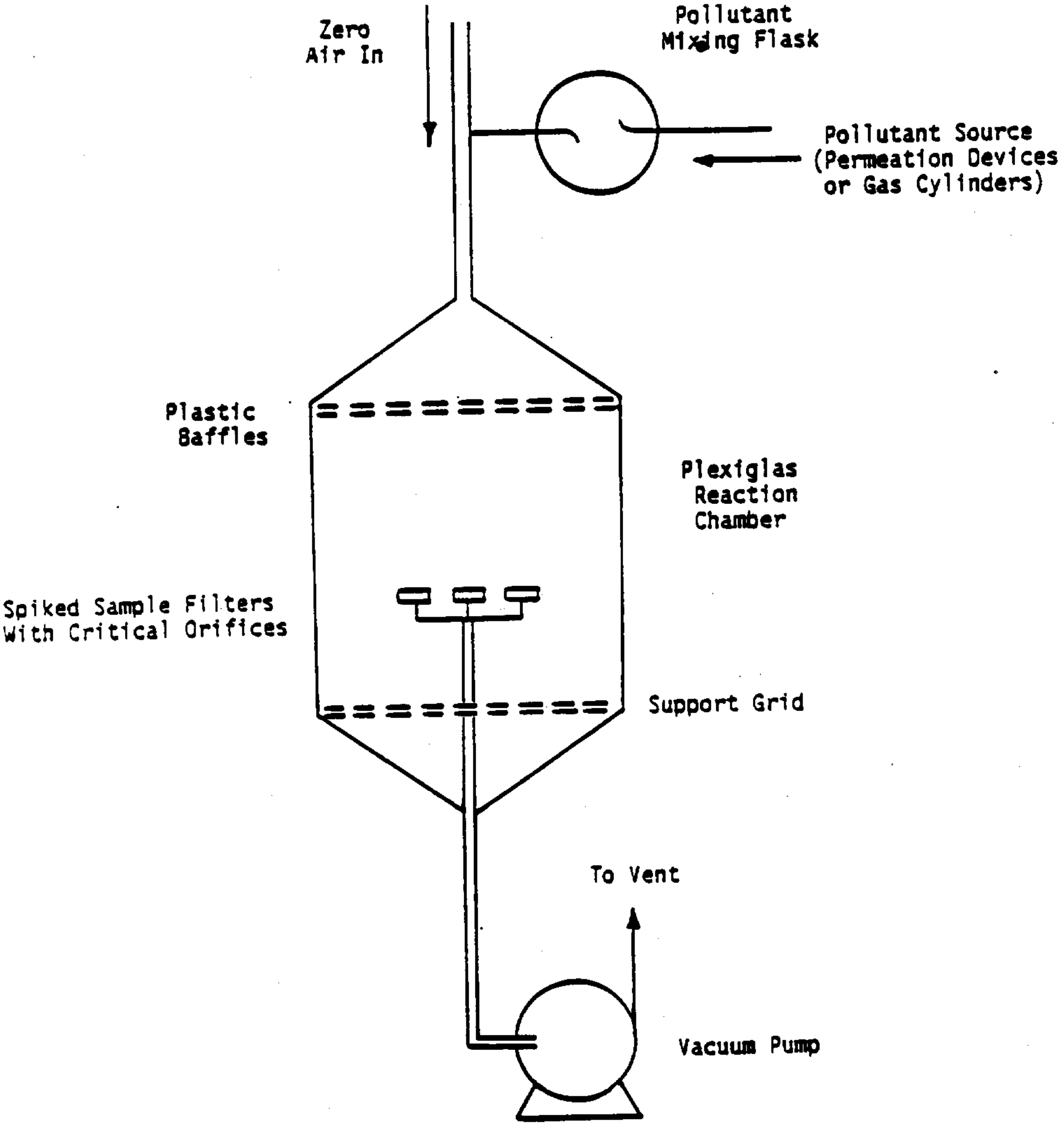


FIGURE 6-2
PLEXIGLAS REACTION CHAMBER

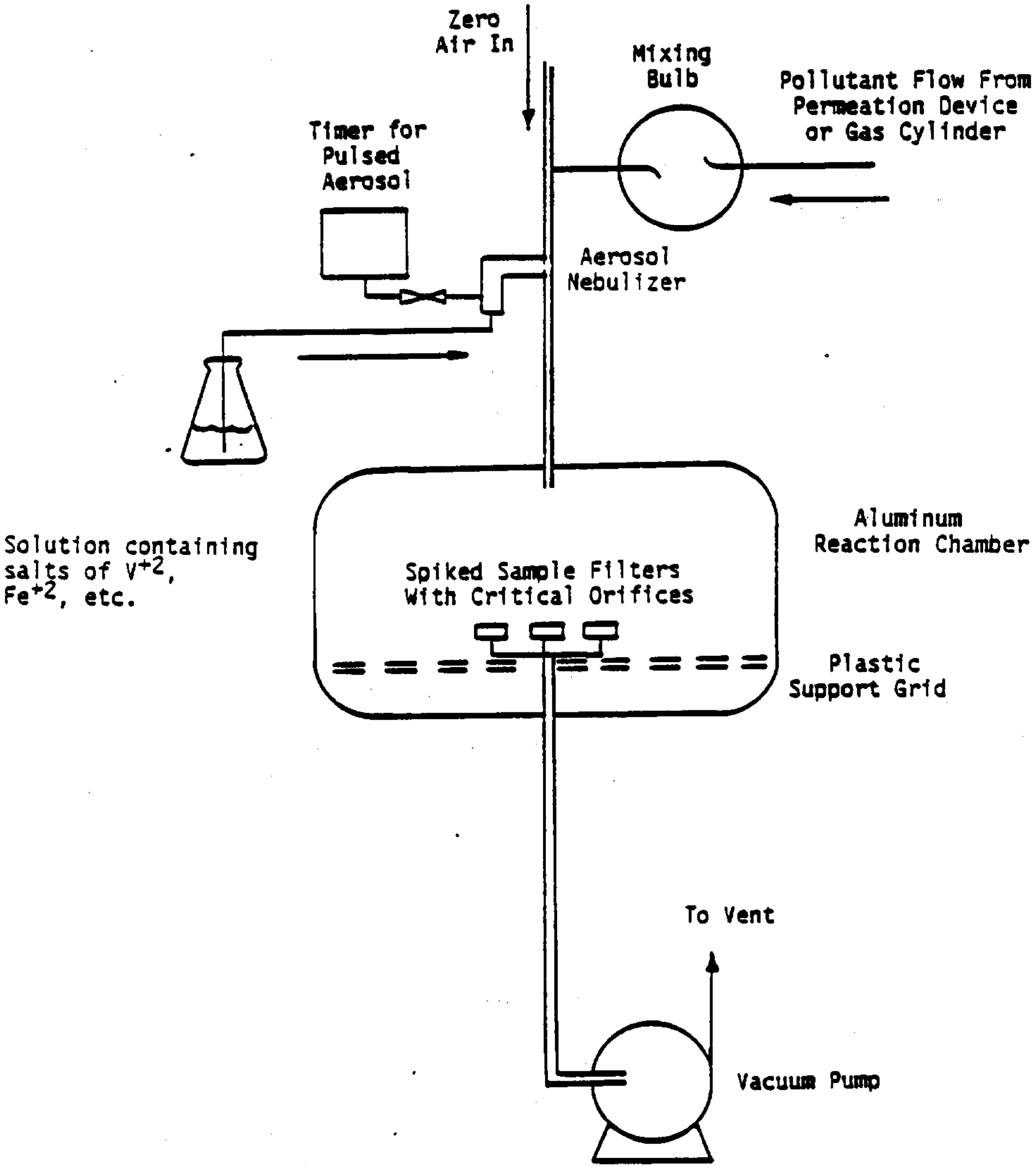


FIGURE 6-3
ALUMINUM REACTION CHAMBER

4. During exposure to the various test reactants, a sampling flow of 3 to 5 Lpm was maintained through each filter. A calibrated critical orifice was used to regulate flow through each filter.
5. Pollutants were introduced into the top of the chamber by a variety of means. Ozone was generated by an ozone generator utilizing pure oxygen irradiated by an ultraviolet source. Atmospheres of species such as SO_2, NO_2, xylene, and benzene were prepared from dilutions of gas cylinder concentrations. Nitric acid (HNO_3) and formaldehyde (HCHO) were generated from permeation devices available from Vici-Metronics (Santa Clara, CA). The verification of HNO_3 concentration was performed by sampling in parallel with a nylon filter, desorbing the filter in an aqueous medium, and performing an ion chromatographic analysis of the resultant nitrate ion. Formaldehyde levels were monitored using hydrogen peroxide impinger samples and subsequent ion chromatographic analysis of the formate ion. A number of other species were evaluated in these tests, and test conditions regarding these potential reactants will be described in detail later in this section.
6. During the test, two filters were removed at each predesignated time interval. For instance, it may have been decided to remove the first two filters after eight hours, two more after 20 hours, and the last two after 40 hours.
7. The filters were then analyzed using CARB Method ADDL006. A portion of the Cr(VI) extract was saved and analyzed for the lithium content to correct for any variability in the aerosol deposition.

6.2 EXPERIMENTAL

The individual tests will be described in detail in this section. Initial tests were conducted to identify the major actors in Cr(VI) reactivity. Levels used were not intended to closely simulate ambient conditions. Also, the early tests served to evaluate the experiment test design and equipment. For instance, after Test 16, the aluminum chamber was used because of large levels of reactive organic species off-gassing from the plastic chamber and adhesives causing considerable Cr(VI) conversion, <u>but</u> only in the presence of HNO_3 or HCl species. It was therefore learned in these early tests that low pH and the presence of reactive oxidizable species were the major factors in Cr(VI) reduction. Later tests simulated more closely those ambient conditions found in the Los Angeles area in 1986. Table 4-1 provided a basis for the later chamber experimental conditions. However, for simplicity, only one oxidizable species was used at any one time. Since levels of organic species in Los Angeles might be expected to reach more than 200 ppb, this was represented by one compound at the 200-300 ppb level. Generally, species such as HNO_3, O_3, and formaldehyde were maintained at realistic levels. HCl was used in place of HNO_3 in one test to determine if the H^+ contribution from HNO_3 was the major issue or if HNO_3 was playing a more direct role in the oxidation/reduction scenario. (The former appeared to be the case.)

Summary data for the thirty-two test runs are included in Table 6-1. Also, plots of each test showing Cr(VI) loadings versus time are shown in Figures 6-4 through 6-28.

Test 1. Eight filters were spiked with 1 µg Cr(VI) each by means of a 1 mL pipet. The filters were then exposed in the plexiglas chamber to a nitric acid aerosol concentration of eight parts per billion by volume (ppbV) and formaldehyde at a concentration of 68 ppbV. Due to incorrect experimental calculations, an unrealistic level of 3 ppm NO_2 was added to the system. The relative humidity ranged from 78 to 95%. Air temperature in this test and subsequent tests was 25°C. The test atmosphere was drawn through the filters at a rate of 4.7 Lpm. Two filters each were removed and analyzed for Cr(VI) content, after 8, 24, and 48 hours. Two additional unexposed filters were analyzed for a "time zero" reference value (t_0). After 8 hours, 28% conversion was observed, and nearly 98% conversion was detected after 24 hours. It was subsequently determined that the Cr(VI) species ($K_2Cr_2O_7$) had been inadvertently spiked onto cellulose ester membranes instead of PVC. This was significant in light of the following two test results.

Test 2. The test conditions were similar to those for Test 1 except that PVC membranes were spiked (1 µg) and the humidity was less than 10%. Filters were removed at 4, 7, and 24 hours. Eleven (11) percent conversion was observed after 24 hours.

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES

Chamber[a] Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
1	HNO_3--7.7 ppbV HCHO--68 ppbV O_3--100 ppbV NO_2--3,000 ppbV SO_2--25 ppbV RH--80 to 90%	1,000	470 (8 hr)	20 (24 hr)	20 (48 hr)	98
2	HNO_3--6.7 ppbV HCHO--41 ppbV RH--<10%	1,000	870 (4 hr)	830 (7.5 hr)	890 (24 hr)	11
3	HNO_3--8.1 ppbV HCHO--50 ppbV RH--60-90%	1,000 (4 hr)	~1,000 (7 hr)	~1,000 (24 hr)	920	8
4	HNO_3--46 ppbV HCHO--35 ppbV RH--<10%	750	708 (4 hr)	788 (8 hr)	760 (24 hr)	<5
5	HNO_3-none added HCHO--671 ppbV RH--80%	671	601 (4 hr)	636 (8 hr)	555 (24 hr)	17
6	HNO_3--46 ppbV HCHO--35 ppbV RH--70%	21.3	9.3	3.4	1.2	90

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Continued)

Chamber[a] Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
7	HNO_3--46 ppbV HCHO--35 ppbV RH--<10%	158	10.1 (16 hr)	2.2 (20 hr)	1.2 (24 hr)	99
8	NOT RUN					
9	HNO_3-none added HCHO--108 ppbV RH--<10%	13.5	23.7 (4 hr)	22.7 (21 hr)	25.6 (24 hr)	<5
10	NOT RUN					
11	HNO_3--43 ppbV HCHO-none added RH--<10%	18.0	9.2 (4 hr)	12.7 (8 hr)	4.4 (24 hr)	76
12	HNO_3--38 ppbV HCHO-none added RH--<10%	54.8	43.5 (4 hr)	35.1 (7 hr)	13.6 (24 hr)	75
13	HNO_3--7 ppbV HCHO-none added RH--25%	117	64 (4 hr)	59 (7 hr)	13 (22 hr)	89

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Continued)

Chamber Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_o	t_1	t_2	t_3	
14[a]	HNO_3--12.8 ppbV HCHO-none added RH--19%	303	245 (4 hr)	218 (7.5 hr)	73 (24 hr)	76
15[a]	HNO_3--24 ppbV HCHO-none added RH--20%	(---)[e]	35 (4 hr)	18.3 (7 hr)	5.8 (23 hr)	>80
16[a,f]	$KMnO_4$--~1000 ng O_3--110 RH--20% Cr^{+3}--~100 ng	3.9 NO MEASURABLE Cr^{+6} FORMED	5.0 (4 hr)	1.3 (7 hr)	0.1 (24 hr)	<5% (Cr^{+3} o Cr^{+6})
17[g]	HNO_3--18.4 ppbV HCHO-none added RH--23%	50	43 (4 hr)	47 (7 hr)	44 (23 hr)	~10
18	HNO_3--18 ppbV HCHO--15 ppbV RH--20%	71	56 (4 hr)	50 (7 hr)	50 (23 hr)	30
19	HNO_3--18 ppbV HCHO--173 ppbV RH--20%	37	24 (4 hr)	17 (8 hr)	5.6 (72 hr)	~80

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Continued)

Chamber Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
20	HNO_3--22 ppbV Propylene-314 ppbV RH--35%	62	54 (16 hr)	25 (24 hr)	22 (40 hr)	60
21[h]	HNO_3-none added Benzene-293 ppbV RH--15%	21	12 (7 hr)	10 (34 hr)	18 (72 hr)	<20
22[h]	HNO_3-none added m-Xylene-315 ppbV RH--15%	96	(180)[i] (7.3 hr)	80 (18 hr)	75 (21 hr)	<20
23	HNO_3-none added m-Xylene-207 ppbV RH--18%	33	29 (6 hr)	21 (24 hr)	13 (95 hr)	~35
24	NOT RUN					
25	HNO_3-none added V^{+2}--~80 ppbV RH--18%	57	57 (5 hr)	65 (21 hr)	70 (45 hr)	<10

TABLE 6-1
REACTION CHAMBER TEST SUMMARIES (Continued)

Chamber Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
26	HNO_3--22 ppbV V^{+2}--~80 ppbV RH--18%	23	6 (6 hr)	5 (22 hr)	0.1 (92 hr)	78
27	HNO_3-none added Fe^{+2}--~80 ppbV RH--20%	180	198 (5 hr)	200 (21 hr)	162 (46 hr)	<10
28[j]	HNO_3--17 ppbV HCHO--173 ppbV RH--12% Cr^{+6} from Cooling Tower Water	78	44 (6 hr)	31 (25 hr)	19 (48 hr)	60
29	HNO_3--20 ppbV m-Xylene-337 ppbV RH--15%	NOT RUN Cr^{+6} Aerosol Generator Failure				
30	HNO_3--20 ppbV benzene-315 ppbV RH--20%	NOT RUN Cr^{+6} Aerosol Generator Failure				
31	HNO_3--15 ppbV m-Xylene-313 ppbV RH--30%	50	38 (8 hr)	24 (24 hr)	10 (71 hr)	52

TABLE 6-1

REACTION CHAMBER TEST SUMMARIES (Concluded)

Chamber Test No.	Reactant	Cr^{+6} Recovered (ng)[b]				Approximate Percent Conversion After 24 Hrs
		t_0	t_1	t_2	t_3	
32[k]	HNO_3--15 ppbV HCHO--320 ppbV RH--30%	55	50 (7 hr)	38 (23 hr)	---	30

[a] Using plastic chamber

[b] analysis by CARB Method ADDL006

[c] n = 2; normalized to Lithium Internal Standard where applicable

[d] Cr^{+6} loading via aerosol deposition for this and subsequent tests

[e] Analytical problem with t_0 filters

[f] Filters spiked w/$KMnO_4$, Cr^{+3} as $CrCl_3$; Cr^{+6} measured

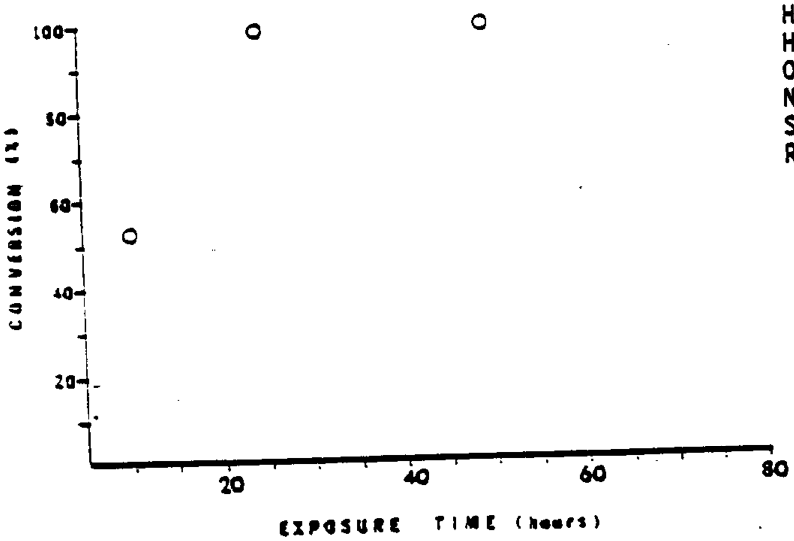
[g] Aluminum chamber used thereafter instead of plastic to minimize "organics" contribution from chamber.

[h] Cr^{+6} results not normalized; no lithium internal standard analysis.

[i] Suspected contamination in one of the t_0 filters.

[j] Filters were aerosol-spiked using actual cooling tower water.

[k] Filters were pipette-spiked using actual chrome plating bath solution



HNO_3--7.7 ppbV
HCHO--68 ppbV
O_3--100 ppbV
NO_2--3,000 ppbV
SO_2--25 ppbV
RH--80 to 90%

FIGURE 6-4: CHAMBER TEST 1

HNO_3--6.7 ppbV
HCHO--41 ppbV
RH, >10 %

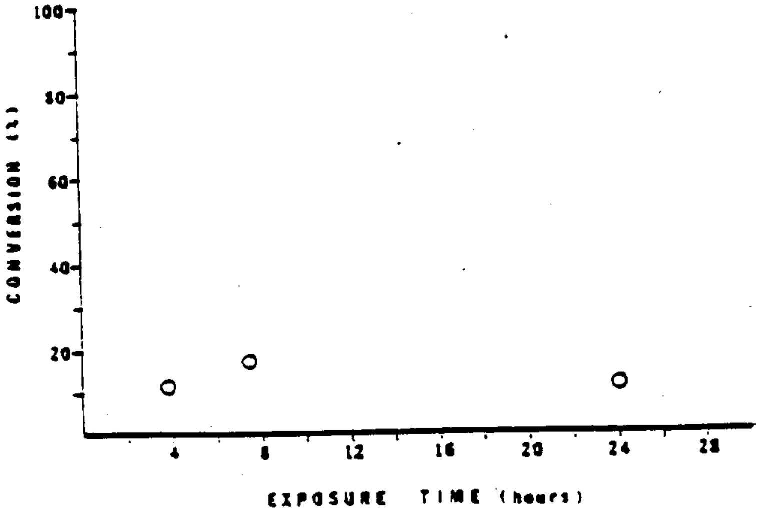
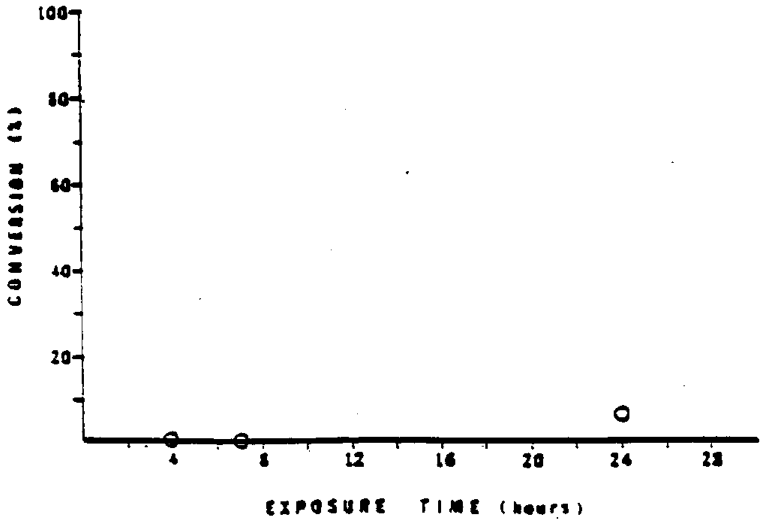
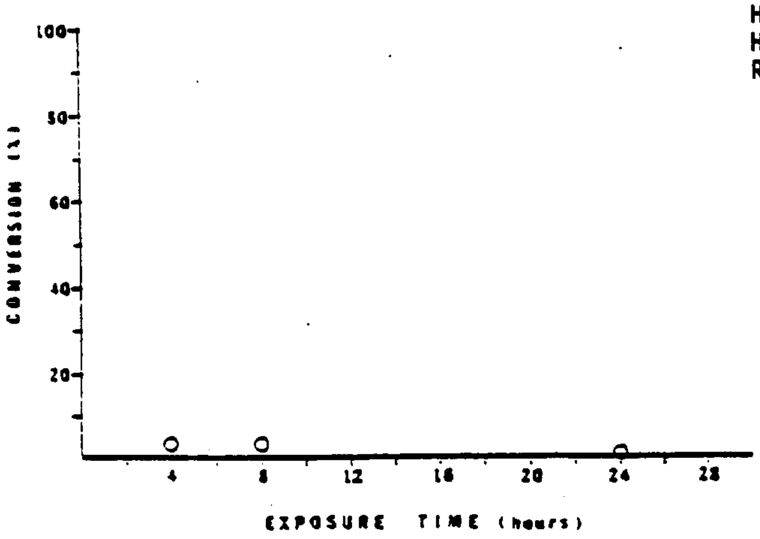


FIGURE 6-5: CHAMBER TEST 2



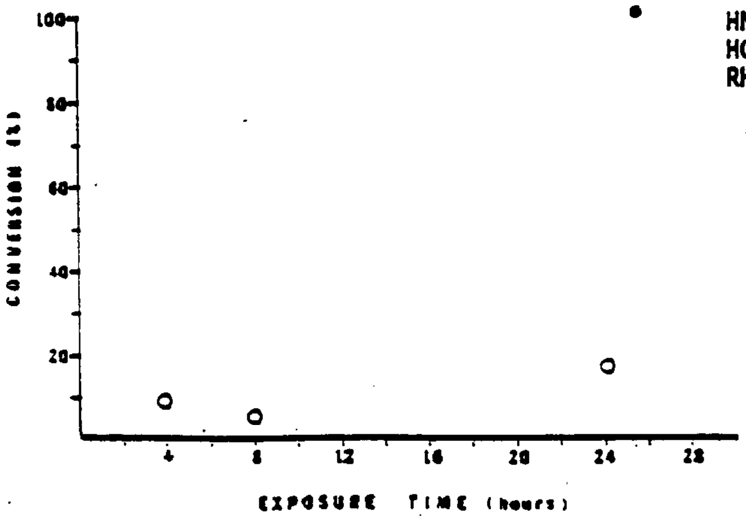
HNO_3--8.1 ppbV
HCHO--50 ppbV
RH--60-90 %

FIGURE 6-6: CHAMBER TEST 3



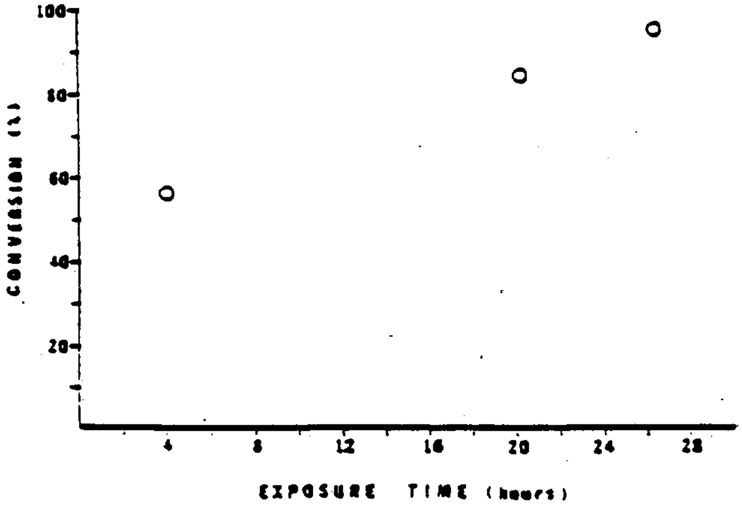
HNO_3--46 ppbV
HCHO--35 ppbV
RH--<10 %

FIGURE 6-7: CHAMBER TEST 4



HNO_3--none added
HCHO--671 ppbV
RH--80%

FIGURE 6-8: CHAMBER TEST 5



HNO_3--46 ppbV
HCHO--35 ppbV
RH--70%

FIGURE 6-9: CHAMBER TEST 6

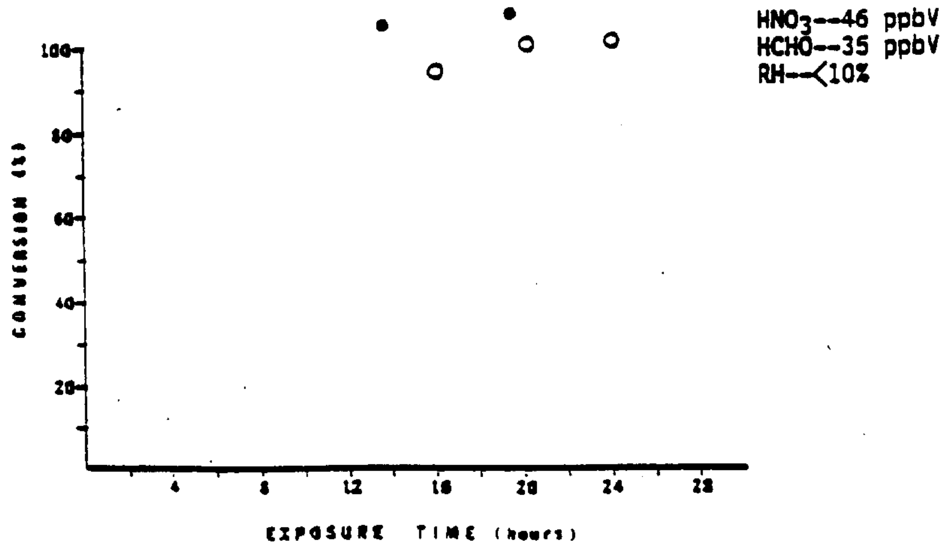


FIGURE 6-10: CHAMBER TEST 7

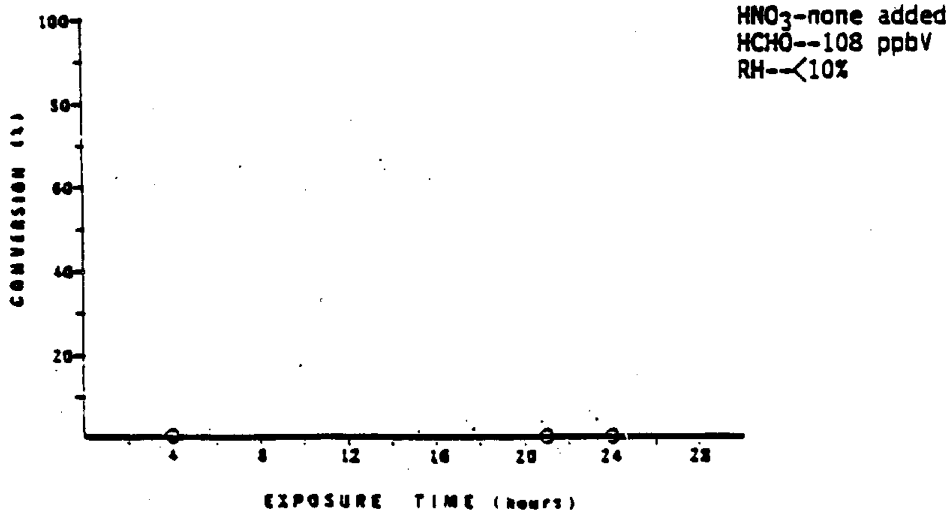


FIGURE 6-11: CHAMBER TEST 9

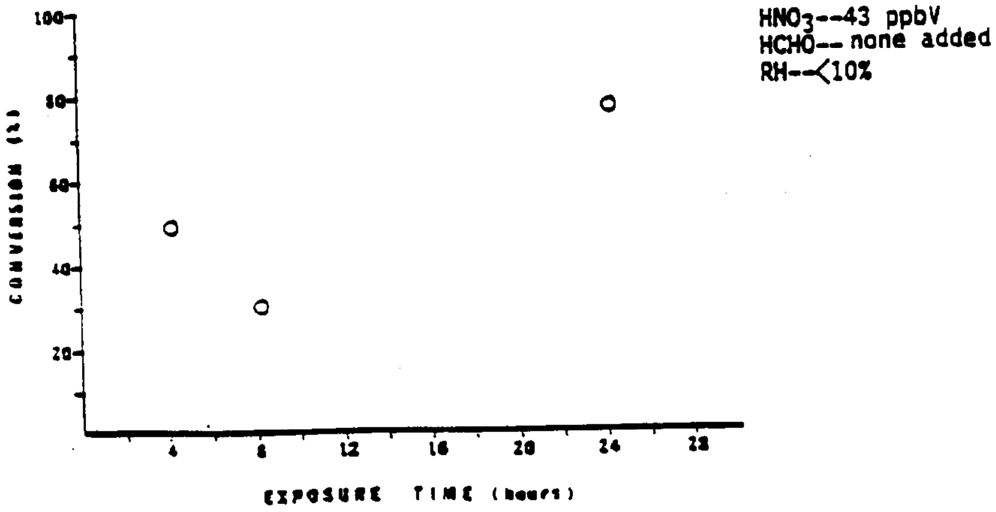


FIGURE 6-12: CHAMBER TEST 11

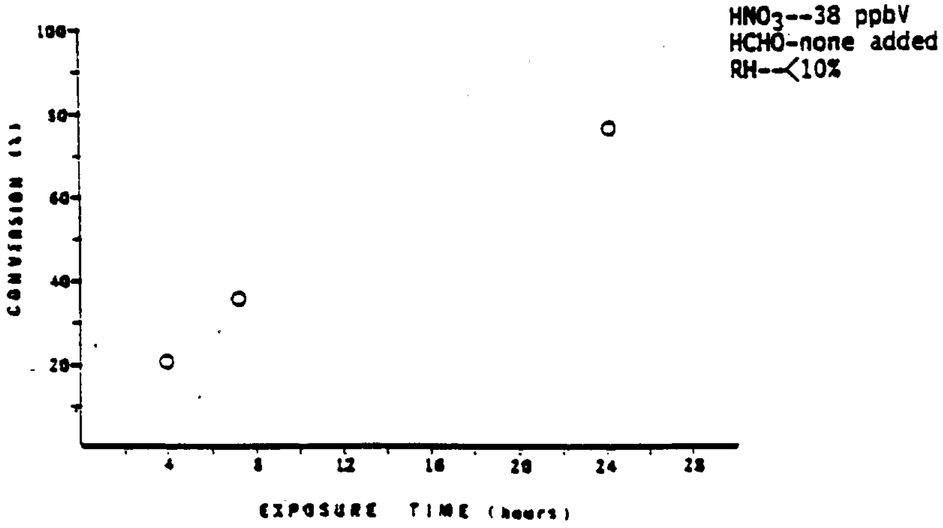
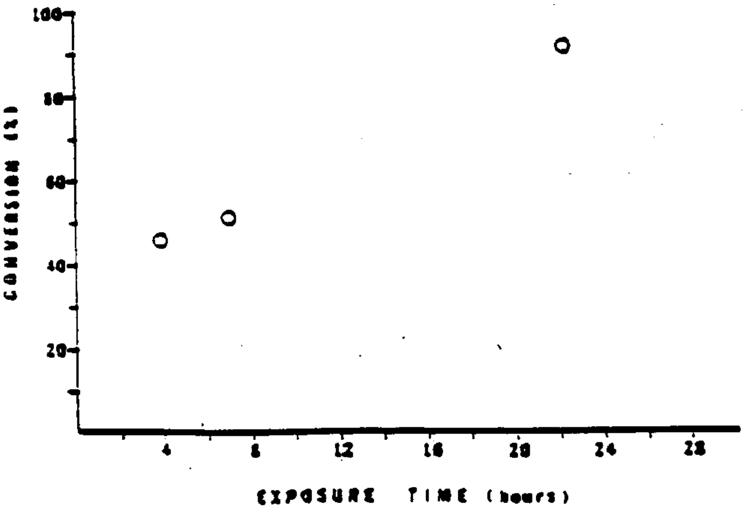
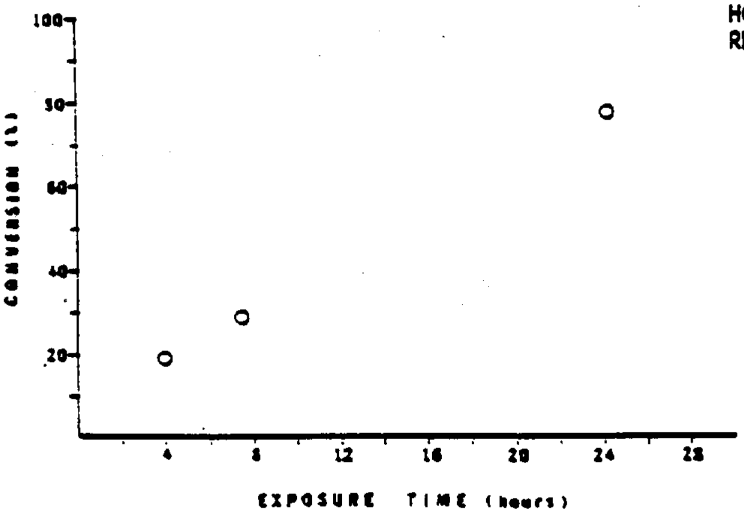


FIGURE 6-13: CHAMBER TEST 12



HNO_3--7 ppbV
HCHO-none added
RH--25%

FIGURE 6-14: CHAMBER TEST 13



HNO_3--12.8 ppbV
HCHO-none added
RH--19%

FIGURE 6-15: CHAMBER TEST 14

HCl--24 ppbV
HCHO--none added
RH--20%

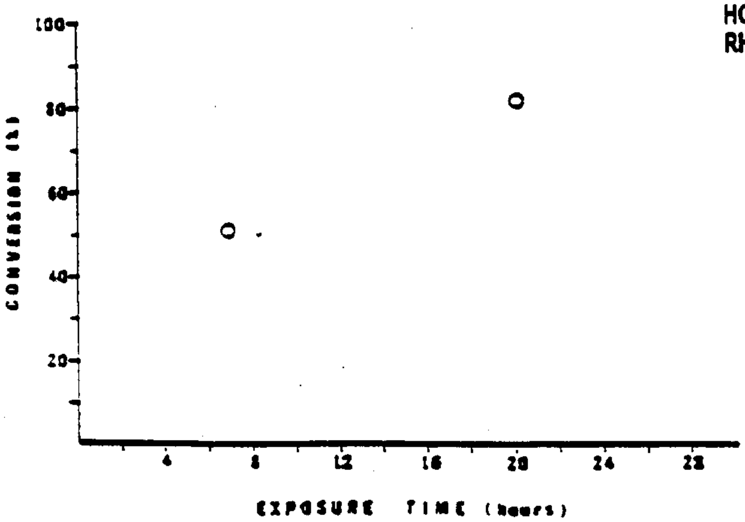


FIGURE 6-16: CHAMBER TEST 15

HNO_3--18.4 ppbV
HCHO-none added
RH--23%

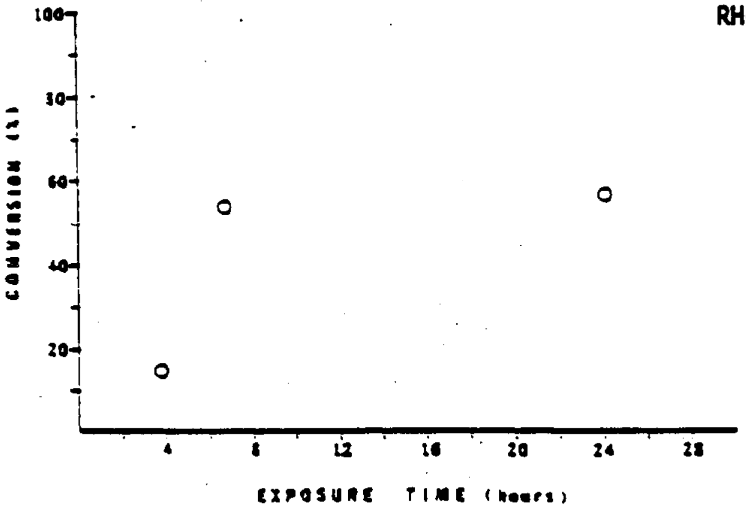


FIGURE 6-17: CHAMBER TEST 17

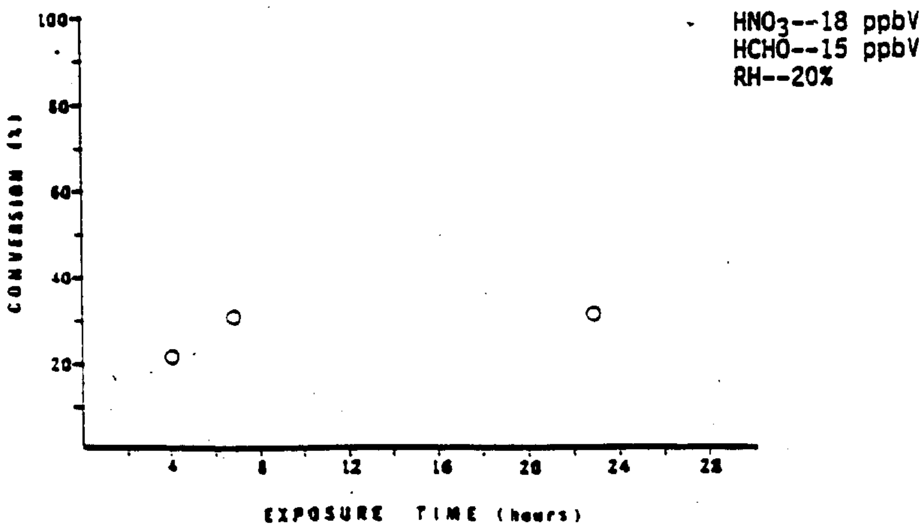


FIGURE 6-18: CHAMBER TEST 18

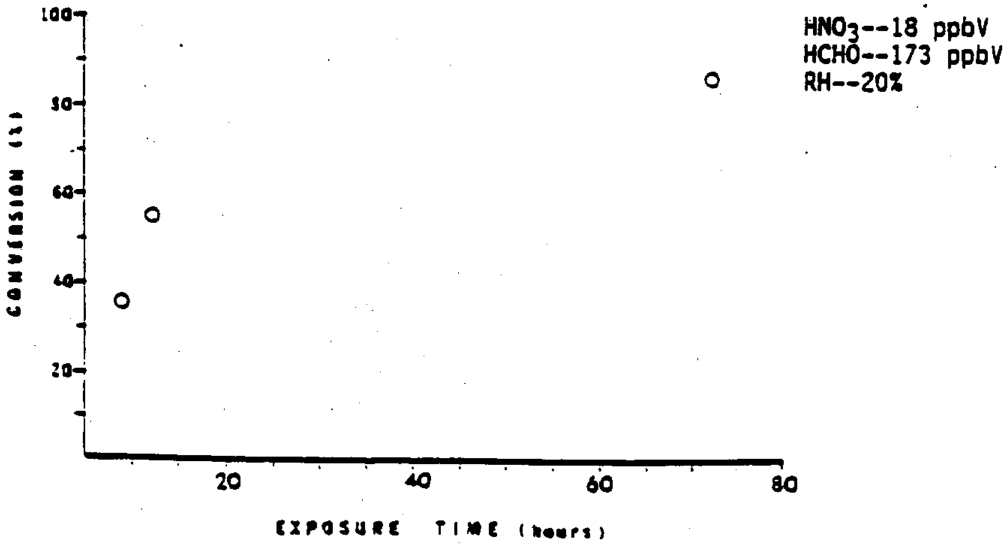
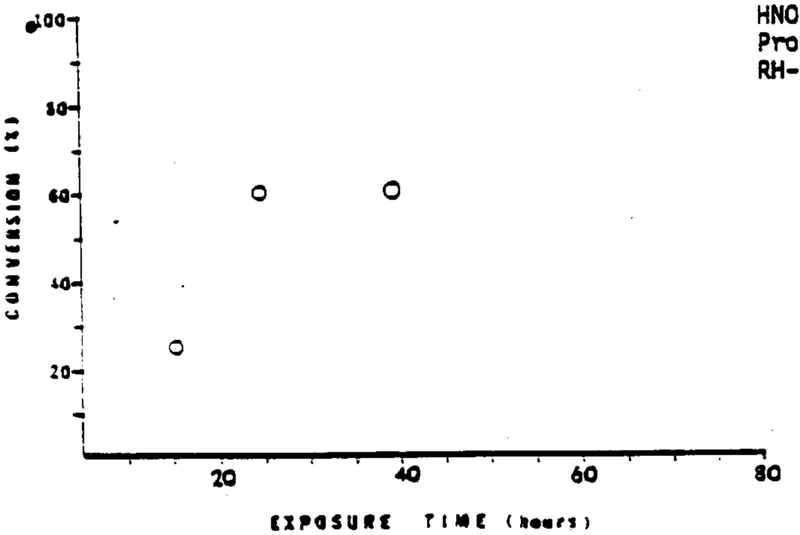
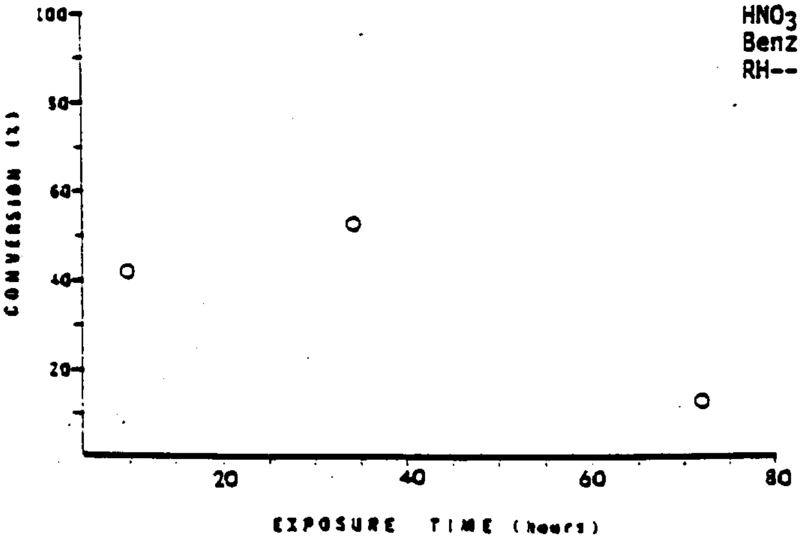


FIGURE 6-19: CHAMBER TEST 19



HNO$_3$--22 ppbV
Propylene-314 ppbV
RH--35%

FIGURE 6-20: CHAMBER TEST 20



HNO$_3$-none added
Benzene-293 ppbV
RH--15%

FIGURE 6-21: CHAMBER TEST 21

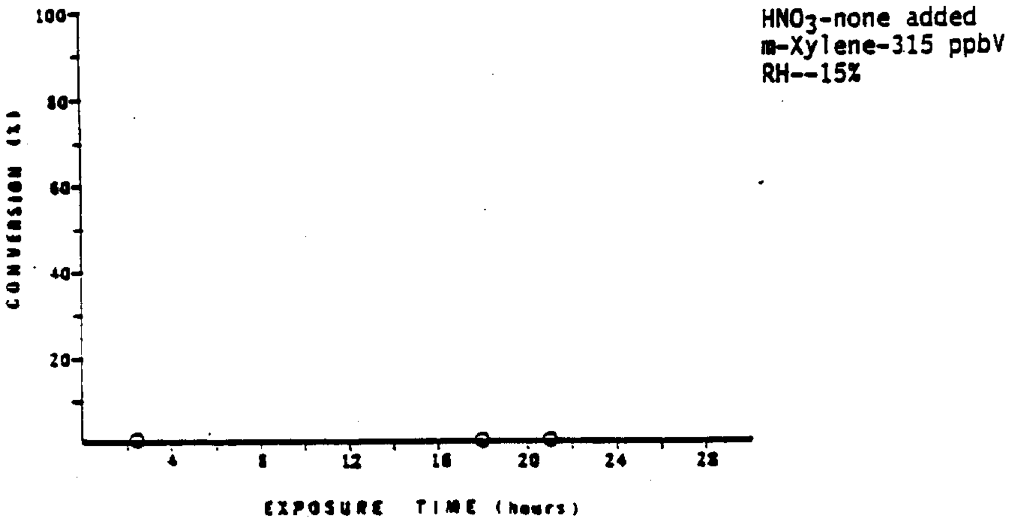


FIGURE 6-22: CHAMBER TEST 22

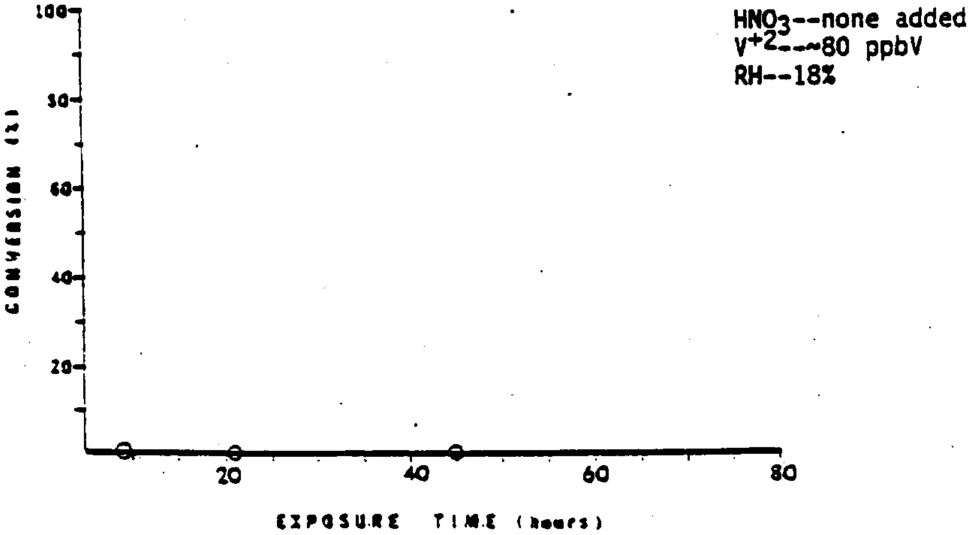


FIGURE 6-23: CHAMBER TEST 25

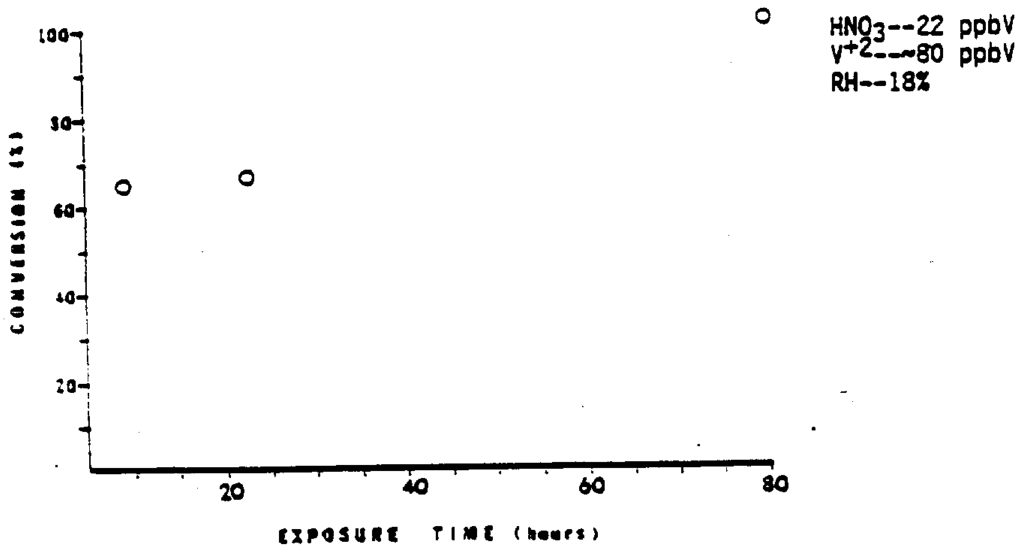


FIGURE 6-24: CHAMBER TEST 26

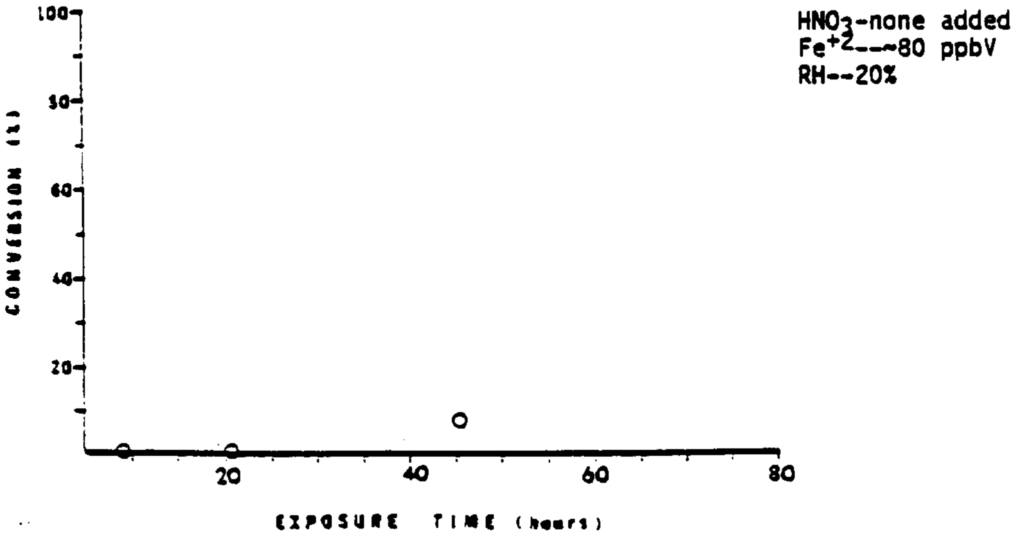


FIGURE 6-25: CHAMBER TEST 27

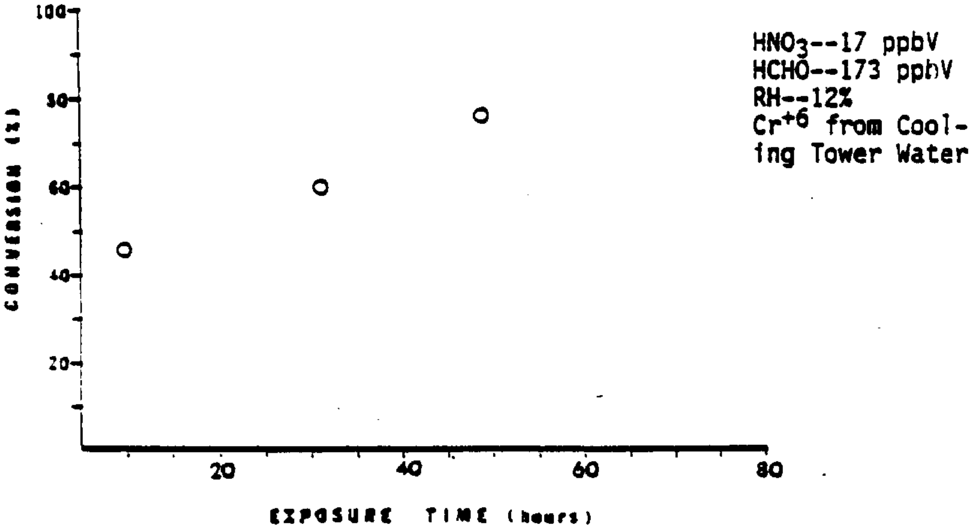


FIGURE 6-26: CHAMBER TEST 28

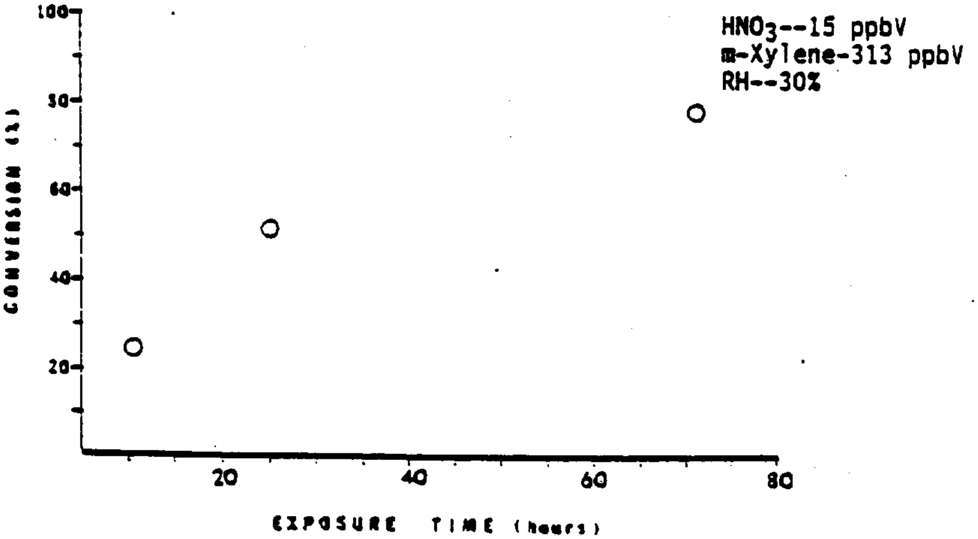


FIGURE 6-27: CHAMBER TEST 31

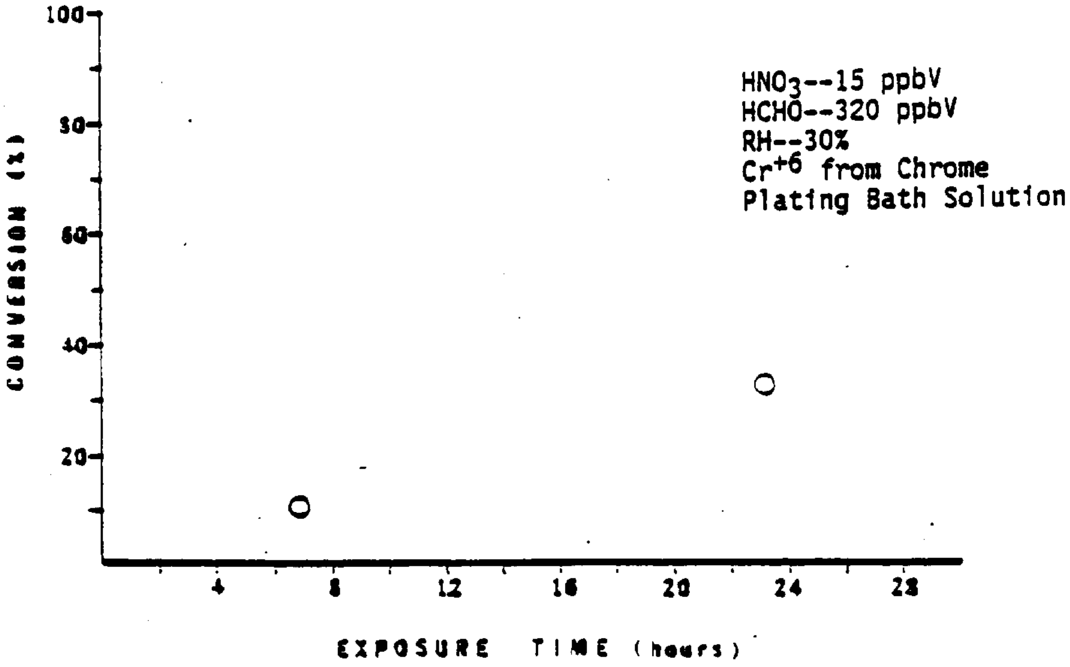


FIGURE 6-28: CHAMBER TEST 32

Test 3. The test conditions were similar to those for Test 2 except that the relative humidity was in the 60-90% range. Filters were removed at 4, 7, and 24 hours. Again, less than 10% conversion was observed after 24 hours. At this point it was assumed that whatever conversion had taken place was minimal in relation to the large quantity of spiked chromium, compared to typical ambient levels. Apparently, the erroneously used cellulose ester membrane (Test 1) provided a considerably reactive surface for the chromium species.

Test 4. The experimental conditions were similar to those of Test 2 (dry conditions). Again, the results indicated that no measurable conversion had taken place. These results are in considerable conflict with Test 7. Two possible explanations are the following:

1. The Cr(VI) level used in Tests 1 to 5 was extremely high (closer to source emission levels). Any Cr(VI) conversion under ambient conditions might well be difficult to measure at the 1 μg Cr(VI) level.
2. The method for Cr(VI) deposition (pipet) may have resulted in a dried droplet that may not have been as easily accessed by the experimental reactants.

As a result of the problems noted above, the aerosolization approach for Cr(VI) deposition was taken after Test 5. This may explain why 150 ppb Cr(VI) was far more reactive than 1,000 ppb Cr(VI).

Test 5. The experimental conditions employed in Test 3 (humid conditions) were repeated in this test. Seventeen (17) percent conversion was observed after 24 hours.

At this point, efforts were made to assemble the aerosol generation system described previously (Figure 6-1). Initially, five filters were exposed to the test aerosol. An aerosol of LiCl generated by aspiration of a 1,000 ppm solution of LiCl showed poor distribution: ± 60% represented by lithium loadings ranging from 51 to 130 μg (see Table 6-2). To determine if the internal standard technique was feasible for monitoring fluctuations in the aerosol distribution, a solution containing 1,000 ppm lithium and 100 ppm copper was aerosolized. The distribution ratios were quite acceptable, resulting in a correlation coefficient $r = 0.994$ (see Table 6-3).

TABLE 6-2
AEROSOL DISTRIBUTION STUDY USING A LITHIUM INTERNAL STANDARD

Filter No.	μg/mL Lithium[a]	Total μg
1	13.0	130
2	5.1	51
3	9.0	90
4	12.8	128
5	12.0	120

[a] determined by extraction with 10% HNO_3 and measurement by flame atomic absorption

TABLE 6-3
AEROSOL DISTRIBUTION STUDY DETERMINATION OF LITHIUM/COPPER RATIO

Filter No.	μg/mL Lithium	μg/mL Copper	Ratio Li/Cu
1	7.9	0.86	.109
2	4.5	0.43	.096
3	7.4	0.77	.104
4	2.6	0.28	.108
5	9.3	1.06	.114

r Li/Cu = correlation coefficient
= 0.994

When an atmosphere containing Li, Cu, and Cr was generated, the correlation was not as acceptable, as shown in Table 6-4. The correlation coefficient between chromium and copper was 0.976, between chromium and lithium was 0.977, but 0.996 between copper and lithium. This implied scatter in the chromium data, possibly due to the much lower levels of Cr. However, it was decided that these data nevertheless provided a means of at least determining a trend in the Cr(VI) data over the 24- to 48-hour period. All subsequent filter loadings for chamber tests were performed in this manner.

Test 6. Using a solution containing 5 µg/mL Cr(VI) (as potassium dichromate) and 1,000 ppm Li (as LiCl), a low level Cr(VI) aerosol was deposited on eight PVC filters (~ 20 ng). Again, two filters were saved for t_0 determination, and additional pairs of filters were removed at 4, 20, and 26 hours. The test atmosphere used contained approximately 50 ppb HNO_3 and 35 ppb formaldehyde. Also, a relative humidity of 70% was used in this test. Fifty-six percent conversion was observed after 4 hours and 84% after 20 hours. Ninety-five percent conversion was indicated after 26 hours.

Test 7. Using a test atmosphere containing similar levels of HNO_3 and formaldehyde, but under dry conditions (<10% RH), six filters containing approximately 150 ng Cr(VI) were exposed and removed after 16, 20, and 24 hours. Ninety-four percent conversion was noted after 10 hours, and greater than 95% was observed after 20 hours.

Test 8. This test was cancelled due to problems with the test atmosphere generation.

Test 9. Samples spiked with the aerosol generator for ten minutes and exposed for up to 24 hours to formaldehyde in the absence of nitric acid indicated no measurable conversion of the Cr(VI) species. Approximately 25 ng were loaded onto the filters. The relative humidity was <10%.

Test 10. This test was cancelled due to problems with the test atmosphere generation.

TABLE 6-4
AEROSOL DISTRIBUTION STUDY USING LITHIUM/COPPER/CHROMIUM AEROSOL

Filter No.	Cr	Cu	Li	Cr/Li
1	0.55	1.03	26.4	.0210
2	0.50	0.76	19.7	.0253
3	0.62	1.59	38.0	.0163
4	0.52	0.84	21.0	.0247
5	0.63	1.34	33.0	.0191
1B	0.68	1.93	43.5	.0156
2B	0.51	0.73	17.9	.0284
6	0.53	0.84	21.2	.0250

r Cr/Li = 0.977

r Cr/Cu = 0.976

r Cu/Li = 0.996

Test 11. Filters spiked with approximately 20 ng were exposed with nitric acid in the absence of the formaldehyde species but otherwise under the same conditions used in Test 9. After eight hours, 29% of the Cr(VI) species had been reduced. After 24 hours, 76% conversion had taken place.

Test 12. The above conditions (Test 11) were repeated. After seven hours, 36% conversion was observed, while 75% of the Cr(VI) species had undergone decay after 24 hours. These results were regarded as similar to those of Test 11. The relative humidity was $<10\%$.

Test 13. When conducting another test under similar conditions (except relative humidity of 25%), 45% conversion was observed after four hours and 89% after 22 hours.

Test 14. This test was again conducted under similar conditions to establish a chemical explanation for the conversion in the absence of formaldehyde. Since significant conversion was observed in this test as seen in Tests 11 and 12, it was decided that the plexiglas chamber was contributing significant levels of reactive organic species through some off-gassing process. Nevertheless, it was decided to determine if similar results were obtained using an HCl atmosphere instead of the HNO_3 atmosphere in order to determine if the conversion mechanism of the acid species used was essentially a pH phenomenon as opposed to the redox characteristics of HNO_3.

Test 15. When filters were loaded with approximately 30 ng Cr(VI) and exposed to 24 ppb HCl and relative humidity of 20%, the same trends found in Tests 11 to 14 were seen. Approximately 50% conversion was seen after seven hours, and 84% conversion after 23 hours. This appeared to indicate that the H^+ contribution was the major contribution of the HNO_3 species used in previous and subsequent tests, not the HNO_3 molecule itself.

Test 16. In this test, filters were aerosol-spiked with a 5 ppm solution of Cr(III) ($CrCl_3$) in the presence of 50 ppm $KMnO_4$ and exposed to ozone (~100-200 ppb). Exposed filters removed after 4, 7, and 24 hours were analyzed for Cr(VI) content to determine if any Cr(III) oxidation had occurred. However, after 24 hours, none had taken place.

In response to the possibility of contribution of organic species by the plexiglass chamber materials, an alternate chamber (shown in Figure 6-3) was constructed of all aluminum as described previously. At the same time, the atmosphere inside the plexiglass chamber was sampled in an evacuated stainless steel can designed for this application and analyzed for individual gaseous organic compounds by gas chromatography in the flame ionization detection. Organic species found included a variety of unsaturated carbonyl and aromatic organic compounds. The total concentration of these latter species exceeded 300 ppbV, thereby accounting for the measurable Cr(VI) conversion rate, even in the absence of added organic species.

Test 17. Utilizing the new aluminum "chamber," spiked filters were exposed to HNO_3 vapors in the absence of added organic species. Over a 24-hour period, only approximately 10% conversion of the Cr(VI) species was observed. This latter result verified the necessity for the presence of an organic or other oxidizable species under low pH conditions to promote reduction of Cr(VI) species. All subsequent tests were conducted in this aluminum device.

Test 18. Under conditions similar to those in Test 17 but with 15 ppb formaldehyde added, 20% conversion was observed after four hours and 30% conversion was observed after 23 hours. However, the level of formaldehyde used was considered unrealistically low in relation to typical atmospheric organic species concentrations.

Test 19. Noting that the total organic species employed is Test 18 was far below that normally encountered in ambient (200 ppbV or greater), it was decided to utilize far more concentrated HCHO atmospheres. Test 19 results reflect an atmosphere containing approximately 20 ppbV HNO_3 and 175 ppbV formaldehyde. After eight hours, a conversion of 55% was measured. After 72 hours, 85% conversion had taken place.

Test 20. Using an alternate organic species, propylene (at 300 ppb), the following test results were observed. Thirteen percent conversion was observed after 15 hours, 60% after 24 hours, and 65% after 40 hours.

Tests 21 through 23 were inadvertently conducted in the absence of nitric acid. Benzene and meta-xylene were selected as the "oxidizable" organic species. Although a small amount of unexplained conversion was nevertheless observed, the m-xylene test was repeated later (Test 31) to determine what increased effect nitric acid would demonstrate in the reduction process.

Test 25. Divalent or trivalent vanadium species are suspected of promoting Cr(VI) reduction. Efforts to generate an aerosol of V^{+2} were made by pulsing an aspirated 0.5 µg/mL solution of VCl_2 onto exposed filters. It was determined that an approximately 15-hour time period was required to produce a total of 100 µg exposure to the Cr(VI) species. Utilizing no HNO_3 atmosphere, Cr(VI)-spiked filters were exposed to an approximately 200 ng loading of V^{+2}. No measurable conversion was observed.

Test 26. The conditions for Test 25 were reproduced for Test 26, but HNO_3 was added. Seventy-five percent conversion was observed after six hours and no Cr(VI) was detected after 94 hours (>99.5%) conversion). These tests indicated that the V^{+2} compounds were the most reactive species tested to date.

Test 27. Substituting Fe^{+2} species ($FeSO_4$) for V^{+2} species and utilizing an atmosphere containing HNO_3 (nominal 20 ppb) no conversion of the Cr(VI) species was observed.

Test 28. Filters were loaded with an actual cooling tower solution supplied by Entropy Environmentalists. Filters spiked with this solution were exposed to HNO_3 and 300 ppb formaldehyde in the aluminum chamber. Forty-five percent conversion was observed after six hours, 60% after 25 hours, and 75% after 48 hours.

Test 31. Fifty (50) nanograms of Cr(VI) was deposited onto PVC filters by pipette (due to problems with the aerosol generator). The filters were exposed to 310 ppb m-xylene to repeat Test 23 but with 15 ppb HNO_3 added. Fifty-two (52) percent conversion was observed after 24 hours (compared to 35% without HNO_3), and 75% conversion was observed after 71 hours.

Test 32. Hexavalent chromium from an actual chrome plating bath solution was deposited by pipette on filters and subjected to exposure to 320 ppbV formaldehyde and 15 ppbV HNO_3. Thirty percent conversion was observed after 24 hours.

A summary of individual Cr(VI) half life values for those chamber tests deemed to most closely approximate actual ambient conditions is shown in Table 6-5. To qualify for this criteria, the test had to incorporate both an acid species (5 to 50 ppb) and an easily oxidizable species in the 50 to 400 ppb range. The average half life was found to be 12.9 hours (± 5.8 hours).

Additional experiments correlating individual particle behavior with reactivity were planned in this study through the use of an electrodynamic balance (32). However, difficulties with the particle balance operation forced RTI investigators to abandon this set of experiments and concentrate efforts more fully on more important questions, such as the chamber reactivity tests.

TABLE 6-5
ESTIMATED Cr(VI) HALF LIFE DURING CHAMBER TESTS

Chamber Test No.	Cr(VI) ng	Estimated Half Life (Hrs)	Comments[a]
6	21	9	Plastic chamber organics ~300-400 ppb
7	158	7	Plastic chamber organics ~300-400 ppb
11	18	10	Plastic chamber organics ~300-400 ppb
12	55	12	Plastic chamber organics ~300-400 ppb
13	117	7	Plastic chamber organics ~300-400 ppb
14	303	15	Plastic chamber organics ~300-400 ppb
15	35 (est.)	7	Plastic chamber organics ~300-400 ppb
19	37	11	173 ppb HCHO[b]
20	62	24	314 ppb C_3H_6[b]
26	23	15	80 ppb V^{+2}[b]
28	78	15	173 ppb V[b]
31	50	23	313 ppb m-Xylene[b]

Average Half life = 12.9 hrs. (± 5.8 hrs.)

---

[a] HNO_3 concentration ranged from 7 to 46 ppb; Organics were a variety of species resulting from off-gassing of plastic chamber and adhesives.
[b] Aluminum chamber

7.0 FIELD STUDY

7.1 INTRODUCTION

The third major phase of the study was designed to verify the general Cr(VI) reactivity trends observed in the laboratory reaction chamber tests through the use of actual field samples. This was carried out using two approaches:

- An ambient sampling study near two Cr(VI) sources, a chrome plating facility and a cooling tower, measuring Cr(VI) at distances up to 2 km from each source
- A field reaction study to verify the laboratory chamber tests through the use of true ambient air samples typical of the Los Angeles area

Each analytical method employed in the measurement of the field samples was subjected to a series of quality control/quality assurance procedures. These included the analysis of duplicate aliquots of quality control solutions, spikes, and reagent blanks. Duplicate aliquots of impinger solutions were not available. The entire solution was utilized for each result to provide maximum sensitivity. Spikes results were judged acceptable in the 80-120% recovery range. Duplicates were ± 10% (except at the lower quantifiable limit), quality control sample values were within 10% of the expected value, and blanks in Method ADDL006 were in the 1-3 ng range. Duplicate filter analyses were utilized for the field reaction study.

Quality assurance procedures utilized during field test sampling are indicated in Appendix F.

7.2 THE AMBIENT SAMPLING STUDY

At each Cr(VI) source, one upwind and four potential downwind ambient stations were employed. A meteorological data station was set up near each source to determine wind speed and direction. In addition, sulfur hexafluoride (SF_6) tracer experiments were conducted at each site to verify emission or plume location. Plot plans of each site are shown in Figures 7-1 and 7-2. Each station contained two ambient sampling units for filter sampling and one set of three impinger trains. One filter sampling unit

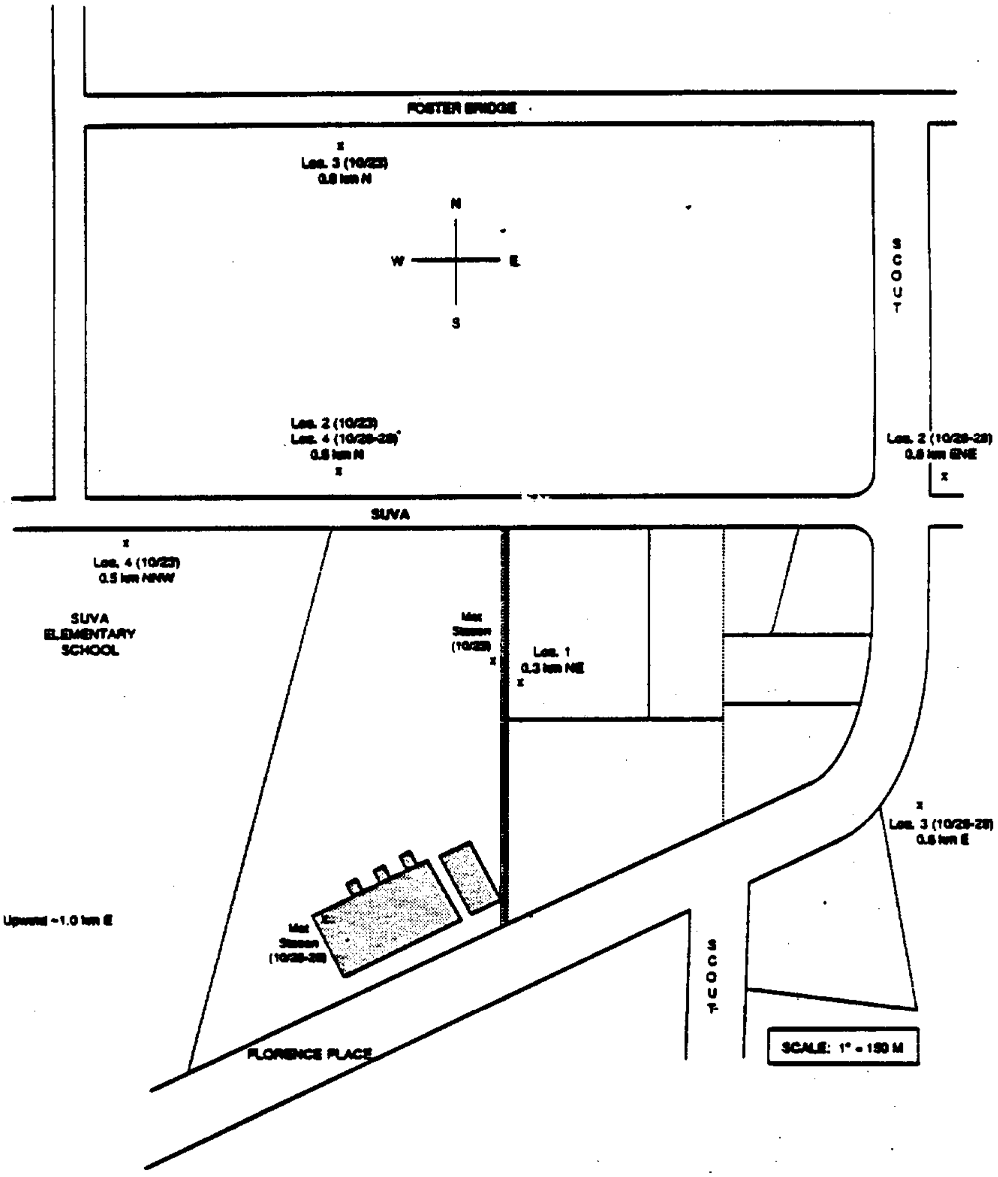


FIGURE 7-1
PLOT PLAN OF CHROME CRANKSHAFT SHOWING SAMPLING LOCATION

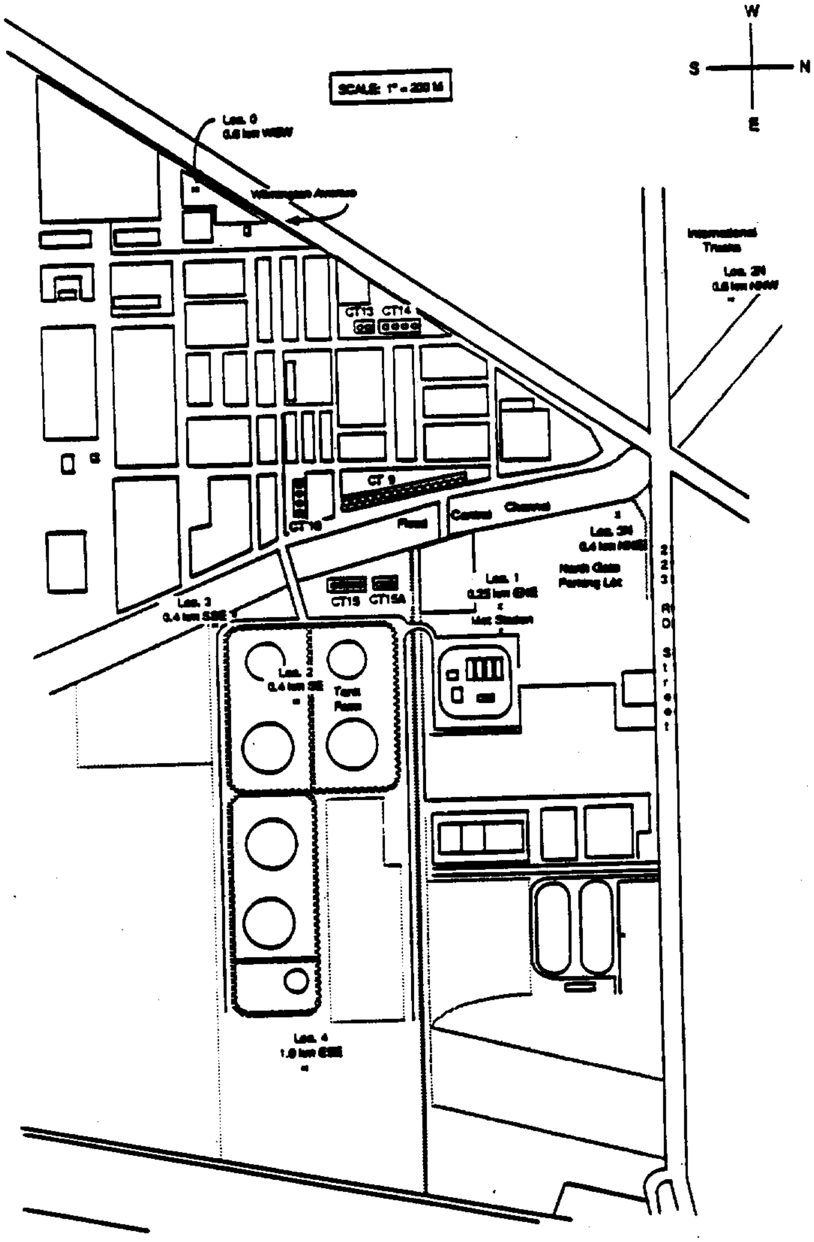


FIGURE 7-2
PLOT PLAN OF THE ARCO REFINERY
SHOWING SAMPLING LOCATIONS (RELATIVE TO CT9)

used polyvinylchloride (PVC) membranes, while the other used Teflon membranes. Teflon membranes were used for total chromium measurements, while PVC membranes were intended for both total chromium and Cr(VI) collection. Impinger samplers were taken using Smith-Greenburg impingers filled with 0.01 M sodium acetate reagent. These devices (depicted in Figure 7-3) were used as a reference method for Cr(VI) sampling. It was expected that some total chromium information might be obtained from these devices, but initial tests indicated a great difficulty in obtaining low blank chromium values.

The information obtained from the ambient study was intended to provide:

- Cr(VI) and Cr(III) levels near the sources
- Some comparison of PVC filters versus sodium acetate impingers in terms of Cr(VI) sampling efficiency
- Some measure of the Cr(VI)/Cr(III) ratio at each downwind sampling site in order to quantitate the rate of conversion

The details of the field test conducted by Entropy Environmentalists are included in the field test report in Appendix F.

7.3 RESULTS

Samples obtained in the vicinity of the chrome plating facility generally contained measurable levels of hexavalent chromium, especially at the "near downwind" sites approximately 0.5 km from the emission source. Of seven tests run at this site, four (4) were judged complete and, from these, Cr(VI) concentrations ranged from 26.3 ng/m^3 to 315 ng/m^3. Results of these four tests are shown in Table 7-1. Although not part of the work plan, the ambient data were also used to calculate the relationship of Cr(VI) to total chromium in order to determine if the ambient data might be used to estimate Cr(VI) conversion rates as a function of distances from the source. Due to the lack of (1) useful total chromium data at the source, and (2) measurable Cr(VI) levels farther than the near downwind sampling position, it is felt that, with the exception of Run 8, the ambient data could not be used to provide conversion estimates. In Run 8, the ratios are likewise somewhat unreliable but indicate that the Cr(VI) levels

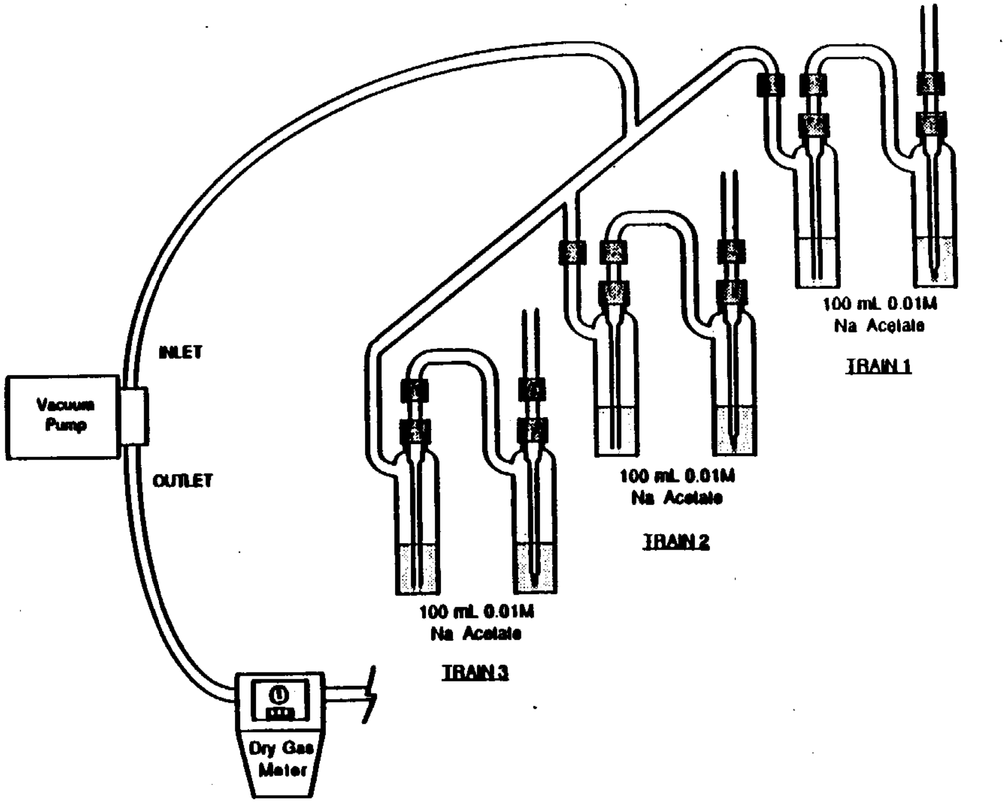


FIGURE 7-3
AMBIENT SAMPLING STATION IMPINGER TRAINS

TABLE 7-1
AMBIENT SAMPLING TEST RESULTS NEAR CHROME PLATING SOURCE[a]

Run No.	Position No.	Cr(VI)(ng/m^3)	Total Cr (ng/m^3)	Cr(VI)/Total Cr
3	0-Upwind	2.7	10.3	N/A
	1-Predicted DW	2.3	8.4	0.27
	2-Near DW	33.5	[c]	---
	3-Far DW	3.7	19.1	0.19
5	0-Upwind	2.6	(153)	N/A
	1-Predicted DW[b]	110	102	~1.0
	2-Far DW	7.6	18.3	0.42
	3-Location 3	1.2	10.9	0.11
	4-Location 4	<0.5	4.8	<0.1
7	0-Upwind	1.9	51.3	N/A
	1-Location 1	26.4	74.7	0.35
	2-Location 2	<0.5	11.7	<0.1
	3-Location 3	<0.5	16.6	<0.1
	4-Location 4	<0.5	4.1	<0.1
8	0-Upwind	2.4	<3	N/A
	1-Predicted/ Near DW	316	340	0.93
	2-Far DW	14.3	24.7	0.58
	3-East of Source	10.3	28.3	0.36
	4-North of Source	13.8	20.7	0.67

[a] Impinger samplers used with Method ADDL006 measurement

[b] Downwind

[c] Defective Sample (no flow)

N/A - Not Applicable

are a significant portion of the total chromium levels at all sampling locations (see Table 7-2).

An additional aspect of the field sampling study was the evaluation of the analytical methodology. There were two goals:

- That the tentatively developed sampling method using the acetate impinger could be compared to the PVC membrane filter presently being used by CARB
- That the CARB Method ADDL006 could be compared to the ion chromatographic methods

It was decided that data from the CARB field test of October 1987 could be utilized for the sampling method comparison. This test did, in fact, involve a comparison of the two methods and indicated that, in general, the impinger technique provided a Cr(VI) estimate of three to 27 times that provided by the PVC membrane. These data are included as Appendix A of this report, and are summarized in Table 7-3. The measurement component of Method ADDL006 was used for all field samples since the method was amenable to both impinger and filter samples. Samples from Runs 2 and 3 were analyzed by both ADDL006 and ion chromatography. The results, shown in Table 7-4, indicate that the IC results are biased 18% higher with respect to Method ADDL006. It should be noted that the IC analyses were conducted using direct injection, which is relatively insensitive. The resulting data are close to the lower quantifiable limit (LQL) for this particular IC method. Additional field sample measurement comparison data, shown in Table 7-5, were obtained from a subsequent Los Angeles area field test in a cooperative effort with the South Coast Air Quality Management District. By contrast, these data show Method ADDL006 to be biased high by an average of 8.8%. These data are perhaps more reliable due to the larger volumes taken for IC analysis. The IC analysis utilized preconcentration prior to sample injection. These data are presented for purposes of measurement comparison only. The sampling data are not available at this time. As a consequence, results from Table 7-5 are unavailable for the purposes of providing ambient test data.

Ambient sampling at the cooling tower facility provided an added difficulty due to Cr(VI) levels that were, in general, close to the detection limit. Measurable levels of Cr(VI) on two days could be provided.

TABLE 7-2
FIELD TEST NUMBER 8

Results in ng (Normalized for flow)*

Sample	Cr(VI)	Total Cr	Cr(VI)/Total Cr
Position 1	1104	1193	0.93
Position 2	93	158	0.59
Position 3	65	179	0.36
Position 4	77	116	0.66

*Cr(VI) results from acetate impinger
Total Cr results from Teflon filters

TABLE 7-3
FIELD TEST COMPARISON OF Cr(VI) COLLECTION DEVICES
PVC FILTERS VS. 0.05 M NA_2CO_3 IMPINGER

Results in ng/m^{3a}

Field Site No.	PVC	Na_2CO_3 Buffered Impinger	Factor (Imp/PVC)
1	1.3	13.9	10.7
2	10.2	47.3	4.6
3	6.5	30.2	4.6
4	0.9	13.3	14.8
5	1.5	41.5	27.7
6	6.9	25.0	3.6
7	4.7	19.2	4.1
8	2.6	26.0	10.0
9	2.4	8.6	3.6
10	7.4	29.0	3.9
11	4.6	19.8	4.3

[a] Method ADDL006

TABLE 7-4
MEASUREMENT METHOD COMPARISON USING FIELD SAMPLES CARB METHOD ADDL006 VERSUS ION CHROMATOGRAPHY

[ng Cr(VI) Per Sample]

Sample No.	Ion Chromatography[a]	ADDL006
CC-02-IS-11	850	640
CC-02-IS-12	825	600
CC-03-IS-21	175	161
CC-03-IS-22	50	38
CC-03-IS-41	175	165
CC-03-IS-61	200	183
CC-03-IS-62	150	123

[a] Direct injection

TABLE 7-5
MEASUREMENT METHOD COMPARISON--ADDL006 VERSUS ION CHROMATOGRAPHY

Results in ng Cr(VI)

Sample No.	Ion Chromatography	ADDL006
1	185	229
2	434	423
3	149	190
4	306	353
5	988	1203
6	4550	4260
7	1060	1300
8	270	307
9	133	121

Five (5) other tests were conducted. Hexavalent chromium values were too low to be detected. Total chromium values (obtained from Teflon filters) are provided in Table 7-6. The field test personnel believe that several factors may have contributed to these low Cr(VI) values. The dilution rate from the cooling tower(s) was so great it was difficult to provide adequate quantities of SF_6 to verify the plume location (see Table F-4 in Appendix F).

A summary of wind direction data can be found in Table F-4 of Appendix F. The wind was expected out of the east in the morning. In the afternoon the wind generally came off the ocean. Deviations to this pattern are found in Appendix F(C), which contains wind direction data. An examination of these data indicates that the wind direction at the chrome plating facility was generally steady, while winds at the cooling tower site were highly variable. There were other occasions where sampling personnel felt that they were located downwind of the cooling towers (at least for short periods) but may have not sampled the emission plume due to its altitude. In one test (Run 10), field test personnel could actually feel the mist (drift) from the cooling tower(s). This was not the case during the other tests. However, even for this test, the Cr(VI) values were close to the lower quantifiable limit, or about five to ten times the detection limit.

In general, it was felt that the SF_6 data correlated well with the Cr(VI) ambient data. For example, SF_6 levels for Run 8 were the highest of the chrome plating tests, as were the Cr(VI) levels. This is true also for the cooling tower Run 10. Here again, the levels were among the highest of the cooling tower tests. Runs 11 to 15 yielded nearly nondetectable levels of SF_6. A summary of SF_6 tracer results can be found in Table F-4 of Appendix F. Again, the SF_6 tracer tests were used to verify, not locate, the emission plume. Had more personnel been available, the SF_6 test may also have provided additional means of locating the plume.

Cr(III) concentrations were high enough to be easily measured but did not correlate well with wind direction and sampler location in relation to nearby cooling towers. Two observations of the total chromium data are

TABLE 7-6
AMBIENT SAMPLING TEST RESULTS NEAR REFINERY COOLING TOWER[a]

Run No.	Position No.	Cr(VI)(ng/m^3)	Total Cr (ng/m^3)	Cr(VI)/Total Cr
9	0-Upwind	---[b]	77	---[b]
	2-DW	10.4	33	0.32
10	0-Upwind	1.0	42	0.02
	1-Due West of Tower Bank	2.1	30	0.07
	2-Straight DW	9.3	No data	
	3-Drift from Another Tower	8.0	99	0.08
11	0-Upwind	ND (<2)	39	
	1-	ND (<2)	52	
	2-	ND (<2)	43	
	3-	ND (<2)	24	
	4-	ND (<2)	102	
12	0-Upwind	ND (<2)	38	
	1-	ND (<2)	15	
	2-	ND (<2)	22	
	3-	ND (<2)	17	
	4-	ND (<2)	59	
13	0-Upwind	ND (<2)	23	
	1-	ND (<2)	10	
	2-	ND (<2)	179	
	3-	ND (<2)	128	
	4-	ND (<2)	766	
14	0-Upwind	ND (<2)	29	
	1-	ND (<2)	52	
	2-	ND (<2)	2	
	3-	ND (<2)	60	
	4-	ND (<2)	46	
15	0-Upwind	ND (<2)	77	
	1-	ND (<2)	76	
	2-	ND (<2)	241	
	3-	ND (<2)	133	
	4-	ND (<2)	38	

[a] Impinger samplers used with Method ADDL006 measurement

[b] Impinger sample not available

perhaps worthy of note. First, those samples considered indicative of upwind or background conditions (Location 0) provided chromium values usually equal to or greater than the near downwind samples (Runs 9, 10, 12, 15). Since there were no cooling towers west of Location 0 and this location was probably out of any potential plume from nearby cooling towers, this location probably provided chromium values indicative of the area background levels; i.e., 20 to 80 ng/m^3. Also, the sampling location originally designated as far downwind (4) frequently yielded higher chromium values than those locations considered near downwind (Runs 11, 12, 13). Actually, due to wind shifts, Location 4 frequently was the upwind position. Cooling towers due south and east of location 4 (>1 km) may have contributed to the chromium levels measured at that position. In general, it appears that, due to high dilution rates and variable wind conditions, no distinct plume could be located in this area. This is supported by the SF_6 tracer studies. The Run 13 value of 766 ng/m^3 total chromium [Cr(III)] cannot be explained in light of any of the above mentioned sampling conditions. Run 14 Cr(III) results were slightly lower than those of other tests, probably due to rainy conditions that day.

7.4 THE FIELD REACTION STUDY

The primary goal of the field reaction study was the corroboration of laboratory chamber reactivity tests: "Was the Cr(VI) half life of approximately 13 hours determined from chamber tests applicable to actual field conditions?" An additional goal of the field reaction study was to determine if there was any significant photochemical input in the Cr(VI) conversion process.

As a consequence, the field reaction study was conducted in a manner similar to the laboratory chamber tests. PVC and Teflon membrane filters were "preloaded" at each source with levels ranging from approximately 10 to 60 ng of Cr(VI). Twelve filters were loaded simultaneously in this manner for each run. A diagram depicting the filter holder for this test is shown in Figure 7-4. Two days were spent at each source to determine the optimum filter loading time to achieve the appropriate Cr(VI) loading. Based on samples immediately sent to RTI for Cr(VI) analysis, a five-second filter loading period was determined to be adequate at the chrome plating

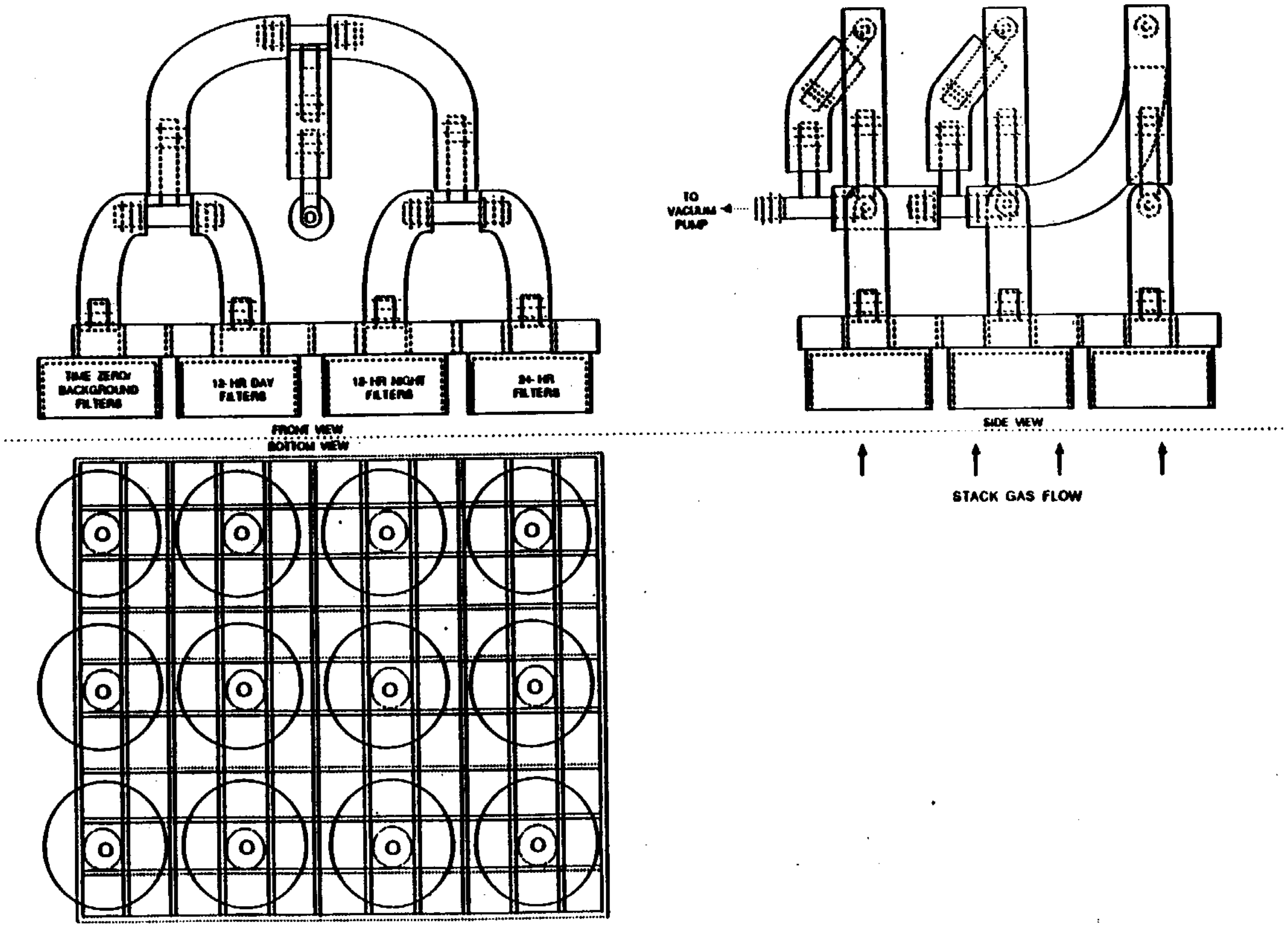


FIGURE 7-4
FIELD REACTION FILTER HOLDER

site, and a 30-minute period was determined to be appropriate at the cooling tower facility. However, in retrospect, the five-second exposure at the chrome plating site may have been too short, since all filter loadings of Cr(VI) after the first day were less than 20 ng, near the lower quantifiable limit (by Method ADDL006). Once the membrane filters were loaded at the source, they were exposed to ambient air at an upwind or isolated site according to the following scheme:

1. Three (3) filters were set aside for a "t_0" reference Cr(VI) value.
2. Three (3) filters were exposed for 12 hours to night conditions only.
3. Three (3) filters were exposed for 12 hours to daylight conditions only.
4. The remaining three (3) filters were exposed for 24 hours to combined day/night conditions.

Two of three filters for each exposure time were used to provide the average values reported in Table 7-7. The details of the field reaction sampling study sampling are included in Appendix F.

Air quality in the Los Angeles area was generally good with levels of nitrogen oxides (as well as ozone and carbon monoxide) below the clean air standard during the entire field test. From this it could be inferred that potentially reactive species were not at levels that would promote usually rapid Cr(VI) reduction. General air quality indicator data are included in Appendix F(D).

Results of seven (7) field reaction experiments from the chrome plating sites and three (3) from the cooling tower facility are shown in Tables 7-7 and 7-8. Plots depicting Cr(VI) conversion versus time are found in Figures 7-5 through 7-11. Filter loadings ranged from 11 to 49 ng for the chrome plater and 29 to 63 ng for the cooling tower. Over a 24-hour period, the conversion ranged from 49 to 80% for the chrome plating facility and from 39 to 74% for the cooling tower samples. A summary of the estimated Cr(VI) half life for each field reaction test is shown in Table 7-9. Results indicate an average half life of 16 hours (± 6.9 hours), in good agreement with that obtained during the laboratory chamber tests. The Run 9 half life value of 30 hours may appear to be somewhat outside of the

TABLE 7-7
FIELD REACTION TESTS OF CHROME PLATING SAMPLES[a]

Run No.	Sample No.	Cr(VI) Recovered (ng)	Percent Conversion
2	Unexposed (t_o)[b]	48.6[c]	---
	12 hr. night	44.3	<10
	12 hr. day	24.8	49
	24 hr.	27.0	44
	Background	<2	
3	Unexposed (t_o)	11.1	---
	12 hr. night	18.3	55
	12 hr. day	34.4	28
	24 hr.	21.1	>80
	Background	<2	
4	Unexposed (t_o)	11.6	
	12 hr. night	9.6	(Inadequate Sample)
	12 hr. day	13.3	
	24 hr.	11.3	
	Background	9.8	
5	Unexposed (t_o)	12.6	---
	12 hr. night	12.3	<10
	12 hr. day	12.3	<10
	24 hr.	4.7	63
	Background	<2	
6	Unexposed (t_o)	24.1	
	12 hr. night	18.3	(Indeterminate Data)
	12 hr. day	34.4	
	24 hr.	21.1	
	Background	<2	
7	Unexposed (t_o)	18.6	---
	12 hr. night	13.5	27
	12 hr. day	15.0	19
	24 hr.	5.2	72
	Background	<2	
8	Unexposed (t_o)	17.5	---
	12 hr. night	5.5	69
	12 hr. day	11.9	32
	24 hr.	5.6	68
	Background	<2	

[a] Values "corrected" for background

[b] Unexposed (t_o)--initial loading at source

[c] All Cr(VI) values are averages of duplicate filter analyses for each time period.

TABLE 7-8
FIELD REACTION TESTS OF COOLING TOWER SAMPLES[a]

Run No.	Sample No.	Cr(VI) Recovered (ng)	Percent Conversion
9	Unexposed (t_o)[b]	62.9 (25)[c]	---
	12 hr. night	43.4 (2.6)[c]	31
	12 hr. day	58.9 (2.6)[c]	<10
	24 hr.	24.2	39
	Background	<2	
10	Unexposed (t_o)	28.5	---
	12 hr. night	13.5	53
	12 hr. day	10.0	65
	24 hr.	7.4	74
	Background	<2	
11	Unexposed (t_o)	31	---
	12 hr. night	17.4	44
	12 hr. day	16.0	48
	24 hr.	23.4	(25)
	Background	4.0	

[a] Values "corrected" for background

[b] Unexposed (t_o)--initial loading at source

[c] Ion chromatographic results 16 days later--these values reflect the instability of Cr(VI) in the acetate impinger

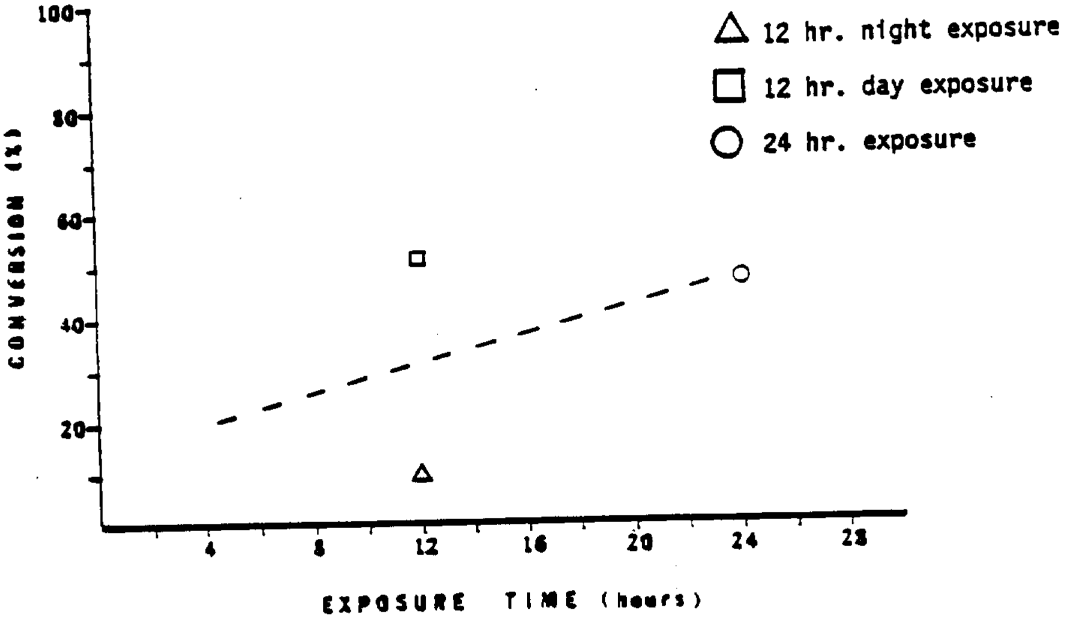


FIGURE 7-5: FIELD REACTION - RUN 2

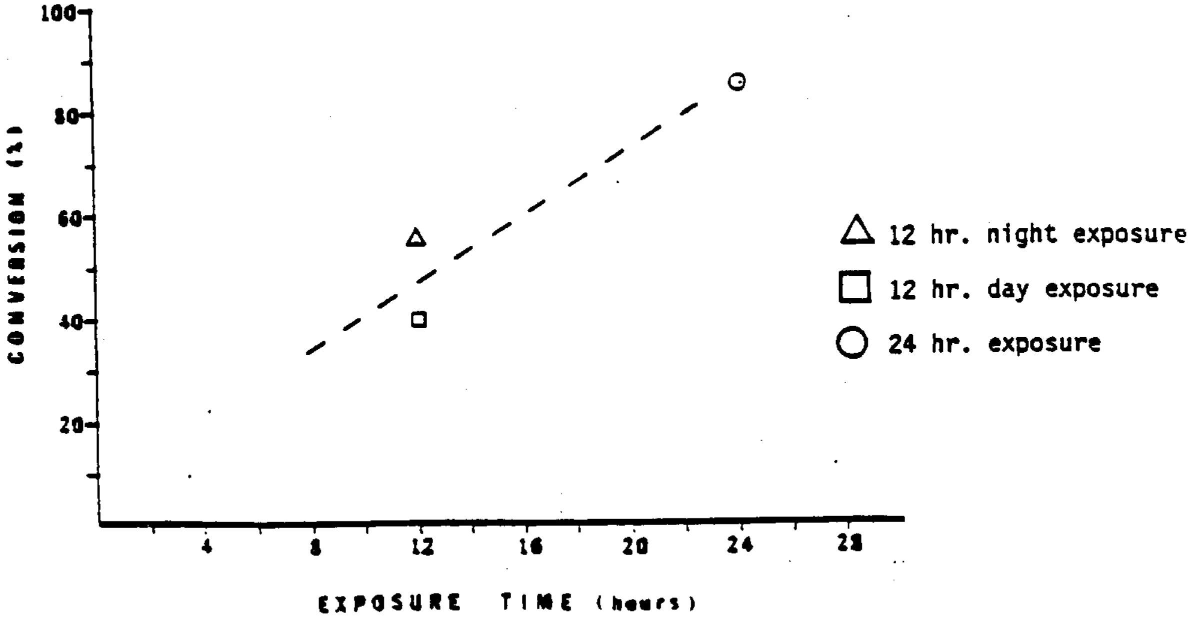


FIGURE 7-6: FIELD REACTION - RUN 3

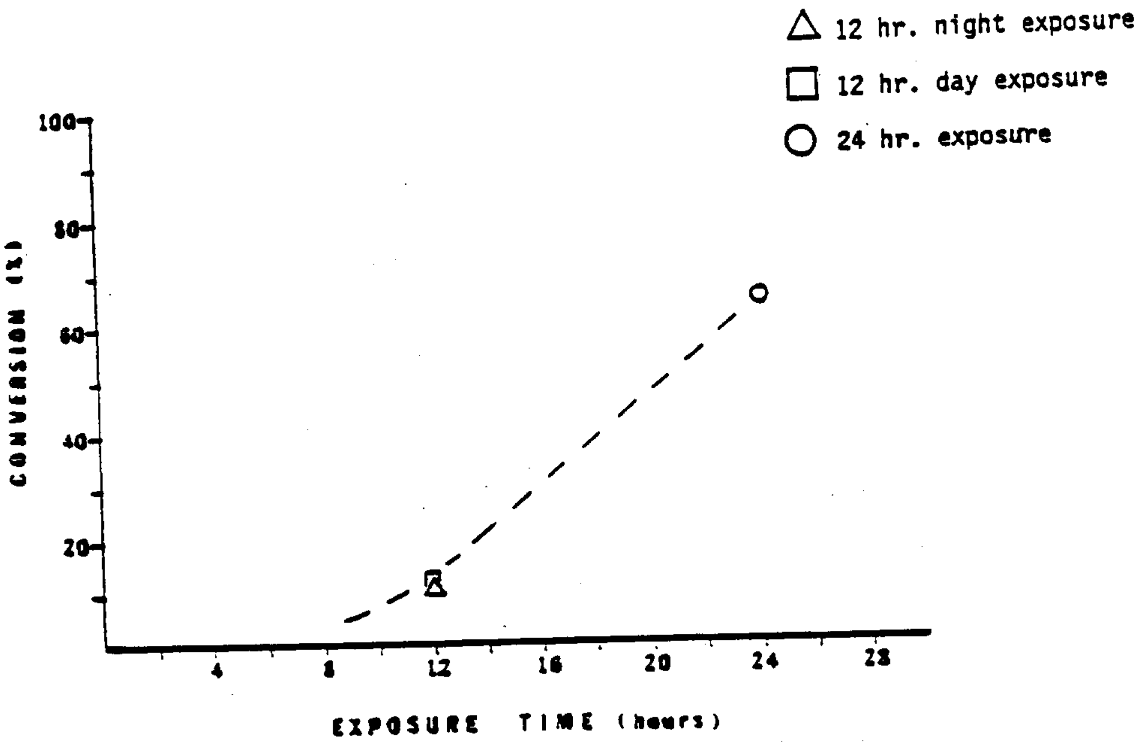


FIGURE 7-7: FIELD REACTION - RUN 5

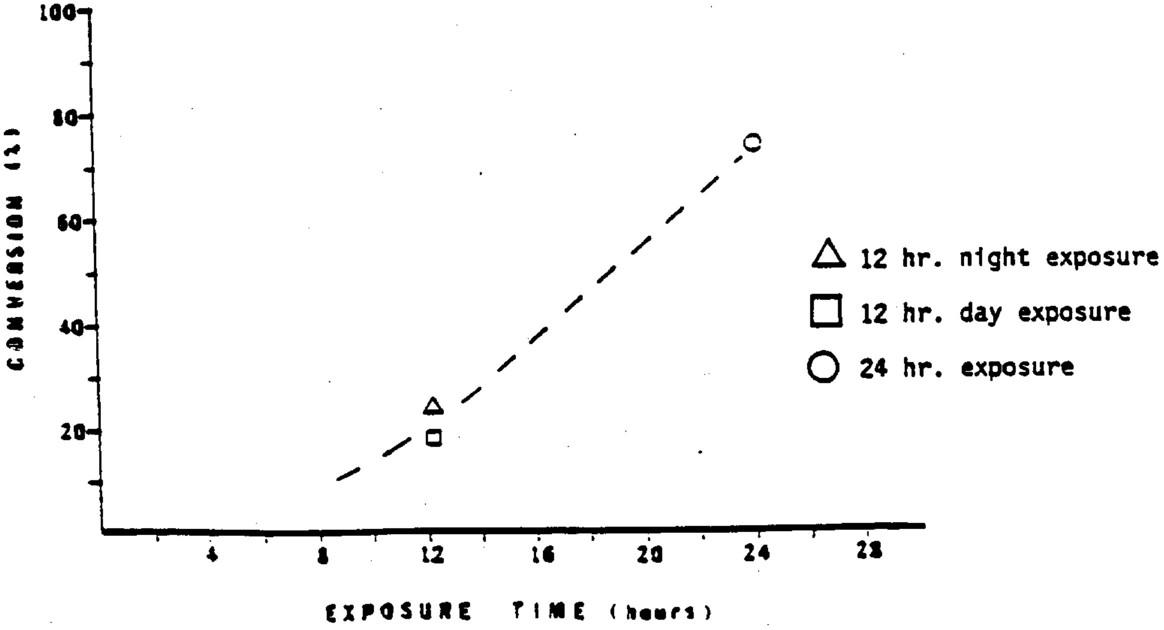


FIGURE 7-8: FIELD REACTION - RUN 7

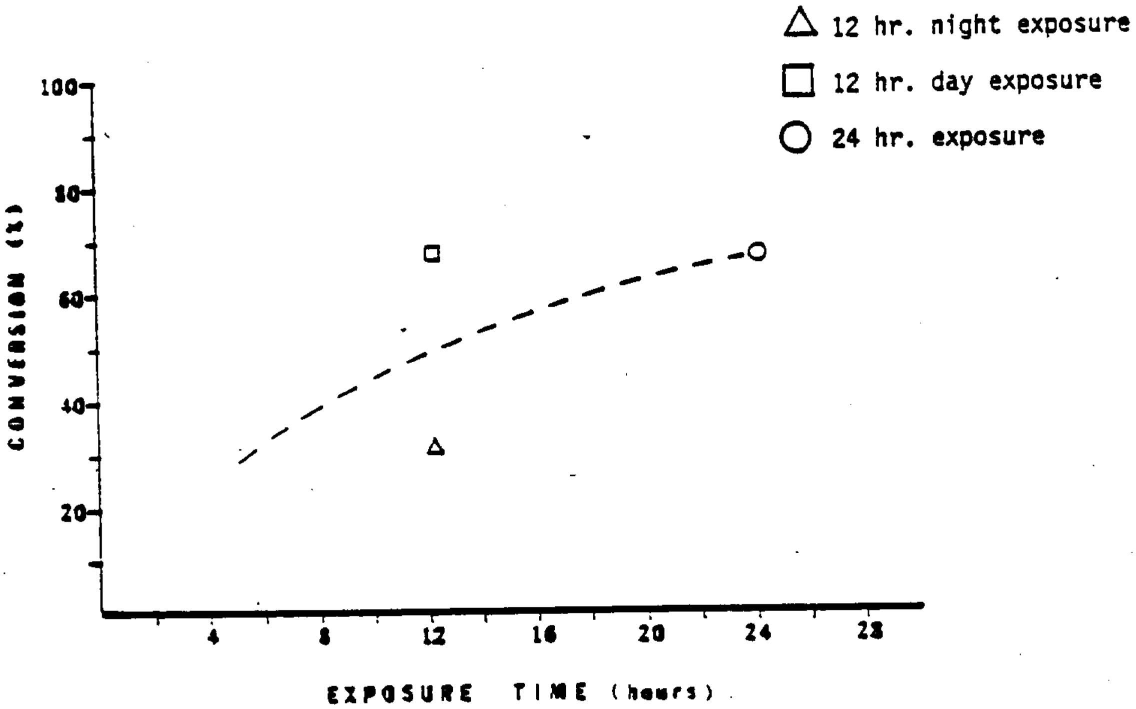


FIGURE 7-9: FIELD REACTION - RUN 8

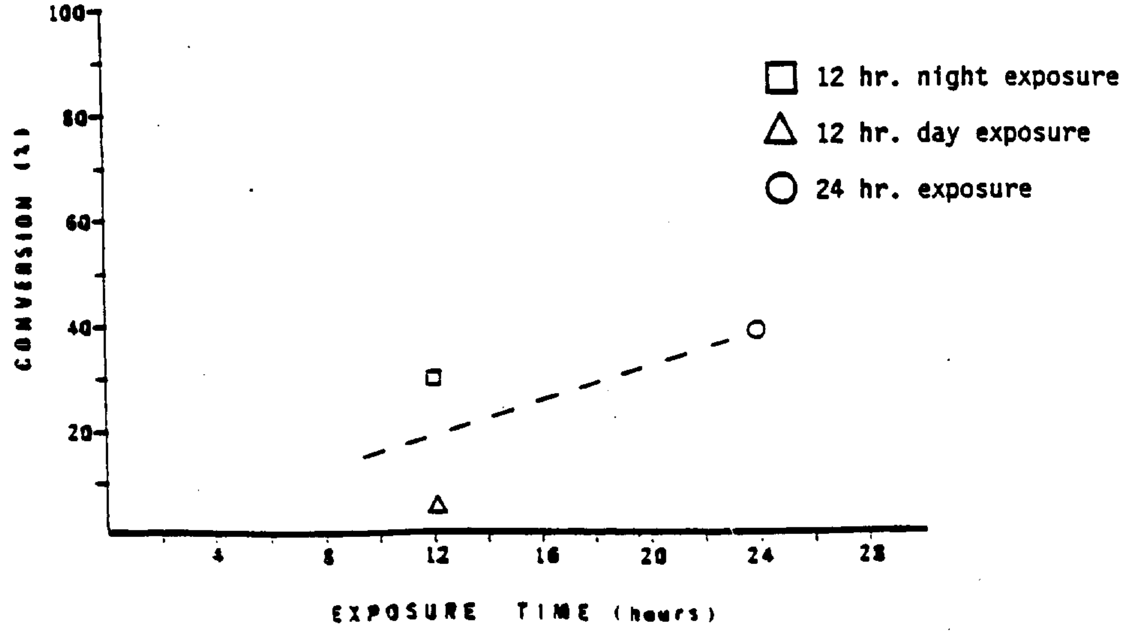


FIGURE 7-10: FIELD REACTION - RUN 9

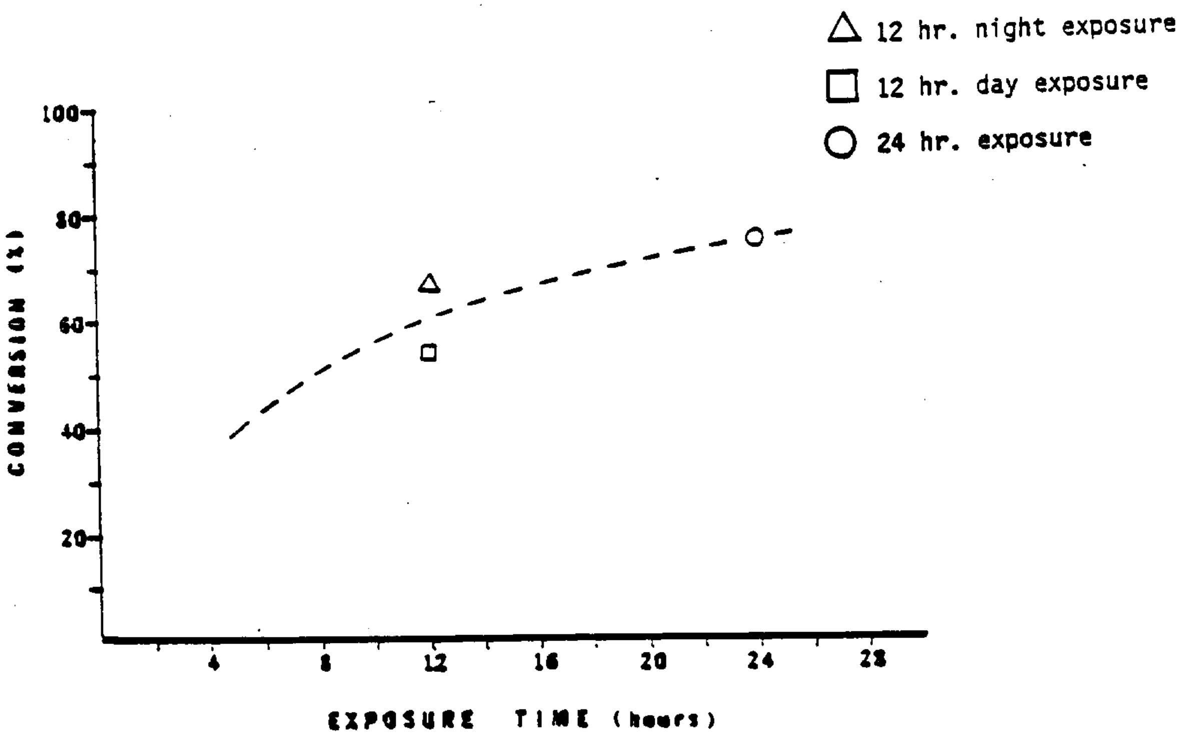


FIGURE 7-11: FIELD REACTION - RUN 10

TABLE 7-9
ESTIMATED Cr(VI) HALF LIFE DURING FIELD REACTION TESTS

Field Reaction Test No.	Estimated Half Life (Hrs.)	Comments
2	12	Chrome Crankshaft
3	14	Chrome Crankshaft
5	21	Chrome Crankshaft
7	20	Chrome Crankshaft
8	13	Chrome Crankshaft
9	~30 (est.)*	ARCO
10	9	ARCO
11	12	ARCO
	Average Half life = 16.4 hrs (± 6.9 hrs.)	

*Possible outlier--if excluded the average half life is 14.4 hrs (± 4.4 hrs)--still in excellent agreement with the laboratory results.

expected range over all of the field test results. Analytical problems were evident in this particular run. Duplicate filter results for each time period (T_O, T_{12N}, T_{12D}, T_{24}) demonstrated much more variability than that usually encountered during these analyses. Subsequent IC analyses of the same Run 9 samples indicated Cr(VI) values that had decreased by approximately 30 ng for each time period over that originally obtained by Method ADDL006 due to Cr(VI) instability in the acetate medium. Data from this run might be considered suspect. If the Run 9 data point is discarded, the average Cr(VI) half life for the field test is 14.4 hours (± 4.4 hours), remarkably close to the laboratory half life value of 13 hours. However, this close agreement must be evaluated in relation to previously mentioned rates regarding the generally "good" air quality during the entire study.

Study of the data indicates the following:

- In the absence of more accurate ambient data, field reaction studies indicate that significant reduction of Cr(VI) is likely to take place over hours instead of minutes.
- There is no apparent correlation between photochemical input and Cr(VI) reactivity.
- Both chromium sources demonstrated similar Cr(VI) reduction trends.
- There is a strong parallel between the field reaction study data and that obtained in laboratory tests.

8.0 REFERENCES

1. Lovett, R. J., and G. F. Lee; Environ: Sci. Technol. (1976) 1, 67-71.

2. Thompson, K. C., and K. Wagstaff; Analyst, London (1979), 104, 114-231.

3. National Institute of Occupational Safety and Health, "NIOSH Manual of Analytical Methods." U.S. Department of Health, Education and Welfare; Public Health Service; Center for Disease Control; Atlanta, GA (1977). NIOSH OHEN (NIOSH) Publication No. 77-157C, 2nd Ed., Vol. 3, Method S-317 and S-323.

4. U.S. Environmental Protection Agency, "Method for Chemical Analysis of Water and Wastes." EPA 600/4-79-020 (March 1979), Section 9.2, Methods 218.4 and 218.5.

5. U.S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste," 2nd Ed. (1982). SW-849 Methods 1310, 3020, 3050, 3060, 7190, 7195, and 7196.

6. National Institute of Occupational Safety and Health, "NIOSH Manual of Analytical Methods." U.S. Department of Health, Education and Welfare; Public Health Service; Center for Disease Control; Cincinnati, Ohio (1984), DHHS (NIOSH) Publication No. 84-100, 3rd Ed., Vol. 1, Method 7600.

7. "Method Evaluation, Improvement and Development for Hazardous Waste Analysis and Characterization." Work Assignment No. 4, "Evaluation of Methods for Determinating Hexavalent Chromium in Waste." RTI Interim Report; U.S. EPA Contract No. 68-23-3099 (March 1983), 85-98.

8. Moreton, J., J. Bettelley, H. Mathers, A. Nichols, R. W. Perry, D. B. Rutcliff, and L. Svensson, Ann. Occup. Hyg. (1983), 27, 137-156.

9. U.S. Environmental Protection Agency, "Method for Chemical Analysis of Water and Wastes." EPA 600/4-79-020 (March 1979), Section 9.2.

10. California Air Resources Board Proposed Method 106A.

11. Sickles, J. E., L. Ripperton, W. C. Eaton, R. S. Wright, "Oxidant-Precursor Relationships Under Pollutant Transport Conditions." Outdoor Smog Chamber Study, U.S. EPA Publication No. EPA-600/3-79-078 (1979).

12. Sickles, J. E., and R. E. Wright, "Atmospheric Chemistry of Selected Sulfur-Containing Compounds. Outdoor Smog Chamber Study--Phase I," U.S. EPA Publication No. EPA 60/7-79-227 (1979).

13. Private Communication with Dr. Peter McMurry, University of Minnesota.

14. "Sampling and Analytical Methods Development for Dry Deposition Monitoring." RTI Project in Progress. U.S. EPA Contract No. 68-02-4079.

15. Gutknecht, W. F., M. B. Ranade, P. M. Grohse, A. Damle, and D. O'Neal, "Heavy Metal Aerosols: Collection and Dissolution Efficiencies," RTI Final Report, NIOSH Contract No. 210-79-0048, pp. 24-46 (1981).

16. *Locating and Estimating Air Emissions from Source of Chromium*, EPA-450/4-84-007g, July 1984.

17. *Health Assessment Document for Chromium--Final Report*, EPA-600/8-83-014F, (PB85-115905), August 1984.

18. *Medical and Biologic Effects of Environmental Pollutants. Chromium*, National Academy of Sciences, PB237-183, May 1974.

19. R. M. Riggin, E. J. Mezey, and W. M. Hendry, *A Literature Review on Occurrence and Methodology for Determination of Nickel, Chromium, Manganese and Arsenic Species in Air*, EPA-600/4-84-026, March 1984.

20. Christian Seigneur, "A Theoretical Study of the Atmospheric Chemistry of Chromium," SYSAAP-85/209, USEPA Contract 68-02-3889, December 1985.

21. G. Cainelli and G. Cardilla, *Chromium Oxidations in Organic Chemistry*, Springer-Verlag, New York, 1984.

22. H. J. M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, 1979, p. 23.

23. Grohse, P. M. and J. E. Sickles, II, *Sampling and Analysis Methods for Particulate Sulfate and Nitrate--A Literature Review*. Research Triangle Institute Report on EPA Contract 68-02-4079 (1985).

24. Lippman, M. and T. J. Kneip, "Exchange of Comments: Measurement of Sulfuric Acid Aerosol, Sulfur Trioxide and the Total Sulfate Content of the Ambient Air," *Anal. Chem. 48:* 2269-2270 (1976).

25. Pate, J. B., J. W. Lodge, Jr., and M. P. Neary, "The Use of Impregnated Filters to Collect Traces of Gases in the Atmosphere," *Anal. Chim. Acta. 28:* 341-348 (1963).

26. Adams, D. F., W. L. Bamesberger, and T. J. Robertson, "Analysis of Sulfur Containing Gases in the Ambient Air Using Selective Prefilters and Microcoulometric Detector," *Air Pollu. Control Assoc. J. 18:* 145-148 (1968).

27. Tanaka, S., Y. Hashimoto, M. Darzi, and J. W. Winchester, "Sampling Method and PIXE Analysis for Atmospheric Sulfur Dioxide with Alkali Coated Filters, *Nucl. Inst. and Meth.* 181: 509-515 (1981).

28. Sickles, J. E., II and P. M. Grohse, Literature Review: Methods for Sampling and Analysis of Sulfur Dioxide and Nitrogen Dioxide. Research Triangle Institute Report on EPA Contract 68-02-4079 (1984).

29. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1979 (Dec. 1982 revision).

30. Private Communication with Robert Joyce, Dionex Corporation (Sunnyvale, California) (September 1987).

31. Ehman, D. L., V. C. Anselmo, and J. M. Jenks, "Determination of Low Levels of Airborne Chromium (VI) by Anion Exchange Treatment and Inductively Coupled Plasma Spectroscopy," Spectroscopy 3: 32-35 (1988).

32. Davis, E. James, P. Ravindran, and A. K. Ray, "Single Aerosol Particle Studies," Advances in Colloid and Interface Science 15: 1-24 (1981).

9.0 GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

CARB	California Air Resources Board
Cr(VI), Cr^{+6}	Hexavalent chromium
Cr(III), Cr^{+3}	Trivalent chromium
ng/m^3	Nanograms per cubic meter
C.V.	Precision, as Coefficient of Variation
PVC	Polyvinylchloride
Fe^{+2}	Ferrous ion
V^+, V^{+2}	Reduced vanadium species
Organics	Generic expression referring to those oxidizable organic compounds
CO_2	Carbon dioxide
HNO_3	Nitric acid (atmospheric)
Teflon	Generic expression for chlorofluorocarbon materials
MnO_2	Manganese dioxide
in-situ	Measurement--real time analysis of the desired component--a given
Impinger	A dynamic sampler utilizing the collection of a gaseous or particulate species by passing through liquid absorption medium
Parafilm	A polyneric waxy film used to provide a temporary film on containers
mm	Millimeter
Plexiglass	A generic expression referring to acrylic plastics

APPENDIX A

REPORT OF FIELD TEST
PERFORMED BY CARB, OCTOBER 1987

CHROME CRANKSHAFT CO
6845 EAST FLORENCE PLACE • BELL GARDENS, CALIF 90201
TELEPHONE 773-5936 AREA CODE 213

POST OFFICE BOX 2126, BELL GARDENS, CALIF. 90201

LOS ANGELES CAL. • CHICAGO, ILL.

COMPLETE [illegible] RELIA[illegible]

December 9, 1986

Frances Cameron, P.E.
Assoc. Air Resources Engineer
State of California
Air Resources Board
Toxic Pollutants Branch/
Compound Evaluation Section
P.O. Box 2815
Sacramento, CA 95812

Re: Scrubber Test Results

Dear Ms. Cameron,

As per your telecon with Mr. Jerry Miller, I am enclosing copies of our recent wet scrubber test results. I trust that this information is as you require to facilitate the successful evaluation procedures toward air emission guidelines.

Thank you for your assistance in these matters and if we can be of further help, please let me know.

Very Truly Yours,

HHROME CRANKSHAFT CO., INC.

David S. Davies

David S. Davies
Vice President

DSD
encl.

LN 17207

CHROME CRANKSHAFT CO.
10/22/86

Test No: 1(as is make up water)	Scrubber Inlet		Scrubber Outlet
Flue Gas	A	B	
Temperature, °F	73	75	61
Velocity, ft/sec	24.6	21.4	26.3
Static pressure, in. H_2O	-0.95	-0.95	-0.50
Flue Diameter, in.	24x24	24x24	27x35
Flue Area, Sq. ft.	4.00	4.00	6.56
Flow Rate, ACFM	5900.	5140.	10,300.
, SCFM	5750.	5000.	10,300.
, DSCFM	5680.	4930.	10,200.
Moisture, % by vol.	1.2	1.1	1.3
Chromium	(11:10-12:10)	(11:10-12:10)	(11:10-12:10)
Sample Volume, DSCF	28.83	27.18	29.28
Concentration			
Total Cr, PPM	5.06	0.22	0.04
, mg/m^3	11.1	0.48	0.08
Cr^{+6}, PPM	3.75	0.16	0.01
, mg/m^3	8.22	0.35	0.03
Emission Rate, lbs/hr			
Total Cr	0.236	0.009	0.003
Cr^{+6}	0.175	0.006	0.001
Removal Efficiency, %			
Total Cr			98.8
Cr^{+6}			99.4

vol. wt. mean mg/m^3, TCr 6.17
10^{-4} gr/dscf 2.7

LN 17207

CHROME CRANKSHAFT CO.
10/22/86

Test No: 2(ph neutral-make up water)	Scrubber Inlet		Scrubber Outlet
Flue Gas	A	B	
Temperature, °F			
Velocity, ft/sec			
Static pressure, in. H_2O			
Flue Diameter, in.	24x24	24x24	27x35
Flue Area, Sq. ft.	4.00	4.00	6.56
Flow Rate, ACFM			
, SCFM	(from Test 1)		
, DSCFM	5680.	4930.	10,200.
Moisture, % by vol.	1.1	1.5	1.9
Chromium	(13:05-14:05)	(13:05-14:05)	(13:05-14:05)
Sample Volume, DSCF	28.62	26.79	27.94
Concentration			
Total Cr, PPM	3.84	0.39	0.12
, mg/m^3	8.42	0.86	0.27
Cr^{+6}, PPM	2.82	0.28	0.09
, mg/m^3	6.18	0.61	0.20
Emission Rate, lbs/hr			
Total Cr	0.180	0.016	0.010
Cr^{+6}	0.132	0.011	0.008
Removal Efficiency, %			
Total Cr			94.9
Cr^{+6}			94.4
vol. wt. mean mg/m^3	4.91		
10^{-4} gr/dscf	21.4		

TRUESDAIL LABORATORIES, INC.

LN 17207

CHROME CRANKSHAFT CO.
10/29/86

Test No: 3 (clean make up water)	Scrubber Inlet		Scrubber Outlet
	A	B	
Flue Gas			
Temperature, °F	79	81	69
Velocity, ft/sec	23.6	25.2	27.8
Static pressure, in. H_2O	-0.98	-0.98	-0.43
Flue Diameter, in.	24x24	24x24	27x35
Flue Area, Sq. ft.	4.00	4.00	6.56
Flow Rate, ACFM	5660.	6050.	10,900.
, SCFM	5440.	5800.	10,700.
, DSCFM	5300.	5650.	10,400.
Moisture, % by vol.	2.6	2.6	2.7
Chromium	(12:20-13:20)	(12:19-13:19)	(12:20-13:20)
Sample Volume, DSCF	34.71	29.78	32.38
Concentration			
Total Cr, PPM	1.54	0.25	0.01
, mg/m^3	3.39	0.17	0.02
Cr^{+6}, PPM	1.06	0.08	0.01
, mg/m^3	2.32	0.17	0.01
Emission Rate, lbs/hr			
Total Cr	0.072	0.012	0.001
Cr^{+6}	0.050	0.003	0.001
Removal Efficiency, %			
Total Cr			98.8
Cr^{+6}			98.1

vol. wt. mean mg TCr/m^2 .87
10^{-1} gr/dscf 3.8

respectfully submitted,

Truesdail Laboratories. Inc.
S Hugh Brown
S. Hugh Brown, Supervisor
Air Pollution Testing

EQUIPMENT DESCRIPTION

CHROME CRANKSHAFT CO. 6845 E. Florence Place, Bell Gardens

All tanks have 33 oz./gal. of chromic acid, operating 16 hours/day and 5 days/week, with plating amperage varies between 4000 and 6000 amps.

CHROME PLATING TANKS

TANK 1 - 3'-6"W. X 24'-1"L. X 3'-9"H.
TANK 2 - 3'-4"W. X 20'-0"L. X 3'-8"H.
TANK 3 - 3'-4"W. X 21'-0"L. X 3'-7"H.
TANK 4 - 3'-6"W. X 18'-1"L. X 3'-6"H.
TANK 5 - 3'-6"W. X 18'-0"L. X 3'-6"H.
TANK 6 - 3'-0"W. X 18'-1"L. X 3'-4"H.
TANK 7 - 3'-0"W. X 18'-0"L. X 3'-4"H.
TANK 8 - 3'-0"W. X 18'-0"L. X 3'-5"H.

SCRUBBERS

SCRUBBER 1 - WET SCRUBBER, ERIKSON, 5'-0"W. X 12'-0"L. X 7'-5"H., WITH A 2 HP PUMP AND A 10 HP BLOWER. VENTING TANKS 1 & 2

SCRUBBER 2 - WET SCRUBBER, ERIKSON, 5'-0"W. X 12'-0"L. X 6'-7"H., WITH A 2 HP PUMP AND A 10 HP BLOWER. VENTING TANKS 3 & 4

SCRUBBER 3 - WET SCRUBBER, ERIKSON, 5'-0"W. X 12'-0"L. X 8'-0"H., WITH A 2 HP PUMP AND A 10 HP BLOWER. VENTING TANKS 5 & 6

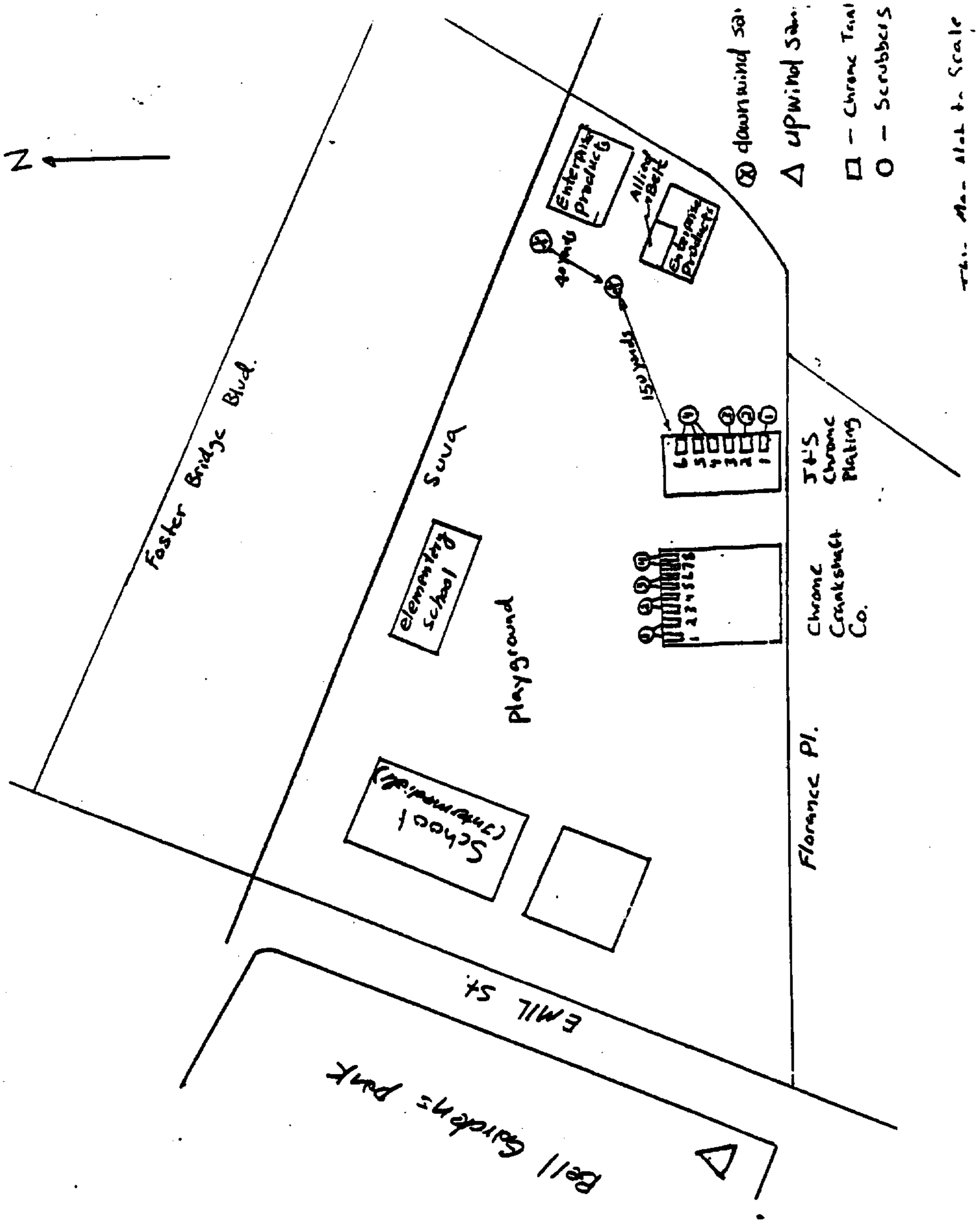
SCRUBBER 4 - WET SCRUBBER, ERIKSON, 5'-0"W. X 12'-0"L. X 7'-11"H., WITH A 2 HP PUMP AND A 15 HP BLOWER. VENTING TANKS 7 & 8

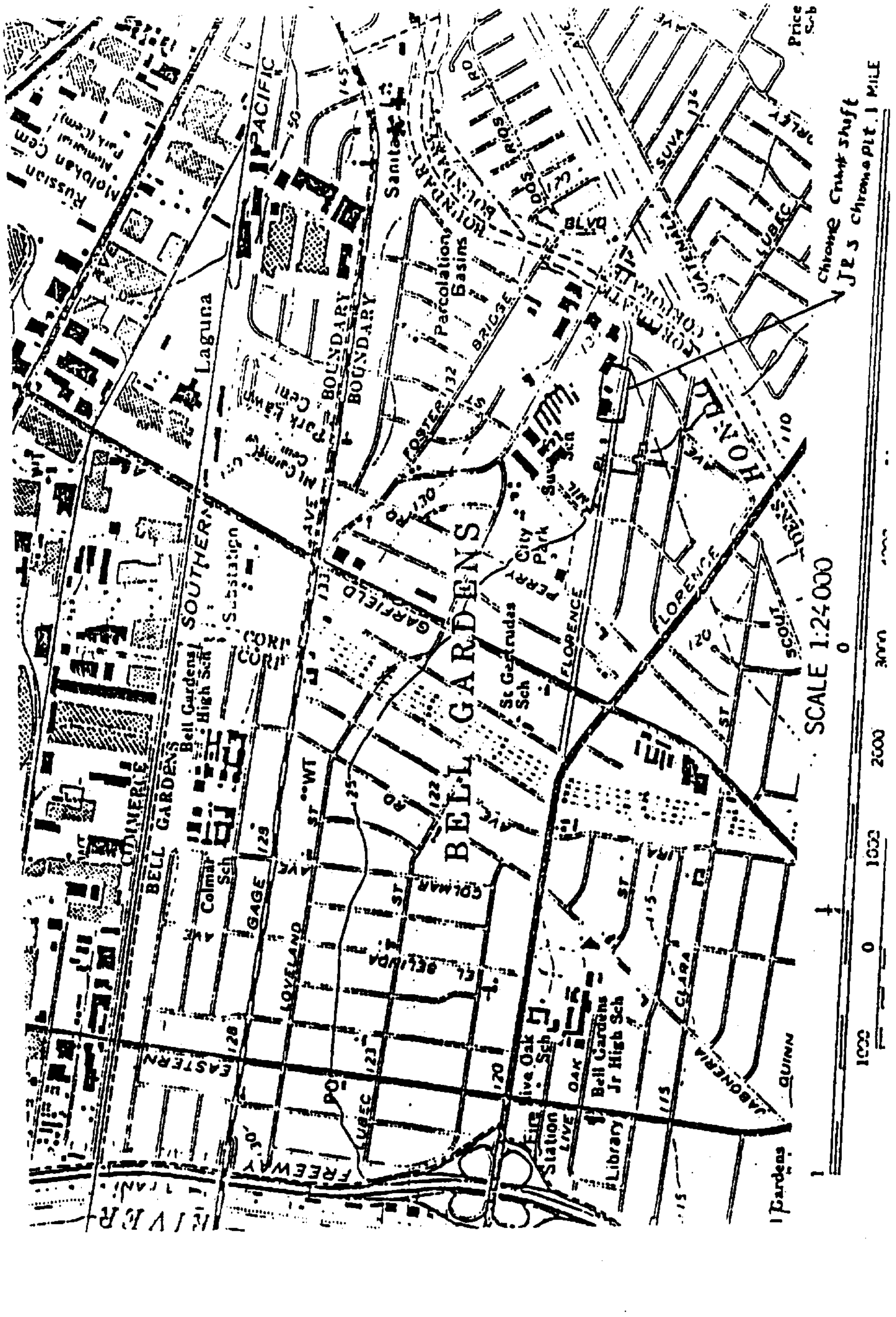
J & S CHROME PLATING CO. 6863 E. Florence Place, Bell Gardens

All tanks have 30 oz./gal.of chromic acid, operating 24 hours/day and 7 days/week, with plating amperage varies between 4200 and 4500 amps.

CHROME PLATING TANKS

TANK 1 - 3'-0"W. X 5'-0"L. X 7'-0"H. VENTED TO SCRUBBER 1.
TANK 2 - 2'-6"W. X 5'-0"L. X 8'-0"H. VENTED TO SCRUBBER 2.
TANK 3 - 2'-6"W. X 7'-0"L. X 7'-0"H. VENTED TO SCRUBBER 3.
TANK 4 - 2'-6"W. X 3'-6"L. X 7'-0"H. VENTED TO SCRUBBER 4.
TANK 5 - 2'-6"DIA. X 2'-7"H. VENTED TO SCRUBBER 4.
TANK 6 - 2'-6"DIA. X 2'-7"H. VENTED TO SCRUBBER 4.


N
Foster Bridge Blvd.
Suva
elementary school
Playground
School (Intermediate)
EMIL St.
Bell Gardens park
Florance Pl.
Enterprise Products
Allied Belt
Enterprise Products
40 yards
150 yards
1 2 3 4 5 6
J&S Chrome Plating
1 2 3 4 5 6 7 8
Chrome Crankshaft Co.
⊗ downwind sa
△ upwind sa
□ – Chrome Tank
○ – Scrubbers
This Map Not to Scale


BELL GARDENS
SCALE 1:24000
1 MILE
1000
0
1000
2000
3000
Chrome Crank shaft
JRS Chrome Plt.
Price Sch
Russian Molokan Cem
Laguna
PACIFIC
SOUTHERN
Substation
CORP
Bell Gardens High Sch
COMMERCE
BELL GARDENS
Colmar Sch
GAGE
LOVELAND
BOUNDARY
Park Lawn Cem
McCormick Cem
Sanita
Percolation Basins
BRIGSE
FOSTER
BLVD
CORONATH
HONDA
SUVA
LUBEC
GUATEMALA
GARFIELD
PERRY
City Park
St Gertrudes Sch
FLORENCE
FLORENCE
SCOUT
COLMAR
EL BELINDA
CLARA
JABONERIA
QUINN
EASTERN
FREEWAY
RIVER
Olive Oak Sch
Fire Station
OAK
LIVE
Bell Gardens Jr High Sch
Library
Gardens

State of California

MEMORANDUM

To : Gary Murchison, Manager
SSD, Process Evaluation Section

Date : November 2, 1987

Subject : Chromium +6 Analysis

Bob Kuhlman, Manager
MLD, Laboratory Services Section

From : Air Resources Board

Attached are the data for chromium +6 analyses you requested for the J & S Plating and Chrome Crankshaft study. Based on our preliminary analysis of the data, the impinger method appears to give consistently higher results than the PVC filter method. This relationship is comparable to that reported by Research Triangle Institute in their September 1987 progress report to Research Division for the Cr+6 methods comparison contract. Note that one point (site A PVC), taken on 10/7/87 appears to be an outlier. It is the only PVC sample that shows a daily site A sample lower than a site B sample. It also showed an abnormally low PVC/impinger ratio. While this sample was re-analyzed and the original result validated, the field sampling conditions are unknown and could not be duplicated. In addition, the analysis of the upwind PVC sample taken on 10/8/87 was below our analytical detection limit of 0.4 ng/M3. These two points were removed and a least squares analysis plot of the remaining points is presented in Figure 1.

Caution should be used in interpreting these results. While the study design included a laboratory blank and a trip blank, no impinger blank was provided. Dr. Peter Grohse of RTI has reported high Cr+6 in impinger blanks analyzed for their current South Coast Air Quality Management District study. Our laboratory has also seen Cr+6 in new glassware and has adopted a cleaning procedure involving a soak with concentrated nitric acid prior to use in Cr+6 analysis methods. In short, we do not know the history of the impinger glassware. It is possible that the impinger sample results reflect a positive Cr+6 artifact.

Based on this preliminary analysis, we recommend that future studies be designed to include an impinger blank. Additional samples should be taken to confirm the validity of the method results.

cc. Todd Wong
Catherine Dunwoody
Mike Poore
Dave Hartmann

Sacramento Laboratory Sample Analysis Request/Report Form
Monitoring & Laboratory Division - Laboratory Services Section

Division/Section Submitting Request: SSD/TPS	Date Submitted: October 1, 1987	Control Number: 13834 - 13872
Name of Requestor: Gary Murchison	Phone Number: 2-8521	Expected Sample Receipt Date: October 12, 1987

Analytical Service Requested:

Expected Sample Turn-Around Time: 2 weeks

AAS quantitative analysis of 12 filter samples, 13 buffered impinger samples and 13 dilute acid impinger rinse samples.

Description of Sample (how and where taken, purpose of sampling):

During the week of October 6-10, 1987, ambient air samples were taken near two sources - J & S Plating and Chrome Crankshaft. An upwind site was monitored for each source. The methods used to collect the samples were the PVC filter method and the impinger method, which uses a buffered solution of sodium acetate. Sample runs averaged 6 hours at an average volume of 7 M^3.

Specific Compounds/Elements/Ions to Analyze for or Identify:

Analysis of PVC filters and impinger solution samples for hexavalent chromium.
Analysis of impinger acid rinse samples for total chromium.

RESULTS

Analyst's Signature:	Phone Number: 4-6863	Date Completed: October 21, 1987	Instrument/Method: AAS/NLS 006

Qualitative Information/Quantitative Data:

See attachment.

Description of Methods Used:

Refer to NLS006 (former ADOL006) for the analytical description. The buffered impinger solution samples were adjusted to pH 5 with 10% HNO_3 before beginning the method's Cr + 6 complexation procedure. The acid rinses did not require preanalytical preparation.

Supervisor's Approval: R. Kuhlman	Phone Number: 2-6042	Date: 10/30/87

cc: Todd Wong
P. Venturini

(9-22-87)

J & S Plating and Chrome Crankshaft Study

Los Angeles - October 6-10, 1987

Hexavalent Chromium Results for PVC and Impinger (Buffer) Solution Samples

Method NLS006

Date	Sample #	Lab #	Sample Type	Cr^{+6} ng/M^3
10/6	001	13834	Upwind Buffer	13.9
	003	13836	Site A Buffer	47.3
	005	13838	Site B Buffer	30.2
	279872	13842	Upwind PVC	1.3
	279872A	13843	Site A PVC	10.2
	279872B	13844	Site B PVC	6.5
10/7	009	13845	Upwind Buffer	13.3
	011	13847	Site A Buffer	41.5
	013	13849	Site B Buffer	25.0
	280872	13852	Upwind PVC	0.9
	280872A	13853	Site A PVC	1.5
	280872B	13854	Site B PVC	6.9
10/8	015	13855	Upwind Buffer	15.2
	017	13857	Site A Buffer	19.2
	019	13859	Site B Buffer	26.0
	281872	13861	Upwind PVC	<0.4[2]
	281872A	13862	Site A PVC	4.7
	281872B	13863	Site B PVC	2.6

10/9	021	13864	Upwind Buffer	8.6
	023	13866	Site A Buffer	29.0
	025	13868	Site B Buffer	19.8
	282872	13870	Upwind PVC	2.4
	282872A	13871	Site A PVC	7.4
	282872B	13872	Site B PVC	4.6

Notes:

1. Trip Blank Buffer 4.2 ng (0.6 ng/M^3*) Cr^{+6}

   Lab Blank Buffer 3.6 ng (0.5 ng/M^3*) Cr^{+6}

   Lab Blank Spiked 25 ng/mL 21.4 ng/mL (86% recovery)

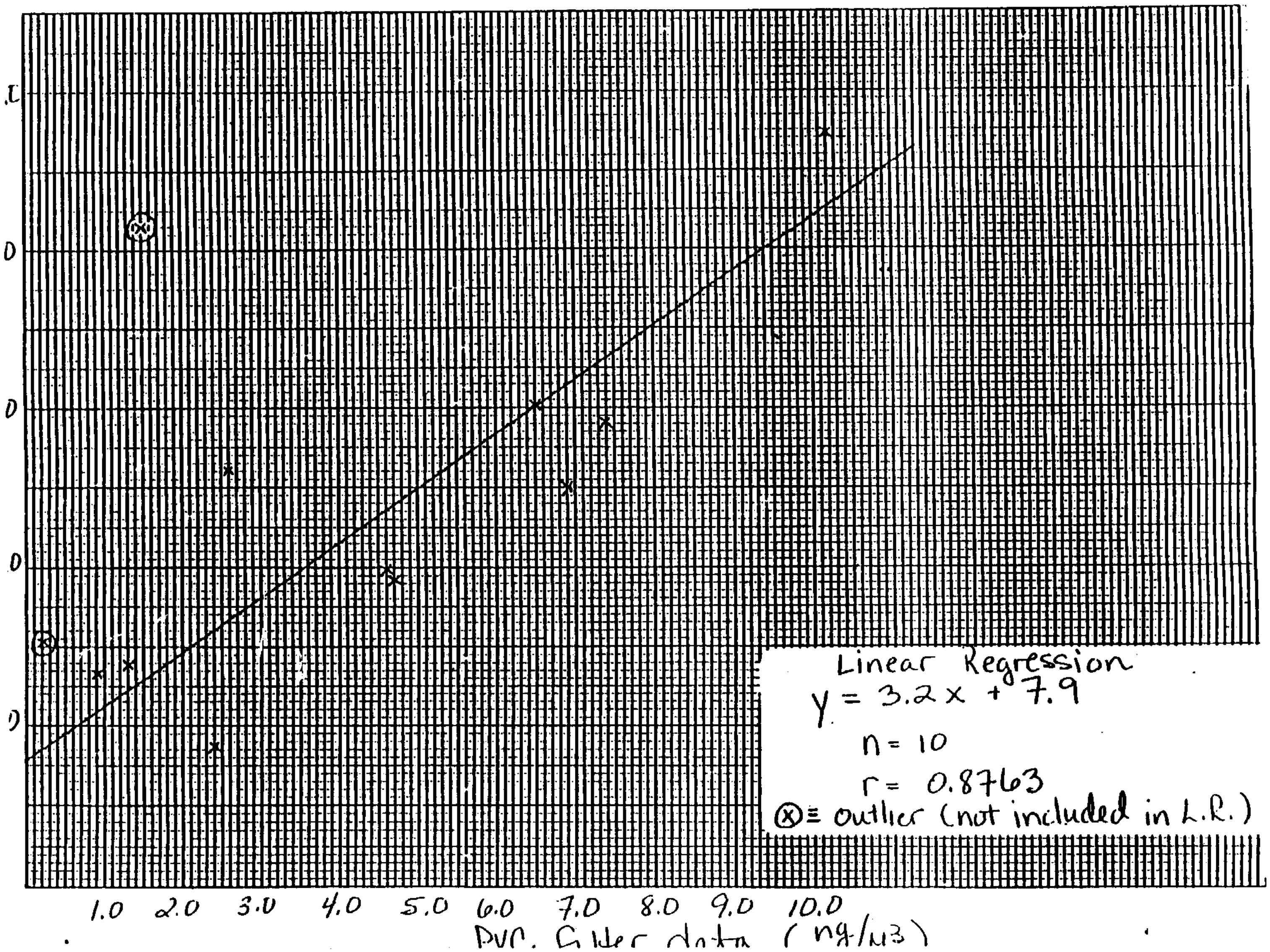
   *equivalent concentration assuming 7M^3 volume

2. Cr^{+6} Method detection limit is 0.4 ng/M^3 based on a volume of 7M^3.

Total Chromium Results for Impinger Acid Rinse Samples

All of the impinger acid rinse analysis total chromium results fell below the Method's detection limit of 3 ng/mL.

Impinger Data vs. PVC Filter Data
J & S Plating and Chrome Crankshaft Study



Linear Regression
$y = 3.2x + 7.9$
$n = 10$
$r = 0.8763$
⊗ ≡ outlier (not included in L.R.)

State of California

AIR RESOURCES BOARD

DRAFT PROTOCOL: Ambient Air Monitoring Study of Hexavalent Chromium Sources in Bell Gardens, California.

I. TEST PROGRAM

A hexavalent chromium air monitoring study near two chrome plating facilities in Bell Gardens, California will be conducted by the Air Resources Board staff during the week of October 5-9, 1987. The two sources have plating operations that can release hexavalent chromium emissions into the ambient air.

The objectives of the study are:

1. Compare the measurement methods and results using the present ARB filter method and the RTI impinger solution method.
2. Measure the ambient concentrations of hexavalent chromium upwind and downwind of the sources.

Specific meterological conditions will also be monitored during the sampling periods.

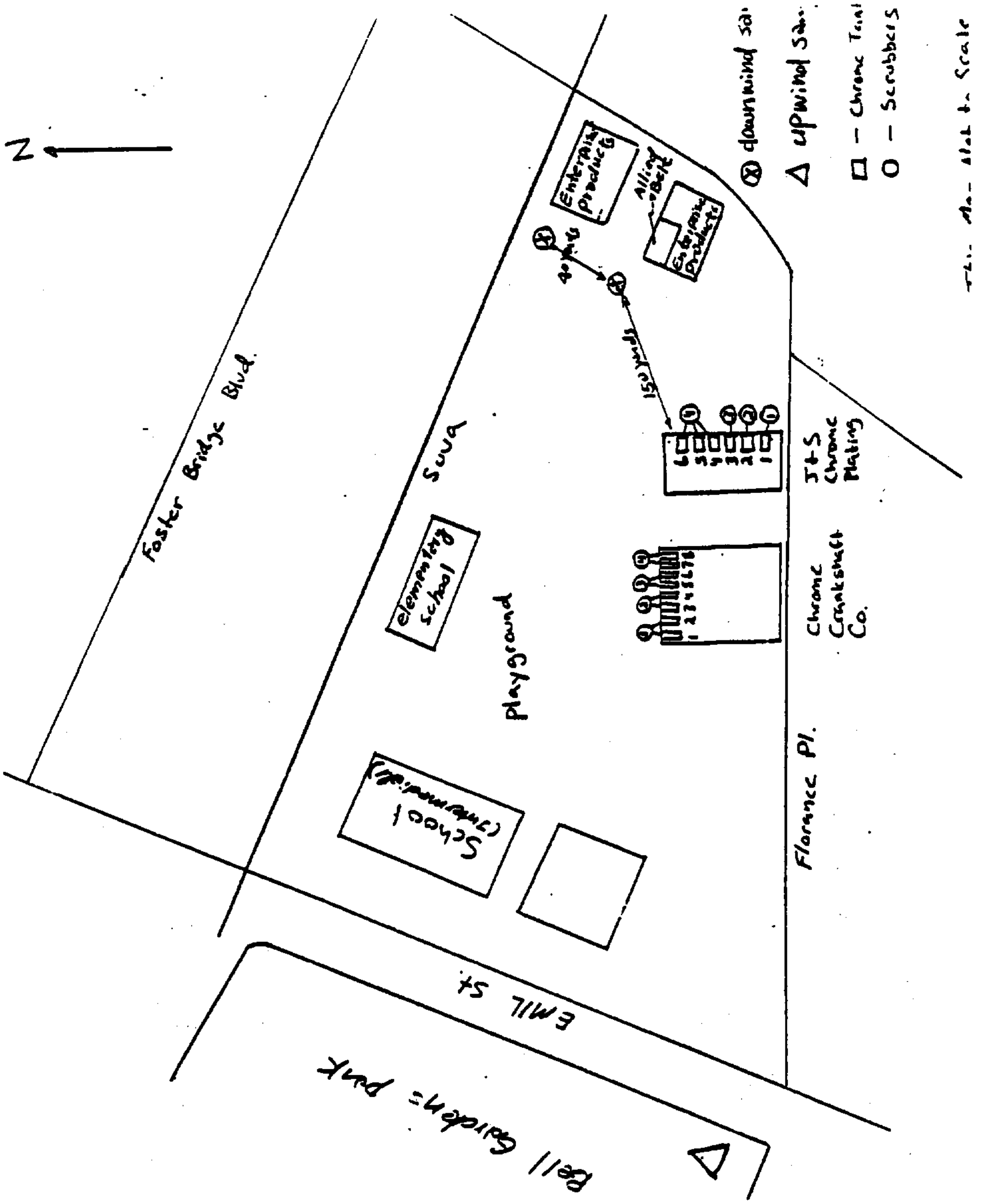
II. SAMPLING LOCATIONS

The sampling plan consists of two downwind monitoring sites which will be located approximately 150 and 200 yards to the east/northeast of the chrome plating facilities in an industrial park parking lot. The upwind site will be placed at the City of Bell Gardens corporation yard. This site is approximately 1/4 mile to the south/southwest of the plating facilities. Figure 1 shows the locations of the monitoring sites.

III. MEASUREMENT METHODS

In this monitoring study, the ARB staff will use two different sampling methods. The first is the filter method which is currently used by the ARB to sample hexavalent chromium for the ARB toxic monitoring network. This will involve the use of Xontech samplers which will contain a 37 mm PVC filter and a 37 mm teflon filter. The second method is the proposed RTI impinger solution method which contains 3 Smith-Greenberg impingers in series, with the first two impingers containing 100 ml of 0.05 M buffered sodium bicarbonate solution.

Both sampler types will operate in parallel at each monitoring site for 5 to 7 hours (depending on prevailing winds) at approximately 20 liters per minute. One run will be conducted each day starting on Tuesday, October 6, 1987 and ending on Friday, October 9, 1987. For the impinger sampling, the impinger will be kept in ice baths and teflon tubing will be used to sample the air at about 8 feet above the ground.


N
Foster Bridge Blvd
Suva
elementary school
Playground
School (Intermediate)
EMIL St
Bell Gardens Park
Florance Pl.
Chrome Crankshaft Co.
1 2 3 4 5 6 7 8
J+S Chrome Plating
1 2 3 4 5 6
150 yards
40 yards
Enterprise Products
Allied Belt
Enterprise Products
⊗ downwind Sa
△ upwind Sa
☐ – Chrome Tank
○ – Scrubbers
This Map Not to Scale

Following the collection of the filter samples, cassettes containing filters will be stored in a refrigerator at the Haagen-Smit Laboratory (HSL). The PVC filters will be analyzed by HSL for total chromium concentrations. The teflon filters will be transported back to Sacramento in a cooler containing ice for hexavalent chromium analysis.

After sampling of the impinger solutions, the contents of the first two impingers will be emptied into clean 250 ml polyethylene bottles. Those impingers will be rinsed 3 times with the sodium bicarbonate solution (25 ml for each rinse). After each wash, the rinse solution is emptied into the polyethylene bottle. The impingers will then be acid rinsed 3 times with 0.1 N nitric acid (30 ml) and emptied into another clean polyethylene bottle. All the collected solutions will be stored in the refrigerator at HSL until transport to Sacramento for hexavalent chromium analysis by the Aerometric Data Division Laboratory (ADD). Clean impingers will be used for each sampling run.

IV. LABORATORY ANALYSIS

See Attachment 1 for ARB Method ADDL006.

V. QUALITY ASSURANCE

A set of filters (1 PVC and 1 teflon) will be retained and given to the appropriate laboratories as field blanks. Field blanks for the sodium acetate and the acid rinse solutions will be prepared by rinsing a clean set of impingers with each solution and retaining it in separate polyethylene bottles for later analysis by ADD.

Attachment 1

ARB Method ADDL006

Standard Operating Procedure for the Speciation and Analysis of Hexavalent Chromium at Ambient Atmospheric Levels

Method ADDL006
Effective Date: December 19, 1986
Revision: 1.0
Approved: 1/12/87
Page 1 of 5

STATE OF CALIFORNIA
AIR RESOURCES BOARD
AEROMETRIC DATA DIVISION LABORATORY

Standard Operating Procedure for the Speciation and Analysis of Hexavalent Chromium at Ambient Atmospheric Levels

1. SCOPE

This document describes the determination of chromium $^{+6}$ in aqueous media after sampling ambient air. The procedure has been tailored to concentrations which would be expected in ambient air. Although the procedure described is known to complex other metal ions, the procedure has not been validated for any metal species other than hexavalent chromium.

2. SUMMARY OF METHOD

A low volume air sampler capable of sampling at a constant rate of 13-15 liters-per-minute for at least 24 hours is fitted with a 37 mm Gelman VM-1 (PVC) membrane filter. After sampling, the filter is added to 50 mL of water and the complexation procedure carried out in the presence of the filter.

The aqueous solution is buffered to pH 4.5 and an aqueous solution of APDC added. After mixing, the solution is filtered through a disposable cartridge containing C_{18}-bonded silica gel. The complex is absorbed onto the gel. The water, remaining ions, and uncomplexed APDC are passed through into a filtering flask and discarded. The absorbed Cr^{+6}-complex is desorbed with acetone, the acetone evaporated, and the resultant residue diluted to 2.0 mL as 10% nitric acid in water.

This solution is then analyzed by flameless atomic absorption spectrophotometry (FAAS) for chromium.

3. LIMITATIONS AND INTERFERENCES

3.1 The concentration ranges expected for Cr^{+6} in ambient air (1-5 ng/M^3) require that <u>extreme</u> care must be taken to insure that glassware and reagents do not contribute to the measured levels. Blanks must be analyzed with every batch of samples.

3.2 Trivalent chromium at levels ten times the Cr^{+6} concentration does not interfere in the method. Iron (Fe+3) does not interfere, except that excess ferric ion will compete with Cr^{+6} for available complexing agent. This effect has been minimized by performing the complexation step at pH 4.5. The other metals known to form APDC complexes at pH 4.5 (copper and cobalt) do not occur at sufficiently high levels to deplete the complexing agent.

3.3 Matrix effects have been reduced or eliminated by the extraction of the complex into an organic solvent and matching the final aqueous diluent to the 10% nitric acid solution used for diluting standards.

4. APPARATUS

4.1 Perkin-Elmer: Model 3030B Atomic Absorption Spectrophotometer, HGA-600 Graphite Furnace, AS-60 Autosampler and PR-100 Printer.

4.2 Vacuum filtering apparatus equipped with Sep-Pak C_{18} cartridge adaptor and teflon tubing.

4.3 Conical, graduated centrifuge tube 15 mL capacity.

4.4 Sep-Pak cartridge: Waters Assoc. #51910. Prepare cartridge for use by first filtering 5 mL of acetone through it, then washing with 10 mL distilled water, then 10 mL of Wash Solution, and repeat the acetone and D.I. washings.

5. REAGENTS

5.1 Nitric acid, Ultrex grade.

5.2 Stock standard, 250 mg/L: Dissolve 141.4 mg $K_2Cr_2O_7$ in 10% nitric acid solution and dilute to 200 mL in a volumetric flask. 1 mL = 0.25 mg Cr^{+6}.

5.3 Intermediate standard (I.S.), 0.5 mg/l: Dilute 100 uL of the stock standard in 50 mL of 10% nitric acid in a volumetric flask. 1 mL = 0.5 ug Cr^{+6}.

5.4 Working standard: Dilute 1.0, 3.0 and 5.0 mL of I.S. in 50 mL of 10% nitric acid. These correspond to 10 ng/mL, 30 ng/mL and 50 ng/mL Cr^{+6}. Prepare working standards daily.

5.5 Buffer, pH 4.5: 50 mL 0.1 M $KHC_8H_4O_4$ and 8.7 mL 0.1 M NaOH.

5.6 APDC solution: Dissolve 2.5 gms ammonium pyrrolidine dithiocarbamate in 50 mL distilled water. Filter the solution through a glass fiber filter to remove the insoluble sediment. The resultant solution will be a clear yellow. The APDC used is J. T. Baker's #3337-2.

5.7 Wash solution: 10 mL D.I. water, 5 mL APDC solution and 10 mL pH 4.5 buffer.

6. INSTRUMENT CALIBRATION

6.1 Optimize the instrument for the flameless analysis of chromium following the manufacturer's instructions.

6.2 Use a pyrocoated graphite furnace tube containing a L'vov platform and condition the tubes as per manufacturer's instructions.

6.3 Set the instrument operating conditions as follows:

Step	Furnace Temp (°C)	Time (seconds) Ramp	Time (seconds) Hold
1 Dry	120	5	35
2 Ash	1650	5	20
3 Cool	100	2	5
4 Atomize	2600	0	5
5 Clean	2700	2	8
6 Cool	20	1	20

Wavelength 357.9 nm; lamp current 24 mA, Slit 0.7 argon gas flow 1.5 L/minute (gas stop at Atomize), 20 ul sample injection.

6.4 The instrument is calibrated using the three working standards. Recalibrate if values differ by more than ±15%.

6.5 Determine the least squares fit of the calibration data; the analysis must result in a slope of 1.00 ± 15%. Perform a reslope calibration at least every ten samples.

7. SAMPLE ANALYSIS

7.1 Place the filter in a 100 mL graduated beaker, add 50 mL deionized water, 2 mL of buffer, and 1 mL of APDC solution, swirl and let stand for 20 minutes.

7.2 Aspirate aqueous solution through a prepared Sep-Pak C_{18} cartridge.

7.3 Using a 10 mL syringe, desorb the trapped Cr^{+6}-APDC complex with 5 mL acetone directly into a 15 mL conical centrifuge tube.

7.4 Using a hot water bath (more than 80°C), concentrate the acetone solution to dryness. Note: There will be a small liquid residual, mostly residual water. As much acetone must be removed as possible, since it causes problems during the analysis step.

7.5 While hot, add 0.2 mL concentrated Ultrex nitric acid (6 drops), and place back in the heating bath for 30 seconds.

7.6 Dilute to 2.0 mL with D.I. water.

7.7 Inject 20 uL of the concentrate in triplicate for analysis using the calibrated FAAS system.

7.8 Print out the analysis results with identifying laboratory identification number. Record results and calculations in the AAS laboratory workbook. Record the calculated concentration in nanograms/M^3 on the laboratory data sheet. The concentration may be calculated as follows:

$$\text{Chromium +6, ng/M}^3 = \frac{\text{Concentration Found, ng/mL}}{\text{Volume Sampled, M}^3} \times \text{Dilution Factor}$$

8. METHOD VALIDATION

8.1 The calibration curve from 10 ng/mL to 50 ng/mL was constructed. The results of this procedure are shown in Table I.

8.2 The complexing solution was spiked with 10 ng, 30 ng and 50 ng Cr^{6}.[1] The analysis results are as follows:

Spike, ng	Recovered,[2] ng	Percent Recovery	RSD (Percent)
10	9.2	92	2.2
30	28.3	94	3.4
50	47.3	95	2.1

---

[1] The Cr^{+6} spike solution had 0.05 M Na_2CO_3 as its matrix.

[2] Results of three separate analysis minus blanks.

8.3 Filters were spiked as above and dried in a dessicator under vacuum. Their analysis resulted in the following:

Spike, ng	Recovered,[3] ng	Percent Recovery	RSD (Percent)
10	10.0	100	2.2
30	24.8	83	1.6
50	43.6	87	5.8

TABLE I

Method Calibration Data

Concentration ng/mL	Average Recovery	RSD (Percent)[4]
10	10.5	1.2
30	31.2	1.8
50	48.6	0.5

---

[3] Results of three separate analysis minus blanks.

[4] Relative Standard Deviation, n = 4
Correlation Coefficient: 0.998
Slope: 1.050
Intercept: -1.5 ng/mL
LOD: (i + 3 SD) = 3.04 ng/mL or 0.2 ng/M^3 based on a 20 M^3 sample

APPENDIX B

STATE OF CALIFORNIA AIR RESOURCES BOARD METHOD ADDL006 FOR THE SPECIATION AND ANALYSIS OF HEXAVALENT CHROMIUM AT AMBIENT ATMOSPHERIC LEVELS

STATE OF CALIFORNIA
AIR RESOURCES BOARD
AEROMETRIC DATA DIVISION LABORATORY

Method for the Speciation and Analysis of Hexavalent•Chromium at Ambient Atmospheric Levels

1. SCOPE

This document describes the determination of chromium $^{+6}$ on membrane filters after sampling ambient air. The method has been tailored to concentrations which would be expected in ambient air. Although the procedure described is known to complex other metal ions, the procedure has not been validated for any metal species other than hexavalent chromium.

2. SUMMARY OF METHOD

A low volume air sampler capable of sampling at a constant rate of 13-15 liters-per-minute for at least 24 hours is fitted with a 37 mm Gelman VM-1 (PVC) membrane filter. After sampling, the filter is added to 50 mL of water and the complexation procedure carried out in the presence of the filter.

The aqueous solution is buffered to pH 4.5 and an aqueous solution of APDC added. After mixing, the solution is filtered through a disposable cartridge containing C_{18}-bonded silica gel. The complex is absorbed onto the gel. The water, remaining ions, and uncomplexed APDC are passed through into a filtering flask and discarded. The absorbed Cr^{+6}-complex is desorbed with acetone, the acetone evaporated, and the resultant residue diluted to 2.0 mL as 10% nitric acid in water.

This solution is then analyzed by flameless atomic absorption spectrophotometry (FAAS) for chromium.

3. LIMITATIONS AND INTERFERENCES

3.1 The concentration ranges expected for Cr^{+6} in ambient air (1-5 ng/M^3) require that <u>extreme</u> care must be taken to ensure that glassware and reagents do not contribute to the measured levels. Blanks must be analyzed with every batch of samples.

3.2 Trivalent chromium at levels ten times the Cr^{+6} concentration does not interfere in the method. Iron (Fe+3) does not interfere, except that excess ferric ion will compete with Cr^{+6} for available complexing agent. This effect has been minimized by performing the complexation step at pH 4.5. The other metals known to form APDC complexes at pH 4.5 (copper and cobalt) do not occur at sufficiently high levels to deplete the complexing agent.

3.3 Matrix effects have been reduced or eliminated by the extraction of the complex into an organic solvent and matching the final aqueous diluent to the 10% nitric acid solution used for diluting standards.

4. APPARATUS

4.1 Perkin-Elmer: Model 3030B Atomic Absorption Spectrophotometer, HGA-600 Graphite Furnace, AS-60 Autosampler and PR-100 Printer.

4.2 Vacuum filtering apparatus equipped with Sep-Pak C_{18} cartridge adaptor and Teflon tubing.

4.3 Conical, graduated centrifuge tube 15 mL capacity.

4.4 Sep-Pak cartridge: Waters Assoc. #51910. Prepare cartridge for use by first filtering 5 mL of acetone through it, then washing with 10 mL distilled water, then 10 mL of Wash Solution, and repeat the acetone and D.I. washings.

5. REAGENTS

5.1 Nitric acid, Ultrex grade.

5.2 Stock standard, 250 mg/L: Dissolve 141.4 mg $K_2Cr_2)_7$ in 10% nitric acid solution and dilute to 200 mL in a volumetric flask.
1 mL = 0.5 ug Cr^{+6}.

5.3 Intermediate standard (I.S.), 0.5 mg/1: Dilute 100 uL of the stock standard in 50 mL of 10% nitric acid in a volumetric flask.
1 mL = 0.5 ug $Cr^{+}6$.

5.4 Working standard: Dilute 1.0, 3.0 and 5.0 mL of I.S. in 50 mL of 10% nitric acid. These correspond to 10 ng/mL, 30 ng/mL and 50 ng/mL Cr^{+6}. Prepare working standards daily.

5.5 Buffer, pH 4.5: 50 mL 0.1 M $KHC_8H_4O_4$ and 8.7 mL 0.1 M NaOH.

5.6 APDC solution: Dissolve 2.5 gms ammonium pyrrolidine dithiocarbamate in 50 mL distilled water. Filter the solution through a glass fiber filter to remove the insoluble sediment. The resultant solution will be a clear yellow. The APDC used is J. T. Baker's #B337-2. It may be necessary to extract the APDC solution with chloroform to remove trace amounts of chromium.

5.7 Wash solution: 10 mL D.I. water, 5 mL APDC solution and 10 mL pH 4.5 buffer.

6. INSTRUMENT CALIBRATION

6.1 Optimize the instrument for the flameless analysis of chromium following the manufacturer's instructions.

6.2 Use a pyrocoated graphite furnace tube containing a L'vov platform and condition the tubes as per manufacturer's instructions.

6.3 Set the instrument operating conditions as follows:

Step	Furnace Temp (°C)	Time (Seconds) Ramp	Time (Seconds) Hold
1 Dry	120	5	35
2 Ash	1650	5	20
3 Cool	100	2	5
4 Atomize	2600	0	5
5 Clean	2700	2	8
6 Cool	20	1	20

Wavelength 357.9 nm; lamp current 24 mA, Slit 0.7 argon gas flow 1.5 L/minute (gas stop at Atomize), 20 ul sample injection.

6.4 The instrument is calibrated using the three working standards. Recalibrate if values differ by more than ± 15%.

6.5 Determine the least squares fit of the calibration data; the analysis must result in a slope of 1.00 ± 15%. Perform a reslope calibration at least every ten samples.

7. SAMPLE ANALYSIS

7.1 Place the filter in a 100 mL graduated beaker, add 50 mL deionized water, 2 mL of buffer, and 1 mL of APDC solution, swirl and let stand for 20 minutes.

7.2 Aspirate aqueous solution through a prepared Sep-Pak C_{18} cartridge.

7.3 Using a 10 mL syringe, desorb the trapped Cr^{+6}-APDC complex with 5 mL acetone directly into a 15 mL conical centrifuge tube.

7.4 Using a hot water bath (more than 80°C), concentrate the acetone solution to dryness. Note: There will be a small liquid residual, mostly residual water. As much acetone must be removed as possible, since it causes problems during the analysis step. The acetone will be removed in 10-15 minutes.

7.5 While hot, add 0.2 mL concentrated Ultrex nitric acid (6 drops), and place back in the heating bath for 30 seconds.

7.6 Dilute to 2.0 mL with D.I. water.

7.7 Inject 20 uL of the concentrate in triplicate for analysis using the calibrated FAAS system.

7.8 Print out the analysis results with identifying laboratory identification number. Record results and calculations in the AAS laboratory workbook. Record the calculated concentration in nanograms/M^3 on the laboratory data sheet. The concentration may be calculated as follows:

$$\text{Chromium}^{+6}\text{, ng/M}^3 = \frac{\text{Concentration Found, ng/mL}}{\text{Volume Sampled, M}^3} \times \text{Dilution Factor}$$

8. METHOD VALIDATION

8.1 The calibration curve from 10 ng/mL to 50 ng/mL was constructed. The results of this procedure are shown in Table I.

8.2 The complexing solution was spiked with 10 ng, 30 ng and 50 ng Cr^6.[1] The analysis results are as follows:

Spike, ng	Recovered,[2] ng	Percent Recovery	RSD Percent)
10	9.2	92	2.2
30	28.3	94	3.4
50	47.3	95	2.1

8.3 Filters were spiked as above and dried in a dessicator under vacuum. Their analysis resulted in the following:

Spike, ng	Recovered,[3] ng	Percent Recovery	RSD Percent)
10	10.0	100	2.2
30	24.8	83	1.6
50	43.6	87	5.8

TABLE I
METHOD CALIBRATION DATA

Concentration ng/mL	Average Recovery	RSD (Percent)[4]
10	10.5	1.2
30	31.2	1.8
50	48.6	0.5

---

[1] The Cr^{+6} spike solution had 0.05 M Na_2CO_3 as its matrix.

[2] Results of three separate analysis minus blanks.

[3] Results of three separate analysis minus blanks.

[4] Relative standard Deviation, n = 4
Correlation Coefficient: 0.998
Slope: 1.050
Intercept: -1.5 ng/mL
LOD: (i + 3 SD) = 3.04 ng/mL or 0.2 ng/M^3 based on a 20 M^3 sample

APPENDIX C

U.S. ENVIRONMENTAL PROTECTION AGENCY
METHOD 218.5--CHROMIUM, DISSOLVED HEXAVALENT (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Chromium, Dissolved Hexavalent (Atomic Absorption, Furnace Technique)—Method 218.5

1. Scope and Application

1.1 This method covers the determination of dissolved hexavalent chromium (Cr^{6+}) in drinking and surface waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that potential interferring substances are taken into account. (See 4.1.)

1.2 The method may be used to analyze samples containing from 5 to 100 µg of Cr^{6+} per liter. The range of the method may be extended upward by dilution.

2. Summary of Method

2.1 The method is based on the separation of Cr^{6+} from the sample by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate is drawn off and the Cr^{6} precipitate resolubilized in nitric acid as trivalent chromium (Cr^{3+}) and quantified by furnace atomic absorption.

2.2 Hexavalent chromium may also be analyzed by the chelation/extraction technique (see Method 218.4 or the procedure described in 9.2 of the Atomic Absorption methods found in this manual).

3. Sample Handling and Preservation

3.1 For sample handling, cleaning glassware and the filtration procedure see part 4.1 of the Atomic Absorption Method section of this manual.

3.2 The sample must not be preserved by acidification, but instead transported and stored until time of analysis at 4°C.

3.3 Stability of Cr^{6+} in environmental samples is not completely understood at this time. The chemical nature of the sample matrix can have a definite affect on the chemistry of chromium. Therefore, the analysis should be carried out as soon as possible but no longer than 24 hours after collection.

4. Interferences

4.1 The possible interference from other elements which form stable chromates is not known at this time.

4.2 Samples with either sulfate or chloride concentrations above 1000 mg/liter should be diluted before analysis.

4.3 The potential reduction of Cr^{6+} from highly reductive substances increases as pH is lowered. When sulfites and sulfides are present the sample aliquot taken for analysis should be neutralized and aerated before beginning.

5. Instrument Parameters (General)

5.1 Drying Time and Temp: 30 sec-125°C.

5.2 Ashing Time and Temp: 30 sec-1000°C.

5.3 Atomizing Time and Temp: 10 sec-2700°C.

5.4 Purge Gas Atmosphere: Argon

5.5 Wavelength: 357.9nm

5.6 Other operating parameters should be as specified by the particular instrument manufacturer.

6. Special Apparatus

6.1 Glassware

6.1.1 Filtering flask, heavy wall, 1 liter capacity

6.1.2 Centrifuge tubes, heavy duty, conical, graduated, glass stoppered, 10 mL capacity

6.1.3 Pasteur pipets, borosilicate glass, 5 ¾ inches.

6.2 Centrifuge: any centrifuge capable of reaching 2000 rpm and accepting the centrifuge tubes described in 6.1.2 may be used.

6.3 pH Meter: a wide variety of instruments are commercially available and suitable for this work.

6.4 Test Tube Mixer: any mixer capable of thorough vortex is acceptable.

7. Reagents

7.1 Lead Nitrate Solution: Dissolve 33.1 grams of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.2 Ammonium Sulfate Solution: Dissolve 2.7 grams of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.3 Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.

7.4 Nitric Acid, conc.: Distilled reagent grade or equivalent to spectrograde quality.

7.5 Acetic Acid, Glacial: ACS reagent grade.

7.5.1 Acetic Acid, 10% (v/v): Dilute 10 mL glacial acetic acid to 100 mL with deionized distilled water.

7.6 Ammonium Hydroxide, 10% (v/v): Dilute 10 mL conc ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with deionized distilled water.

7.7 Hydrogen Peroxide, 30%: ACS reagent grade.

7.8 Potassium Dichromate Standard Solution: Dissolve 2.8285 grams of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in deionized distilled water and dilute to 1 liter. 1 mL = 1 mg Cr (1000 mg/L)

7.9 Trivalent Chromium Working Stock Solution: To 50 mL of the potassium dichromate standard solution (7 8) add 1 mL of 30% H_2O_2 (7.7) and 1 mL conc. HNO_3 (7.4) and dilute to 100 mL with deionized distilled water 1 mL = 0.5 mg Cr^{3+}. Prepare fresh monthly or as needed.

8. Calibration

8.1 At the time of analysis prepare a blank and a series of at least four calibration standards from the Cr^{3+} working stock (7.9) that will adequately bracket the sample. The normal working range covers a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard 1 mL 30% H_2O_2 (7.7), 5 mL CONC HNO_3 (7.4), and 1 mL calcium nitrate solution (7.3) for each 100 mL of prepared solution before diluting to final volume. These calibration standard should be prepared fresh weekly or as needed.

8.2 The listed instrumental conditions (5.) and the stated calibration concentration range are for a Perkin-Elmer HGA-2100 based on the use of a 20μL injection, continous flow purge gas and non-pyrolytic graphite. The use of simultaneous background correction is required for both calibration and sample analysis.

9. Procedure

9.1 Transfer a 50 mL portion of the filtered sample to a 100mL Griffin beaker and adjust to pH 3.5±0.3 by adding 10% acetic acid dropwise. Record the volume of acid added and adjust the final result to account for the dilution.

Note: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to < 3, 10% NH_4OH (7.6) should be used to raise the pH to above 3.

9.2 Pipet a 10 mL aliquot of the adjusted sample into a centrifuge tube (6.1.2). Add 100μL of the lead nitrate solution (7.1), stopper the tube, mix the sample and allow to stand for 3 min

9.3 After the formation of lead chromate, retain the Cr^{3+} complex in solution by addition of 0.5 mL glacial acetic acid (7.5). Stopper and mix.

9.4 To provide adequate lead sulfate for coprecipitation add 100 mL ammonium sulfate solution (7.2), stopper and mix.

9.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2000 rpm in small increments over a period of 5 min. Centrifuge the sample at 2000 rpm for 10 min.

Note 2: The speed of the centrifuge must be increased slowly to insure complete coprecipitation.

9.6 After centrifuging remove the tube and draw off the supernata using the apparatus detailed in Figure 1. As the pasteur pipet is lowered into the tube the supernate is sucked into the filtering flask. With care the supernate can be withdrawn to within approximately 0.1 mL above the precipitate.

9.7 To the remaining precipitate add 0.5 mL conc HNO_3 (7.4), 100μL 30% H_2O_2 (7.7) and 100μL calcium nitrate solution (7.3). Stopper the tube and mix using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10mL mix and analyze in the same manner as the calibration standard (8.2).

9.8 For the general furnace procedure and calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

10. Verification

10.1 For every sample matrix analyzed verification is necessary to determine that neither a reducing condition nor a chemical interference affecting precipitation is present. This must be accomplished by analyzing a second 10mL aliquot of the pH adjusted filtrate (9.1) spiked with Cr^{6+} (7.8). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be of less than 30µg Cr^{6+}/L. To verify the absence of an interference the spike recovery should be between 85% and 115%.

10.2 If the addition of the spike extends the concentration beyond the range of the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

10.3 If the verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

11. Analytical Notes

11.1 Nitrogen should not be used as a purge gas because of possible CN band interference.

11.2 The use of pyrolytic graphite should be avoided when possible. Generally, pyrolytic graphite resulted in a more limited analytical working range and in some situations an enhancement effect.

11.3 Pipet tips have been reported to be a possible source of contamination. (See part 5.2.9 of the Atomic Absorption Methods section of this manual.)

11.4 The method of standard addition should not be required in as much as the Cr^{6+} has been separated from the original sample solution and redissolved in a uniform matrix having an absorption response coincident to the calibration curve.

11.5 Data to be entered into STORET (No. 01032) must be reported as µg/L.

12. Precision and Accuracy

12.1 In a single laboratory (EMSL) using a mixed industrial-domestic waste effluent containing 22 µg Cr^{6+}/L and spiked with a concentration of 50 µg Cr^{6+}/L, the standard deviations were ± 1.0 and ± 2.7, respectively with a spike recovery of 94%.

12.2 Recoveries of a 40 µg Cr^{6+}/L spike in diluted tannery and plating waste effluents were 96% and 93%, respectively.

12.3 Using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 50 µg Cr^{6+}/L the standard deviations were ± 0.7, ±0.6, and ±0.6, respectively. Spike recovery at all three levels was 102%.

12.4 A 1000 µg Cr^{3+}/L standard solution analyzed by this method yielded a result of 8 µg Cr^{6+}/L with a relative standard deviation of 19%.

12.5 The data from 5 µg Cr^{6+}/L tap water spike was used to calculate method detection limit (MDL) with 99% confidence as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, *Environmental Science and Technology*, Vol. 15, Number 12, page 1426, December 1981. The calculated MDL for Cincinnati drinking water is 2.3 µg/L.

APPENDIX D

ION CHROMATOGRAPHIC METHOD FOR THE SPECIATION AND ANALYSIS OF HEXAVALENT CHROMIUM OF AMBIENT ATMOSPHERIC LEVELS

STATE OF CALIFORNIA
AIR RESOURCES BOARD

Proposed Method for the Speciation and Analysis of Hexavalent Chromium at Ambient Atmospheric Levels

Ion Chromatographic Separation, Chromophoric Complexation, Spectrophotometry

1. SCOPE

This document describes the determination of chromium (VI) on membrane filters after sampling ambient air. The method has been tailored to concentrations that would be expected in ambient air. The method is not expected to have significant interferences. While the method is adequately sensitive for ambient air determinations, it has the potential for further significant improvements in sensitivity.

2. SUMMARY OF METHOD

A low volume air sampler capable of sampling at a constant rate of 13-15 liters per minute for at least 24 hours is fitted with a 37 mm Gelman VM-1 (PVC) membrane filter. After sampling, the filter is placed in a container with 10 mL of chromatographic eluent and the hexavalent chromium is extracted using ultrasonication.

The resultant solution is analyzed using an ion chromatographic technique utilizing a separator column normally used for transition metals analysis. The nearly neutral pH of the eluent system ensures that the Cr^{+6} is stabilized. Following chromatographic separation, the Cr^{+6} is reacted with a chromophoric reagent and measured spectrophotometrically at 520 nm.

3. LIMITATIONS AND INTERFERENCES

No significant interferences are expected with this method. Trivalent chromium is separated during the chromatography step.

4. APPARATUS

4.1 Dionex single channel Ion Chromatograph, P/N 37029

4.2 Dionex HPIC-CG5 Cation Guard Column, P/N 37028

4.3 Dionex HPIC-CS5 Cation Separator Column, P/N 37030

4.4 Dionex Reagent Delivery Module (RDM), P/N 35354

4.5 Dionex Membrane Reactor, P/N 35354

4.6 Dionex Visible Detector (VSM), P/N 37044

5. REAGENTS

5.1 2,6-pyridinedicarboxylic acid (PDCA)

5.2 disodium hydrogen phosphate heptahydrate

5.3 sodium iodide

5.4 ammonium acetate

5.5 lithium hydroxide monohydrate

5.6 1,5-diphenylcarbohydrazide (DPC)

5.7 methanol, HPLC Grade

5.8 sulfuric acid, 96%, spectrophotometric grade

5.9 deionized water, 18 M-ohm

5.10 Eluent Stock: Prepare by dissolving the following reagents in 18 M-ohm deionized water. PDCA is slow to dissolve, and heating the solution before addition of the remaining reagents may be used to increase the rate of dissolution.

20.0 mM	(3.34 g/L)	pyridinedicarboxylic acid (PDCA)
20.0 mM	(5.36 g/L)	disodium hydrogen phosphate
100.0 mM	(15.0 g/L)	sodium iodide
500.0 mM	(38.5 g/L)	ammonium acetate
28.0 mM	(1.10 g/L)	lithium hydroxide

5.11 Eluent: Prepare by diluting 100 mL of the eluent stock to 1 L with 18 M-ohm degassed deionized water. The pH of the diluted eluent should be between 6.70 and 6.80.

5.12 Post Column Reagent: Prepare by dissolving 0.49 g of 1,5-diphenylcarbohydrazide (DPC) in 100 mL of methanol. Add to about 500 mL of degassed deionized water containing 25 mL of concentrated sulfuric acid. Dilute to 1 L with degassed deionized water.

6. INSTRUMENT OPERATION

6.1 Assemble the accessories according to the manufacturer's instructions in the individual component manuals.

6.2 Install a 250 μL sample loop on the injection valve.

6.3 Conditions:

Sample Size:	250 µL
Columns:	HPIC-CG5, Cation Guard Column HPIC-CS5, Cation Separator Column
Eluent Flow Rate:	1.0 mL/min
Post Column Reagent Flow Rate:	0.5 mL/min
Detection:	VIS at 520 nm - Filter #5 on wheel

6.4 Establish the recommended eluent and post column reactor flow rates: 1.0 mL/min for the eluent and 0.5 mL/min for the post column reaction reagent are suggested.

6.5 Turn pumps on.

6.6 Set the detector range on 0.005 AU (most sensitive)

7. INSTRUMENT CALIBRATION

7.1 Inject a series of Cr^{+6} standards diluted in eluent reagent in the range of 5 to 50 µg/L.

7.2 Determine the least squares fit. The calibration data should result in a correlation coefficient of 0.995 or better.

7.3 Run a check standard at least every tenth sample.

8. SAMPLE ANALYSIS

8.1 Place the filter in a 100 mL graduated beaker; add 50 mL of eluent, cover with Parafilm.

8.2 Sonicate without heat for 15 minutes.

8.3 Check the pH to ensure that it is 6.8-6.9.

8.4 The resulting solution is now ready for analysis.

8.5 Print out the analysis results with the identifying laboratory identification number. Record results and calculations in the laboratory notebook. Record the calculated concentration in nanograms/M^3 in the laboratory data sheet. The concentration may be calculated as follows:

$$\text{Chromium}^{+6}\text{, ng/M}^3 = \frac{\text{Concentration Found, ng/mL} \times \text{Dilution Factor}}{\text{Air Volume Sampled, M}^3}$$

9. METHOD EVALUATION

To be performed.

APPENDIX E

ION CHROMATOGRAPHIC METHOD FOR THE SPECIATION AND ANALYSIS OF HEXAVALENT CHROMIUM AT AMBIENT ATMOSPHERIC LEVELS WITH SAMPLE PRECONCENTRATION

APPENDIX E
HEXAVALENT CHROMIUM ANALYSIS USING ION CHROMATOGRAPHY
Preconcentration Technique

Reagent Preparation

Eluent Stock: Prepare by dissolving the following reagents in deionized water. PDCA is slow to dissolve, and heating the solution before adding the remaining reagents may be necessary.

Pyridinedycarboxylic acid (PDCA)	3.34 g/L	20.0 mM
Disodium hydrogen phosphate	5.36 g/L	20.0 mM
Sodium iodide	15.0 g/L	100.0 mM
Ammonium acetate	38.5 g/L	500.0 mM
Lithium hydroxide	1.10 g/L	28.0 mM

Eluent: Dilute 100 ml of Eluent Stock to 1 L with deionized water. The pH of the diluted eluent should be between 6.70 and 6.80.

Post Column Reagent: Dissolve 0.49 g of 1,5-diphenylcarbohydrazide (DPC) in 100 ml of methanol. Add to about 500 ml of degassed deionized water containing 25 ml of concentrated sulfuric acid. Dilute to 1 L with degassed deionized water.

Procedure

1. Fill post column reagent reservoir with post column reagent. Degas using helium by bubbling helium through reagent for ten minutes. At the end of the ten-minute period remove helium tube and cover reagent reservoir.
2. Fill eluent container with eluent. Place container in stand on side of ion chromatograph. Open valve on eluent container to allow eluent flow to pump.
3. Turn on eluent pump.
4. Turn on ion chromatograph power switch.
5. Open compressed air cylinder valve.
6. Measure eluent flow at outlet line to waste container using a 5 ml graduated cylinder and stopwatch. Flow should be 0.8 ml/minute. If not, adjust using dial on pump.

7. Turn on post column reagent pump. Measure flow at waste outlet line, again using a 5 ml graduated cylinder and stopwatch. Flow should not be 1.2 ml/minute. If not, adjust flow on post column reagent pump using flow control dial.

8. Turn on detector power using switch at read of instrument. Set filter wheel to #4 (520 nm wavelength setting). Allow detector sufficient time to warm up.

9. Turn on recorder. Adjust baseline zero setting.

10. Place sample inlet tube into a beaker containing deionized water.

11. Set valve switch on chromatograph to "Inject."

12. Turn on sample pump and pump deionized water through side loop for a few minutes. Turn off sample pump.

13. Place sample in small plastic cup. Place sample inlet tube into plastic cup.

14. Turn on sample pump and switch valve on chromatograph to "Load" simultaneously.

15. Allow sample to be pumped into inlet tube. When almost dry, fill plastic cup with deionized water using a squirt bottle. Do not allow sample line to draw in air. Continue pumping in deionized water until total sample inlet time is ten minutes or sample has been completely flashed through the tubing system to the concentrator column.

16. When sample and deionized water flush have been pumped into system, turn off sample pump and switch valve on chromatograph to "Inject." This will begin to pump eluent through the concentrator column and through the system column into the detector.

17. Following elution of peaks, turn on the sample pump and pump deionized water through the side loop for two minutes. The next sample can now be run beginning at Step 10.

EXPERIMENTAL CHAMBER TESTS

INTRODUCTION

The chamber reaction studies, which were designed to simulate those ambient conditions to which Cr^{+6} species would be exposed, were conducted in the following overall manner:

1. Eight or more 37 mm membrane filters (Teflon or PVC) were spiked with levels of Cr^{+6} (ranging from 20 ng to 1,000 ng, depending on the test conditions). Initially, this was performed by pipetting known quantities of solutions onto the filter and then drying at room temperature in a vacuum dessicator. Later, the Cr^{+6} spiking was performed by creating an aerosol with an inhaler device and allowing the aerosol to merely deposit without pumping onto the filter surface (Figure 7). The aerosol was created inside a plastic can with a fan inside to disperse the aerosol as much as possible, thereby optimizing the uniformity. Nevertheless, since some inhomogeneity was anticipated, CARB suggested the use of a lithium internal standard in the solution to be aspirated. In this way, the lithium content could be measured, in addition to the Cr^{+6} species, in order to provide a means of monitoring the variability in the Cr^{+6} loadings. A schematic of the aerosol generator is shown in Figure 5.

2. Six of these filters were placed in a sampling manifold containing 37 mm polystyrene filter holders with backup pads.

3. The sampling manifold was located in the environmental chamber. Initially, the chamber was one constructed of plexiglass or other plastic materials wherever possible. A schematic of the initial test chamber design is shown in Figure 6. Later, the design of the chamber was changed (for reasons to be explained in this section) to that of an all-aluminum design. An aluminum "suitcase" approximately 2 feet x 2 feet x 1 foot was fitted for a gas (reactant inlet and for the sampling manifold (Figure 8).

4. During exposure to the various test reactants, a sampling flow of 3 to 5 Lpm was maintained through each filter. A calibrated critical orifice was used to regulate flow through each filter.

5. Pollutants were introduced into the top of the chamber by a variety of means. Ozone was generated by an ozone generator utilizing pure oxygen irradiated by an ultraviolet source. Atmospheres of species such as SO_2, NO_2, Xylene, and benzene were prepared from dilutions of gas cylinder concentrations. Nitric acid (HNO_3) and formaldehyde (HCHO) were generated from permeation devices available from Vici-Metronics (, CA).?? The verification of HNO_3 concentration was performed by sampling in parallel with a nylon filter, desorbing the filter in an

aqueous medium, and performing an ion chromatographic analysis of the resultant nitrate ion. Formaldehyde levels were monitored using hydrogen peroxide impinger samples and subsequent ion chromatographic analysis of the formate ion. A number of other species were evaluated in these tests, and test conditions regarding these potential reactants will be described in detail later in this section.

6. During the test, two filters were removed at each predesignated time interval. For instance, it may have been decided to remove the first two filters after eight hours, two more after 20 hours, and the last two after 40 hours.

7. The filters were then analyzed using CARB Method ADDL006. A portion of the Cr^{+6} extract was saved and analyzed for the lithium content to correct for any variability in the aerosol deposition.

APPENDIX F

ENTROPY TRIP REPORT: FIELD SAMPLING FOR DETERMINING THE FATE OF HEXAVALENT CHROMIUM IN THE ATMOSPHERIC

DRAFT

TRIP REPORT:

FIELD SAMPLING FOR DETERMINING THE FATE OF HEXAVALENT CHROMIUM IN THE ATMOSPHERE

CARB Contract No. A-6-096-32

Prepared by:

Scott C. Steinsberger, Ph.D.
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Prepared for:

California Air Resources Board

December 1987

Field Sampling for Determining the Fate of Hexavalent Chromium

Field Reaction Samples

The field reaction samples were collected for two purposes: 1) to determine the conversion rate of hexavalent chromium (Cr^{+6}) during a 12-hour daytime period, 12-hour nighttime period, and 24-hour period, and 2) to determine the ratio of hexavalent to trivalent chromium in the emissions being discharged to the atmosphere from the source (time zero samples). The field reaction samples subjected to the conversion studies were collected on filters directly from the source. In addition to the time zero filter samples collected, impinger samples were also collected directly from the source to provide additional time zero Cr^{+6} data. Two impinger samples were collected per day from each source with one being recovered immediately as a time zero sample. The second impinger sample was taken to the upwind ambient sampling site and ambient air was drawn through the second time zero sample simultaneously with the upwind impinger samples. This was done to determine the stability of the hexavalent chromium already present in the impinger reagent.

Preliminary field reaction samples were collected during the first two days of the field study at each source to determine the proper sampling time at that source for optimum chromium loading on the filters. This was done by collecting four sets of three filter samples each over four different time periods. For the hard chrome plating facility, preliminary sampling periods of 5 seconds, 30 seconds, 5 minutes, and 30 minutes were used, with the 5 second sampling time determined to be optimum. For the refinery cooling tower samples, the preliminary sampling periods were 5 minutes, 30 minutes, 1 hour, and 3 hours, with the 30 minute sampling time determined to be optimum.

Each set of field reaction samples consisted of 12 filters fitted to a filter holder (see Figure F.1). The filters were loaded into the filter holders by hand for the first three runs (Runs CC-02-FR, CC-03-FR, and CC-04-FR). After some concern over potential contamination (which turned out to be high blank values for the filters), filter loading was assigned to one individual wearing latex gloves. Initially, 37 mm PVC filters were used exclusively. Later, for the last three field reaction samples collected from the cooling tower, Teflon filters were substituted for two out of each three PVC filters. To collect samples, the loaded filter holder was inserted in the stack directly into the flow of exhaust gas from the source; and the gas sample was simultaneously pulled through all 12 filters for the optimum sampling period using a fiber vane vacuum pump.

The sample flow rate through all 12 filters combined was determined for each run at the cooling tower using a dry gas meter connected to the outlet of the vacuum pump. The flow rate determination during sampling was not conducted at the hard chrome plating facility due to the short sampling period, but was assumed to be the same as the flow rate at the cooling tower. The flow rate during sampling averaged 35.3 liters per minute (lpm) for the filter holder and, assuming even flow distribution, was 2.9 lpm for each filter. The exact flow rate for the field reaction sampling system was not needed since the ratio of hexvalent to trivalent chromium was to be determined, not the actual emission rate of chromium.

Exposure of the field reaction samples to ambient air for the 12-hour day, 12-hour night and 24-hour periods was conducted at the California Air Resources

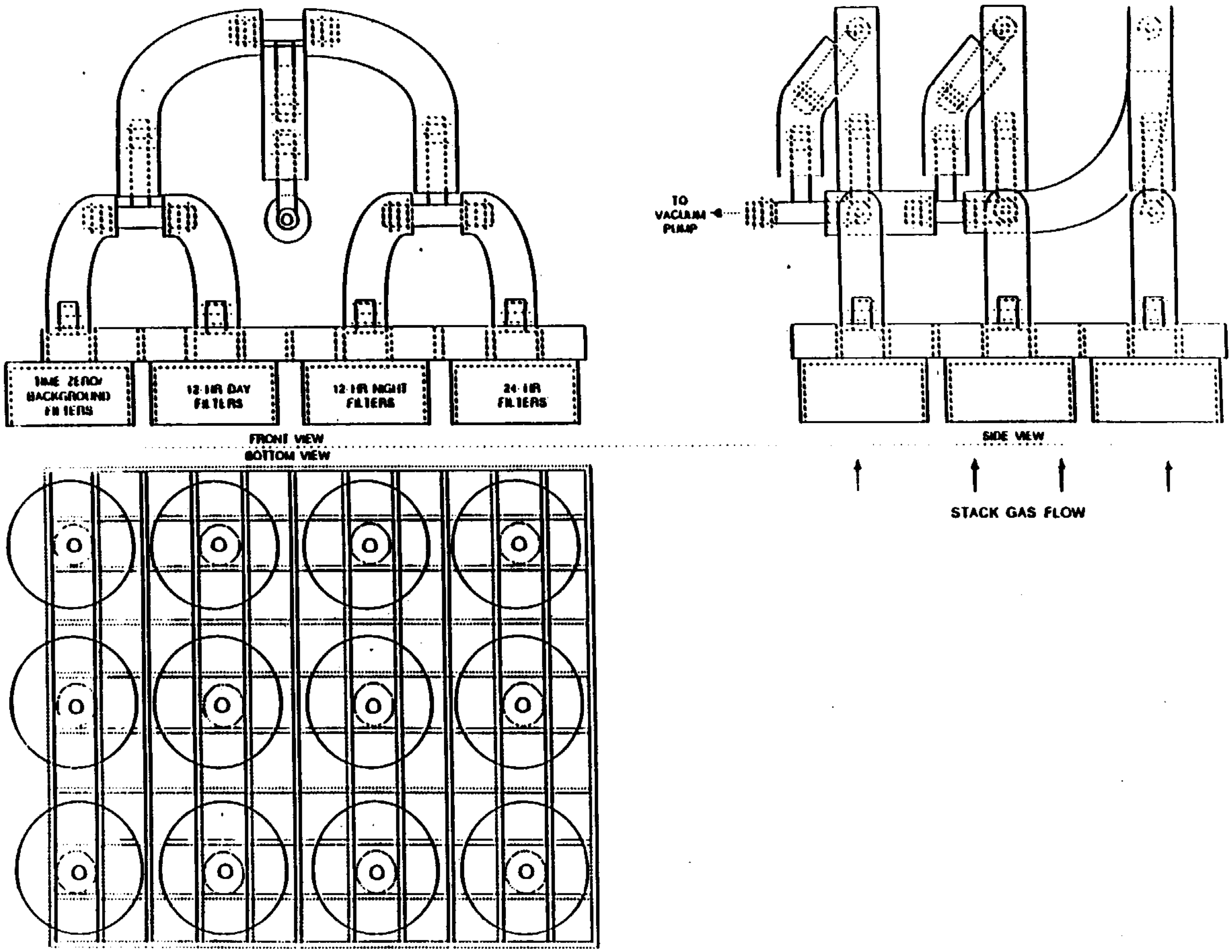

FIGURE F.1 FIELD REACTION FILTER HOLDER

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Board's (ARB) El Monte office. Prior to any ambient exposure, one set of three filters was immediately removed from the filter holder and sealed in the original individual filter holder (see Figure F.1). This set represented both the time zero sample for the ambient study and the time zero sample for the field reaction study. These filters were replaced on the filter holder with new, unexposed filters to determine the background chromium levels over 24-hour ambient exposure period. A positive-displacement vacuum pump was used to pull ambient air through the filters. One set of three filters, designated either 12-hour night or 12-hour day (depending on when the ambient exposure was started), was capped to prevent exposure to ambient air. After 12-hours of exposure to ambient air, the caps were switched to the other set of filters already subjected to a 12-hour exposure. At the end of the 24-hour exposure period, all the filters were removed and sealed.

The flow rate of ambient air through the filters on the holder was determined by measuring the flow at the outlet of the vacuum pump. The flow rate through each filter was intended to reproduce the flow rate used in the original laboratory reaction studies. The flow rate for the filter holder averaged 34.4 lpm and, assuming equal flow through each of the 9 filters, was 3.8 lpm for each filter. Field reaction experiments CC-03-FR and CC-04-FR were run using the XonTech sampling systems with the flow rates set at 1 lpm for each filter. The XonTech channel programmed for the 12-hour day period did not function and no ambient air was pulled through the filters; these 12-hour day period filters were then run concurrently with CC-05-FR.

A total of 14 field reactions were conducted, with 7 field reaction sample sets being collected from each source. A complete sample inventory list for the field reaction study can be found in Appendix A. Efforts to find a source with primarily trivalent chromium emissions in order to conduct additional field reaction studies were not successful.

Ambient Sampling

The ambient sampling portion of the field study involved setting up five ambient sampling stations in the vicinity of each chromium source. The stations were located based on the wind conditions during the afternoon of each test day. Each station consisted of two ambient sampling units (provided by the ARB, El Monte office) for filter samples and one set of three impinger trains (see Figure F.2). Tables F.1 and F.2 summarize the test dates, sampling locations, and sample volumes for the sampling conducted near the chrome plating facilities and at the refinery, respectively.

The Teflon and PVC filter samples were collected using either the newer computer controlled ambient sampling units (XonTechs) or the older units equipped with dry gas meters. The filters were initially loaded into the filter holders with bare hands (Runs CC-02-XT and CC-03-XT). For the remaining runs, the task of filter handling was assigned to one person wearing latex gloves to avoid any potential contamination. (Field blanks and filter blanks collected with bare hands during Run CC-03 did not show any significant contamination). For sample recovery, the filters from the initial runs were placed in nitric acid-rinsed vials; and later the filter samples were placed in the type of plastic petri dishes routinely used by the ARB.

For ambient sampling tests AR-10 through AR-15, three different types of sodium acetate-impregnated filters were used in place of the PVC filters. This was done to evaluate a Cr^{+6} sampling protocol using a filter that would prevent the conversion of the Cr^{+6} collected on the filter.

The impinger sampling trains consisted of a two EPA Reference Method 5 impingers with a Smith-Greenburg tip in the first impinger and a modified Smith-Greenburg tip in the second impinger. The impingers and connecting tubing were prepared prior to the first test run by rinsing with 5% nitric acid followed by deionized water and then a 0.01 M sodium acetate buffer. For sampling, each impinger was charged with 100 ml of the sodium acetate buffer. One train was assembled and immediately recovered for a laboratory proof blank to demonstrate that the sample train components were initially free of contamination.

All three sampling trains at a single location were connected to one fiber vane vacuum pump using a manifold connected to each second impinger outlet. The flow rate for the impinger trains was determined by measuring the flow at the pump outlet using a calibrated dry gas meter. The flow rate was assumed to be equal between the three sampling trains.

Following sampling, impinger samples were recovered into new sodium acetate-rinsed polyethylene storage bottles. Each set of impingers and connecting tubing were rinsed with the sodium acetate buffer and the rinses were added to the appropriate storage bottle. A 5% nitric acid rinse of the impingers and connecting tubing was also performed to remove any insoluble chromium. Initially, the nitric rinses were saved for analysis to determine the total chromium collected; however later rinses were discarded due to a high reagent blank level. Consequently, the impinger samples were used for hexavalent chromium determination only, with the corresponding filter samples providing the total chromium ambient concentration at each sampling location. Deionized water and sodium acetate buffer rinses of the impingers and connecting tubing were performed each day prior to charging the impingers with the sodium acetate reagent.

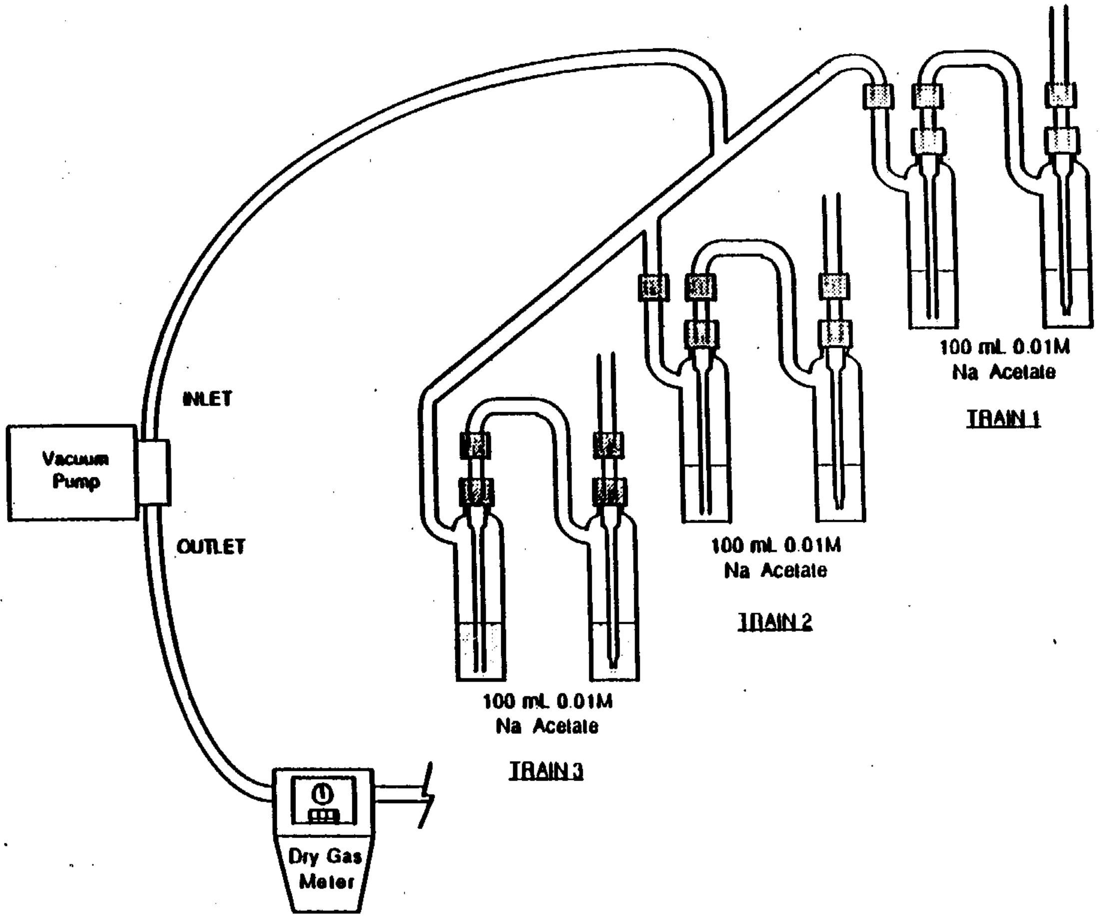

FIGURE F.2 AMBIENT SAMPLING STATION IMPINGER TRAINS

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Table F.1. SUMMARY OF AMBIENT SAMPLING DATA FOR CHROME CRANKSHAFT

Date	Location	Sample Volume (M^3)			T_{sl}[1] (min.)
		Teflon	PVC	Impinger	
10/21	1, 0.3 km NE of CC	4.955		5.95	ND[2]
10/22	0, Upwind	4.668	4.641	7.35	NA[3]
10/22	1, 0.3 km NE of CC	5.575	7.010		11.3
10/23	0, Upwind	3.998	3.974	4.10	NA
10/23	1, 0.3 km NE of CC	3.217	4.548	8.20	2.8
10/23	2, 0.5 km N of CC			4.80	4.7
10/23	3, 0.8 km N of CC	2.462	2.447	5.00	7.5
10/23	4, 0.5 km NNW of CC	5.348	5.043	6.00	4.7
10/26	0, Upwind	3.404	3.309	3.40	NA
10/26	1, 0.3 km NE of CC	4.293	2.270	5.26	1.9
10/26	2, 0.8 km ENE of CC	4.117	4.088	5.41	5.0
10/26	3, 0.6 km E of CC	5.346	5.260	5.65	3.8
10/26	4, 0.5 km N of CC	4.632		5.46	3.1
10/27	0, Upwind	3.999	3.972	4.04	NA
10/27	1, 0.3 km NE of CC	4.316	4.539	6.11	0.9
10/27	2, 0.8 km ENE of CC	5.349	5.257	6.13	2.5
10/27	3, 0.6 km E of CC	5.073	5.112	5.85	1.9
10/27	4, 0.5 km N of CC	5.013		6.19	1.6
10/28	0, Upwind	4.775	4.743	4.90	NA
10/28	1, 0.3 km NE of CC	3.444	3.585	4.30	1.4
10/28	2, 0.8 km ENE of CC	6.459	6.352	6.60	3.8
10/28	3, 0.6 km E of CC	6.336	6.386	6.80	2.8
10/28	4, 0.5 km N of CC	5.610		6.80	2.3

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[1] T_{sl} = Calculated reaction time from source to sample location based on mean wind speed for the predominate wind direction.

[2] ND = No Data

[3] NA = Not Applicable

Table F.2. SUMMARY OF AMBIENT SAMPLING DATA FOR ARCO REFINERY

		Sample Volume (M^3)			T_{sl}[1]
Date	Location	Teflon	PVC	Impinger	(min.)
10/29	2, 0.4 km ESE of CT 9	3.180		3.26	ND[2]
10/30	0, Upwind	4.184	4.352[3]	5.16	NA[4]
10/30	1, 0.25 km ENE of CT 9	5.072	5.117[3]	5.44	1.9
10/30	2, 0.4 km SE of CT 9			5.16	3.0
10/30	3, 0.4 km SSE of CT 9	5.178	5.144[3]	5.28	3.0
11/02	0, Upwind	4.365	4.542[3]	5.21	NA
11/02	1, 0.25 km ENE of CT 9	5.713	5.772[3]	4.60	4.7
11/02	2, 0.4 km SE of CT 9	2.436	4.005[3]	2.60	7.5
11/02	3, 0.4 km SSE of CT 9	5.333	5.292[3]	5.44	7.5
11/02	4, 1.0 km ESE of CT 9	2.220		6.04	18.8
11/03	0, Upwind	5.319	5.529[5]	7.44	NA
11/03	1, 0.25 km ENE of CT 9	7.616	7.678[5]	8.16	1.9
11/03	2, 0.4 km SE of CT 9	5.819	5.323[5]	7.02[6]	3.0
11/03	3, 0.4 km NNE of CT 9	6.664	6.630[5]	7.96	3.0
11/03	4, 1.0 km ESE of CT 9	3.108		7.17	7.5
11/04	0, Upwind	5.999	5.773[5]	8.29	NA
11/04	1, 0.25 km ENE of CT 9	7.615	7.679[5]	9.46	3.1
11/04	2, 0.4 km SE of CT 9	6.066	5.525[5]	6.53	5.0
11/04	3, 0.4 km NNE of CT 9	6.488	6.441[5]	7.37	5.0
11/04	4, 1.0 km ESE of CT 9	2.991		7.54	12.5
11/05	0, 0.6 km WSW of CT 9	5.549	5.773[5]	8.29	4.5
11/05	1, 0.25 km ENE of CT 9	6.239	6.290[5]	6.26	1.9
11/05	2, 0.6 km NNW of CT 9	3.785	4.006[5]	4.98	4.5
11/05	3, 0.4 km NNE of CT 9	6.625	6.588[5]	6.69	3.0
11/05	4, 1.0 km ESE of CT 9	2.649		7.20	7.5
11/06	0, Upwind	4.364	4.614[7]	4.91	NA
11/06	1, 0.25 km ENE of CT 9	7.474	7.548[7]	7.25	1.3
11/06	2, 0.4 km SE of CT 9	5.888	5.937[7]	6.14	2.1
11/06	3, 0.6 km NNE of CT 9[8]	5.485	5.483[7]	7.17	3.2
11/06	4, 1.0 km ESE of CT 9	2.200		6.51	5.4

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[1] T_{sl} = Calculated reaction time from source to sample location based on mean wind speed for the predominate wind direction.

[2] ND = No Data

[3] NA = Not Applicable

[4] First batch of sodium acetate-impregnated filters

[5] Second batch of sodium acetate-impregnated filters

[6] Maximum sample volume. Actual may be less due to loss of power

[7] Third batch of sodium acetate-impregnated filters

[8] At this location 13:22 to 15:40 and moved, due to wind shift, to 0.4 km SSE of CT 9 from 15:43 to 18:15

Several impinger train runs were selected to determine the collection efficiency of the impinger trains. This involved separate recovery and subsequent analysis of each impinger from the selected trains. The trains were selected for the efficiency checks based on which sampling location was thought to have the greatest chromium catch, with two trains typically selected from this location.

Impinger train field blanks were collected at each source. Collection of the field blanks involved preparing a complete impinger train and immediately recovering the train in the normal manner. Field blanks were collected from an impinger train that had been used during the previous days testing and had been subjected to normal handling. They were taken to demonstrate that sample recovery procedures and subsequent rinses were sufficient to prevent any carry over contamination from sampling runs.

Reagent blanks were collected from each 20 liter batch of sodium acetate buffer.

A complete list of all the ambient samples collected, with the corresponding sampling periods, total sampling times, and sample gas volumes, can be found in Appendix B.

Meteorological Data Station

A meteorological data station was set up near each source tested to continuously collect wind speed and wind direction data during the ambient sampling periods. At the hard chrome plating facility, the meteorological data station was located 10 feet off the ground near sampling location 1 (see Figure F.3) for the first run (CC-03). For the last three sampling runs at the plating facility, the meteorological data station was set up on the northwest corner of the facility's roof. The station was relocated to avoid any potential interference from nearby buildings.

At the refinery, the meteorological data station was located 10 feet off the ground, 40 meters east of sampling location 1 (see Figure F.4).

The wind direction, expressed as a percent of time, and the mean wind speed for each wind direction recorded are summarized in Table F.3. Photocopies of the chart recordings from the meteorological data station are presented in Appendix C.

The ambient air quality from 7 a.m. to 6 p.m., as measured by the South Coast Air Quality Management District and published in the Los Angeles Times, are presented in Appendix D.

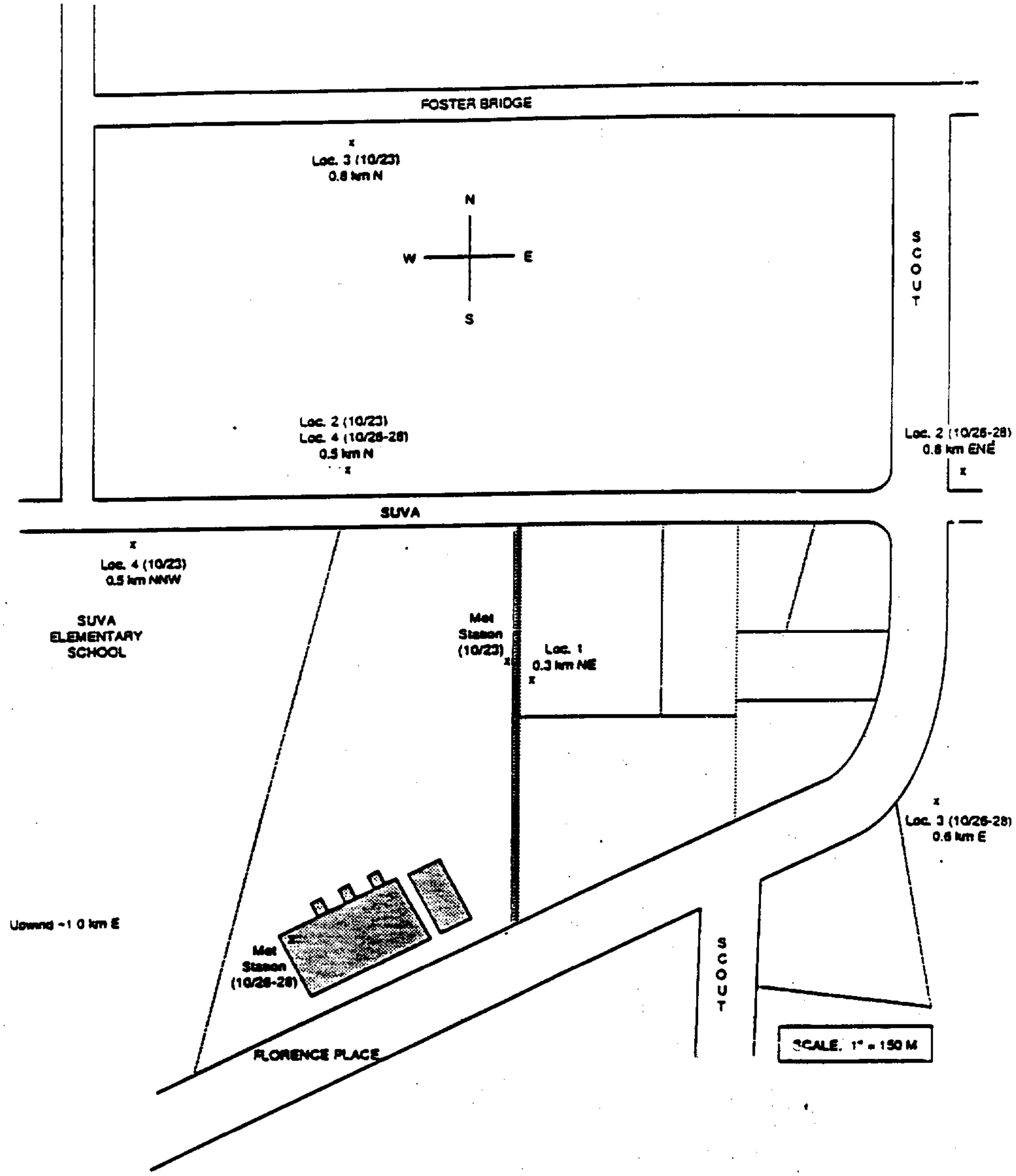

FIGURE F3 PLOT PLAN OF CHROME CRANKSHAFT SHOWING SAMPLING LOCATION

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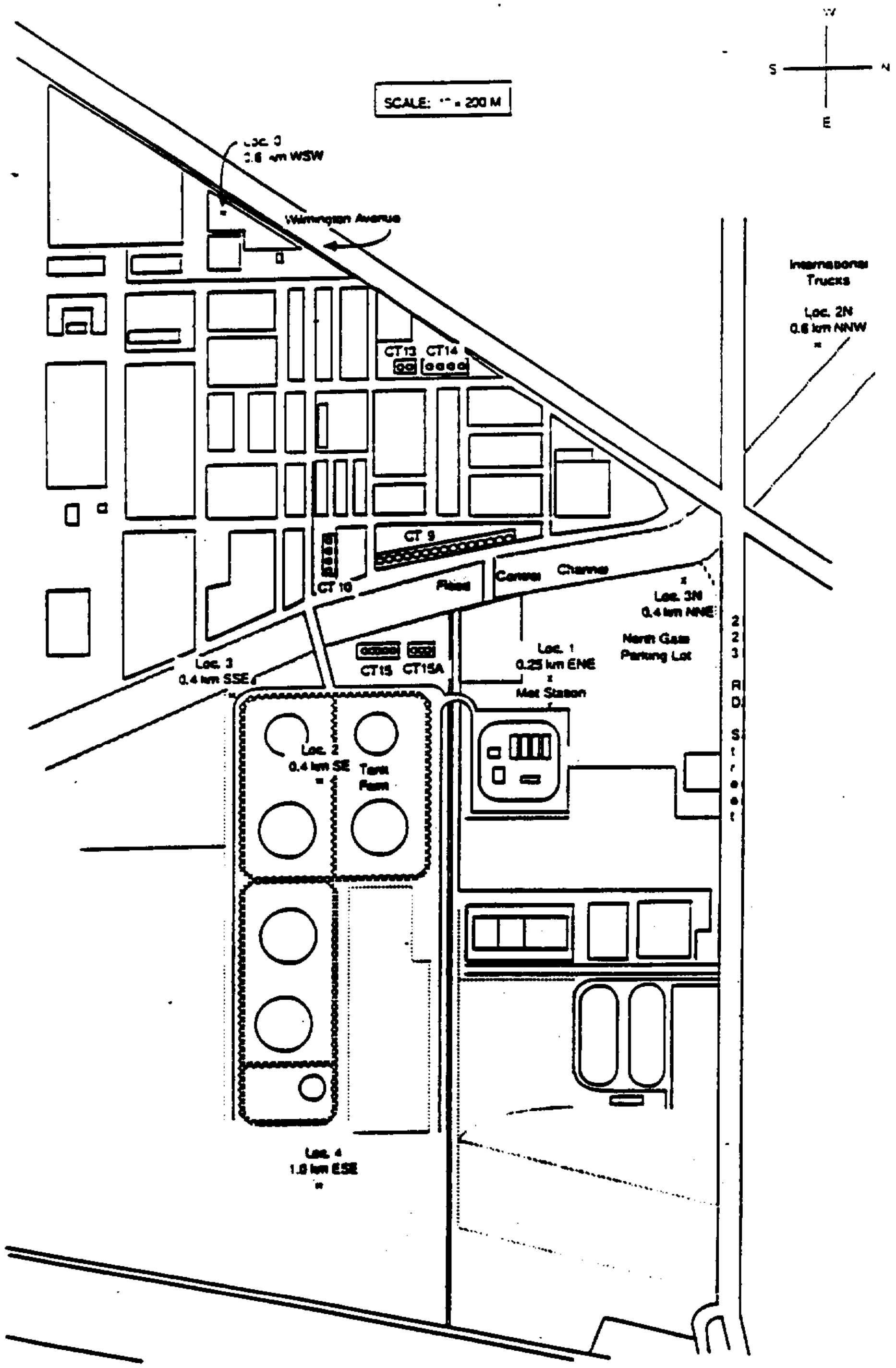

FIGURE F4: PLOT PLAN OF THE ARCO REFINERY SHOWING SAMPLING LOCATIONS (RELATIVE TO CT9).

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Table F.3 WIND DIRECTION AND WIND SPEED DURING AMBIENT SAMPLING

Date	Site	Run	Time Period	Direction	% of Time	Mean Speed
10/23	CC	03	12:00-18:30	SSW	50	4
				E	22	3
				S	20	3
				ESE	4	3
				SE	4	3
10/26	CC	05	12:30-19:00	W	70	6
				SW	15	3
				SE	15	3
10/27	CC	06	12:00-18:00	WSW	56	12
				NNW	13	7
				WNW	10	7
				SW	8	4
				NW	7	6
				W	5	5
				N	1	5
10/28	CC	08	12:00-19:00	W	43	8
				WSW	39	5
				SW	11	4
				WNW	7	5
10/30	AR	10	12:30-18:30	WNW	92	5
				NW	6	5
				W	2	5
11/02	AR	11	12:00-18:00	ESE	41	2
				W	28	5
				S	10	5
				E	8	3
				ENE	7	2
				NE	6	2
11/03	AR	12	12:00-18:00	SE	36	5
				ESE	23	3
				WNW	15	4
				E	15	2
				S	6	2
				N	5	2
11/04	AR	13	12:00-18:30	SE	62	3
				ESE	28	5
				N	7	1
				W	3	1

(continued)

Table F.3 continued

Date	Site	Run	Time Period	Direction	% of Time	Mean Speed
11/05	AR	14	12:00-17:30	SE	64	5
				NNE	29	4
				N	5	3
				E	3	3
11/06	AR	15	12:00-18:00	W	50	7
				SE	36	7
				E	10	3
				ESE	4	3

Daily Sampling Locations

The ambient sampling stations were located as follows:

Upwind of the chromium source (Location 0)
Predicted downwind approximately 0.3 km from source
Actual near downwind approximately 0.5 km from source
Actual far downwind approximately 1.0 km from source
Alternate downwind approximately 0.5 km from source

Some variations on this general deployment scheme were used depending on the wind conditions for a particular day and the logistics of locating an ambient sampling station at the desired location. The typical wind pattern was for the wind to shift from the east to the west around midday as the land mass warmed and the wind would come in off of the ocean. The sampling locations were selected once the wind appeared to be coming steadily out of one direction. The decision was usually made by 13:00.

Chrome Plating Facilities - The first full day of testing at the hard chrome plating facilities (see Figure F.3) was on October 23. At the start of the testing, the wind was primarily out of the south as opposed the predicted westerly direction. The upwind sampling location (Location 0) was located approximately 1.0 km east of the source. The predicted downwind sampling location (Location 1) was set up 0.3 km northeast of the source at the same location used two weeks earlier by the ARB. The near and far downwind sampling locations (Loaction 2 and 3) were set up 0.5 km and 0.8 km, respectively, north of the facility with the alternate downwind location (Location 4) being setup 0.5 km to the north northwest of the facility.

For the testing conducted on October 26 through October 28, the wind was primarily out of the west. This allowed the predicted downwind sampling location (Location 1) to become the actual near downwind location. A far downwind location (Location 2) was setup 0.8 km east northeast of the source, being set up as close as possible in a direct line with the near downwind station and the source. The other two locations were setup 0.6 km to the east and 0.5 km to the north of the source (Locations 3 and 4, respectively).

Refinery Cooling Tower - At the refinery (see Figure F.4) for the first full day of testing (October 30), the wind was primarily out of the west northwest. Location 2 was set up as the near downwind location 0.4 km southeast of cooling tower. Locations 1 and 3 were 0.25 km east northeast and 0.4 km south southeast, respectively, of cooling tower 9. A far downwind sampling station was not set up on this day due to limitations in power supplies. The upwind station was located 0.65 km west southwest of cooling tower 9.

On the second day of testing at the refinery (November 2), the wind was initially out of the west but shifted to the east southeast at about 14:30. Sampling locations 1 and 2 and the upwind station were at the same location as on October 30. Location 3 was moved to 0.4 km north northeast of cooling tower 9 (designated as Location 3N in Figure F.4). A far downwind station was established at 1.0 km east southeast of cooling tower 9.

On November 3, the wind was primarily out of the southeast to east southeast. The wind shifted to the west for the last hour of sampling (17:00 to 18:00). The sampling locations were the same as those used on November 2.

On November 4, the wind was primarily out of the south during most of the test period. Again, the sampling locations were the same as those used on November 2.

On November 5, the wind was primarily out of the southeast. Rain began at 15:30 coinciding with a shift in the wind to out of the north. Sampling Location 2 was set up at the start of the test period 0.6 km north northeast of cooling tower 9 (designated as Location 2N in Figure F.4). All other sampling locations were the same as those used on November 2. Tracer experiments, described below, suggest that cooling tower 9 may have had some impact on the upwind location during this test period. Consequently, location 4 may be considered as the upwind location for this day. However, the impact of some cooling towers due south of Location 4 should also be considered.

On November 6, the wind was initially out of the southeast. At 15:00, the wind changed distinctly and came from the west for the remainder of the test. Initially, the sampling locations were the same as those used on November 2. With the wind shift at 15:00, Location 3N was for the remainder of the test moved back to the original Location 3, used on October 30.

Sulfur Hexafluoride Tracer Experiments

Sulfur hexafluoride (SF_6) was chosen as the compound to conduct tracer experiments at each chromium source. SF_6 is a stable nontoxic gas capable of being detected at sub part-per-billion (ppb) concentrations using a gas chromatograph equipped with an electron capture detector (GC/ECD). The GC/ECD used for the SF_6 tracer experiments was a Hewlett-Packard 5890 equipped with a Porapak Q column. The carrier gas, SF_6 tracer gas, and 100-ppb SF_6 calibration gas were all obtained from a commercial vendor (Scott Specialty Gases, San Bernardino, CA). The output from the GC/ECD was recorded on a strip chart recorder.

Calibration of the GC/ECD was done using the 100-ppb SF_6 calibration gas. A standard curve was established by in-situ dilution of the 100-ppb calibration gas in a gas-tight syringe.

Ambient samples were collected in 250-ml amber low-density polyethylene bottles, each outfitted with screw cap with an integral teflon-lined rubber septa. Samples were collected in the bottles by first repeatedly purging the bottles 30 seconds prior to the sample actual collection time by squeezing and allowing the bottles to refill with ambient air. At the appropriate time the final purge would be made and the bottle sealed with the cap described above.

The SF_6 releases were conducted in-stack at each source. The SF_6 was routed through a rotameter to measure the release flow rate and then flowed through Tygon tubing to the stack for release. At the hard chrome plating facility, the releases were made in stack 4. At the refinery, the releases were made on cooling tower 9 in fan cell 9. The releases were typically 5 minutes in length.

The downwind sampling for SF_6 occurred at one or two minute intervals starting three or four minutes after beginning the release, depending on the wind speed and the distance from the release point. Typically, two of the ambient sampling locations were selected for sampling during each release and five samples were collected at each location. The samples were analyzed on-site immediately after collection with the GC/ECD.

Using the estimated flow rate of the stack receiving the SF_6 and the flow rate of the SF_6 into the stack, an in-stack dilution factor was calculated. The peak concentration at each sampling location was used to calculate the total dilution of the pure SF_6 release gas. The total dilution of SF_6 was divided by the in-stack dilution to calculate the downwind dilution.

A summary of the SF_6 tracer experiments is presented in Table _.4. At the chrome plating facility ground effects were evident presumably caused by neighboring buildings. At the refinery, the in-stack dilution was 20 times higher than at the chrome plating facility even at the maximum release rate of SF_6. As a result, the SF_6 was either not detected or found in trace quantities at only one sampling location (9 ppb at 0.4 km ESE).

For some of the tracer experiments, a Gaussian distribution was seen for the five samples taken at a particular sampling location. An example chromatogram is presented in Figure _.5.

Table F.4. SUMMARY OF SULFUR HEXAFLUORIDE TRACER EXPERIMENTS

Date	Site[1]	Time	Wind Speed and Direction	Location[2]	Peak Conc. (ppb)	Calculated Downwind Dilution
10/26	CC	14:55	SW/WSW 5 mph	0.8 km ENE	ND[3]	------
10/26	CC	14:55	SW/WSW 5 mph	0.5 km N	80	3,364
10/26	CC	16:15	West 7 mph	0.6 km E	ND[3]	------
10/26	CC	16:15	West 7 mph	0.3 km NE	15	16,840
10/27	CC	14:20	W/WSW 15 mph	0.3 km NE	120	2,119
10/27	CC	14:20	W/WSW 15 mph	0.8 km ENE	20	12,870
10/27	CC	15:40	WNW/W 6 mph	0.6 km E	ND[3]	------
10/27	CC	15:40	WNW/W 6 mph	0.5 km N	107	2,361
10/28	CC	13:50	WSW/SW 7 mph	0.3 km NE	25	9,980
10/28	CC	13:50	WSW/SW 7 mph	0.5 km N	trace	------
10/28	CC	15:00	WSW/SW 8 mph	0.8 km ENE	16	14,850
10/28	CC	15:00	WSW/SW 8 mph	0.6 km E	trace	------
10/28	CC	15:55	WSW 9 mph	0.8 km ENE	10	26,260
10/28	CC	15:55	WSW 9 mph	0.3 km NE	500	500
10/30	AR	16:30	WNW 5 mph	0.4 km SSE	ND[3]	------
10/30	AR	16:30	WNW 5 mph	0.4 km ESE	9	1,178
11/03	AR	16:00	SSE 5 mph	0.25 km ENE	trace	------
11/03	AR	16:00	SSE 5 mph	0.4 km NNE	trace	------
11/04	AR	15:10	SSE 2 mph	0.4 km NNE	0.1[4]	100,000
11/04	AR	17:00	SSE 3 mph	0.4 km NNE	0.1[4]	100,000
11/04	AR	17:00	SSE 3 mph	0.65 km WSW	0.1[4]	100,000
11/05	AR	15:00	SSE 5 mph	0.4 km NNE	0.1[4]	100,000
11/05	AR	15:00	SSE 5 mph	0.6 km NW	ND[3]	------
11/06	AR	15:05	W 7 mph	0.4 km NNE	ND[3]	------
11/06	AR	15:05	W 7 mph	0.4 km NE	ND[3]	------

[1] CC = Chrome Crankshaft; AR = ARCO Refinery

[2] Location relative to Chrome Crankshaft or center of cooling tower 9 at ARCO Refinery

[3] ND = Not Detected

[4] Estimated concentration

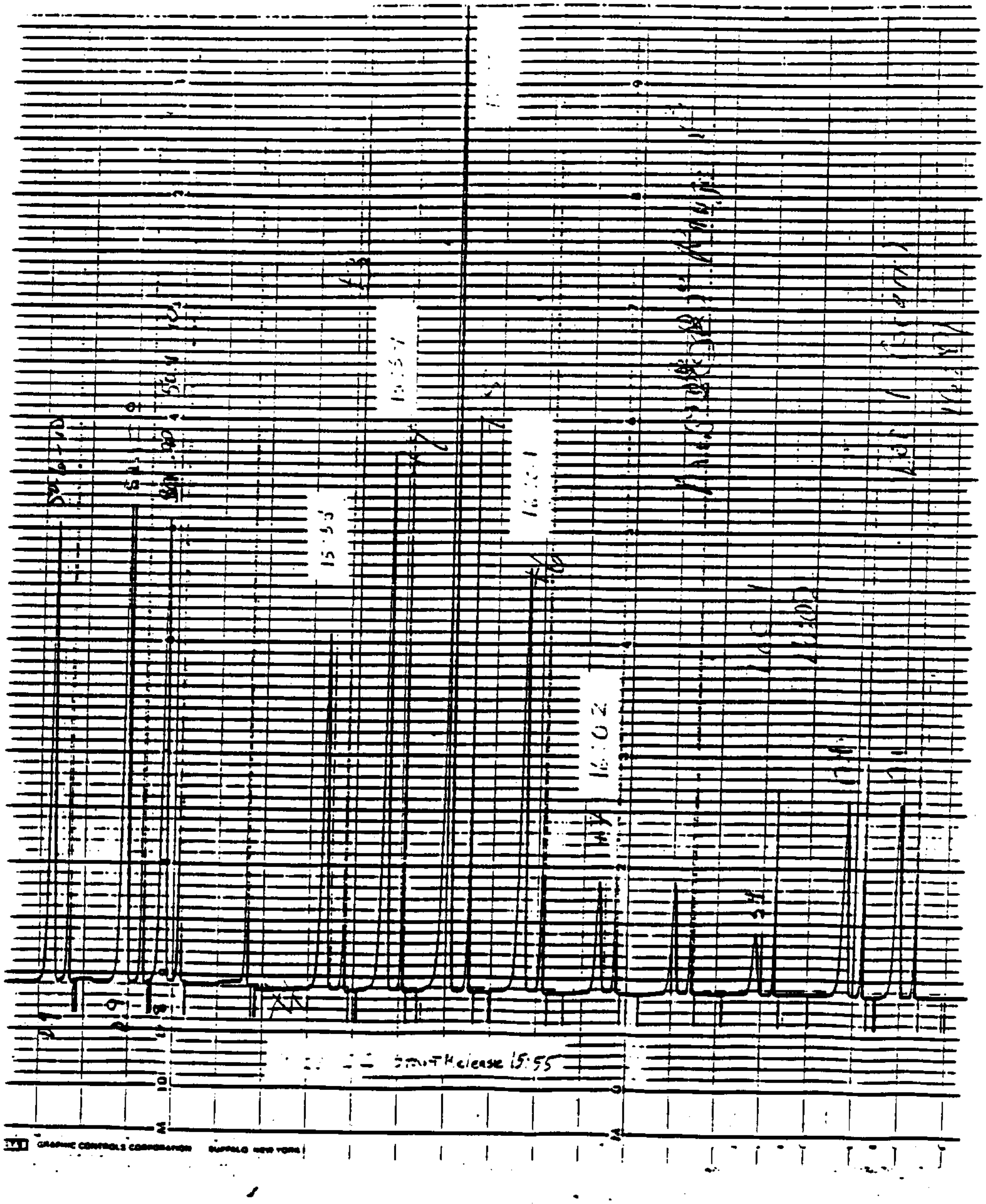

Figure F.5. Example chromatogram showing Gaussian distribution of SF_6

APPENDIX A.

Inventory of Field Reaction Samples

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
10/19	CC 01 FR 01 A	5 Second Exposure - Stack 4	
10/19	CC 01 FR 01 B	5 Second Exposure - Stack 4	
10/19	CC 01 FR 01 C	5 Second Exposure - Stack 4	
10/19	CC 01 FR 02 A	30 Second Exposure - Stack 4	
10/19	CC 01 FR 02 B	30 Second Exposure - Stack 4	
10/19	CC 01 FR 02 C	30 Second Exposure - Stack 4	
10/19	CC 01 FR 03 A	5 Minute Exposure - Stack 4	
10/19	CC 01 FR 03 B	5 Minute Exposure - Stack 4	
10/19	CC 01 FR 03 C	5 Minute Exposure - Stack 4	
10/19	CC 01 FR 04 A	30 Minute Exposure - Stack 4	
10/19	CC 01 FR 04 B	30 Minute Exposure - Stack 4	
10/19	CC 01 FR 04 C	30 Minute Exposure - Stack 4	
10/19	CC 01 FR 00 -	Blank	
10/20	AR 01 FR 01 A	5 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 01 B	5 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 01 C	5 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 02 A	30 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 02 B	30 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 02 C	30 Minute Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 03 A	1 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 03 B	1 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 03 C	1 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 04 A	3 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 04 B	3 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR 04 C	3 Hour Exposure - Stack 13 Tower 9	
10/20	AR 01 FR BLANK	Blank	
10/22	CC 02 FR 01	Time zero - Instack - Top	
10/22	CC 02 FR 02	Time zero - Instack - Middle	
10/22	CC 02 FR 03	Time zero - Instack - Bottom	
10/22	CC 02 FR 11	12 hour night	
10/22	CC 02 FR 12	12 hour night	
10/22	CC 02 FR 13	12 hour night	
10/22	CC 02 FR 21	12 hour day	
10/22	CC 02 FR 22	12 hour day	
10/22	CC 02 FR 23	12 hour day	
10/22	CC 02 FR 31	24 hour	
10/22	CC 02 FR 32	24 hour	
10/22	CC 02 FR 33	24 hour	
10/22	CC 02 FR 41	24 hour - background	
10/22	CC 02 FR 42	24 hour - background	
10/22	CC 02 FR 43	24 hour - background	
10/26	CC 03 FR 01	Time zero Instack (top filter)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
10/26	CC 03 FR 02	12:00 (mid filter)	
10/26	CC 03 FR 03	10/23 (bottom filter)	
10/26	CC 03 FR 11	12 hour night (top filter)	
10/26	CC 03 FR 12	19:00-7:00 (Middle Filter)	
10/26	CC 03 FR 13	10/24-10/25 (Bottom Filter)	
10/26	CC 03 FR 21	12 hour day (top filter)	
10/26	CC 03 FR 22	9:00-21:00 (Middle Filter)	
10/26	CC 03 FR 23	10/26 (Bottom Filter)	
10/26	CC 03 FR 31	24 hour day/night (top filter)	
10/26	CC 03 FR 32	19:00-19:00 (Middle Filter)	
10/26	CC 03 FR 33	10/24-10/25 (Bottom Filter)	
10/26	CC 03 FR 41	24 hour background (top filter)	
10/26	CC 03 FR 42	19:00-19:00 (Middle Filter)	
10/26	CC 03 FR 43	10/24-10/25 (Bottom Filter)	
10/26	CC 04 FR 01	Time zero Instack (top filter)	
10/26	CC 04 FR 02	12:05 (mid filter)	
10/26	CC 04 FR 03	10/23 (bottom filter)	
10/26	CC 04 FR 11	12 hour night (top filter)	
10/26	CC 04 FR 12	19:00-7:00 (Middle Filter)	
10/26	CC 04 FR 13	10/24-10/25 (Bottom Filter)	
10/26	CC 04 FR 21	12 hour day (top filter)	
10/26	CC 04 FR 22	9:00-21:00 (Middle Filter)	
10/26	CC 04 FR 23	10/26 (Bottom Filter)	
10/26	CC 04 FR 31	24 hour day/night (top filter)	
10/26	CC 04 FR 32	19:00-19:00 (Middle Filter)	
10/26	CC 04 FR 33	10/24-10/25 (Bottom Filter)	
10/26	CC 04 FR 41	24 hour background (top filter)	
10/26	CC 04 FR 42	19:00-19:00 (Middle Filter)	
10/26	CC 04 FR 43	10/24-10/25 (Bottom Filter)	
10/26	CC 05 FR 01	Time zero Instack (top filter)	
10/26	CC 05 FR 02	12:10 (mid filter)	
10/26	CC 05 FR 03	10/23 (bottom filter)	
10/26	CC 05 FR 11	12 hour night (top filter)	
10/26	CC 05 FR 12	21:00-9:00 (Middle Filter)	
10/26	CC 05 FR 13	10/26-10/27 (Bottom Filter)	
10/26	CC 05 FR 21	12 hour day (top filter)	
10/26	CC 05 FR 22	9:00-21:00 (Middle Filter)	
10/26	CC 05 FR 23	10/26 (Bottom Filter)	
10/26	CC 05 FR 31	24 hour day/night (top filter)	
10/26	CC 05 FR 32	9:00-9:00 (Middle Filter)	
10/26	CC 05 FR 33	10/26-10/27 (Bottom Filter)	
10/26	CC 05 FR 41	24 hour background (top filter)	
10/26	CC 05 FR 42	9:00-9:00 (Middle Filter)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
10/26	CC 05 FR 43	10/26-10/27 (Bottom Filter)	
10/27	CC 06 FR 01	Time zero Instack (top filter)	
10/27	CC 06 FR 02	(mid filter)	
10/27	CC 06 FR 03	(bottom filter)	
10/27	CC 06 FR 11	12 hour night (top filter)	
10/27	CC 06 FR 12	21:10-9:00 (Middle Filter)	
10/27	CC 06 FR 13	10/27-10/28 (Bottom Filter)	
10/27	CC 06 FR 21	12 hour day (top filter)	
10/27	CC 06 FR 22	9:30-21:10 (Middle Filter)	
10/27	CC 06 FR 23	10/27-10/27 (Bottom Filter)	
10/27	CC 06 FR 31	24 hour day/night (top filter)	
10/27	CC 06 FR 32	9:30-9:00 (Middle Filter)	
10/27	CC 06 FR 33	10/27-10/28 (Bottom Filter)	
10/27	CC 06 FR 41	24 hour background (top filter)	
10/27	CC 06 FR 42	9:30-9:00 (Middle Filter)	
10/27	CC 06 FR 43	10/27-10/28 (Bottom Filter)	
10/28	CC 07 FR 01	Time zero Instack (top filter)	
10/28	CC 07 FR 02	(mid filter)	
10/28	CC 07 FR 03	(bottom filter)	
10/28	CC 07 FR 11	12 hour night (top filter)	
10/28	CC 07 FR 12	21:00-9:00 (Middle Filter)	
10/28	CC 07 FR 13	10/28-10/29 (Bottom Filter)	
10/28	CC 07 FR 21	12 hour day (top filter)	
10/28	CC 07 FR 22	9:00-21:00 (Middle Filter)	
10/28	CC 07 FR 23	10/28-10/28 (Bottom Filter)	
10/28	CC 07 FR 31	24 hour day/night (top filter)	
10/28	CC 07 FR 32	9:00-9:00 (Middle Filter)	
10/28	CC 07 FR 33	10/28-10/29 (Bottom Filter)	
10/28	CC 07 FR 41	24 hour background (top filter)	
10/28	CC 07 FR 42	9:00-9:00 (Middle Filter)	
10/28	CC 07 FR 43	10/28-10/29 (Bottom Filter)	
10/28	CC 08 FR 01	Time zero Instack (top filter)	
10/28	CC 08 FR 02	(mid filter)	
10/28	CC 08 FR 03	(bottom filter)	
10/28	CC 08 FR 11	12 hour night (top filter)	
10/28	CC 08 FR 12	20:15-9:35 (Middle Filter)	
10/28	CC 08 FR 13	10/29-10/30 (Bottom Filter)	
10/28	CC 08 FR 21	12 hour day (top filter)	
10/28	CC 08 FR 22	9:32-20:15 (Middle Filter)	
10/28	CC 08 FR 23	10/29-10/29 (Bottom Filter)	
10/28	CC 08 FR 31	24 hour day/night (top filter)	
10/28	CC 08 FR 32	(Middle Filter)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
10/28	CC 08 FR 33	(Bottom Filter)	
10/28	CC 08 FR 41	24 hour Background (top filter)	
10/28	CC 08 FR 42	9:32-9:35 (Middle Filter)	
10/28	CC 08 FR 43	10/29-10/30 (Bottom Filter)	
10/28	CC 08 FR B	Blank Lot #5288037	
10/29	AR 09 FR 01	Time zero Instack 60 min (top)	
10/29	AR 09 FR 02	(mid filter)	
10/29	AR 09 FR 03	(bottom filter)	
10/29	AR 09 FR 11	12 hour night (top filter)	
10/29	AR 09 FR 12	20:15-9:35 (Middle Filter)	
10/29	AR 09 FR 13	10/29-10/30 (Bottom Filter)	
10/29	AR 09 FR 21	12 hour day (top filter)	
10/29	AR 09 FR 22	9:40-20:15 (Middle Filter)	
10/29	AR 09 FR 23	10/30-10/30 (Bottom Filter)	
10/29	AR 09 FR 31	24 hour day/night (top filter)	
10/29	AR 09 FR 32	20:15-20:15 (Middle Filter)	
10/29	AR 09 FR 33	10/29-10/30 (Bottom Filter)	
10/29	AR 09 FR 41	24 hour Background (top filter)	
10/29	AR 09 FR 42	20:15-20:15 (Middle Filter)	
10/29	AR 09 FR 43	10/29-10/30 (Bottom Filter)	
10/29	AR 09 FR B	Blank, Lot #8002908	
10/30	AR 10 FR 01	Time zero 30 min Instack (top)	
10/30	AR 10 FR 02	(mid filter)	
10/30	AR 10 FR 03	(bottom filter)	
10/30	AR 10 FR 11	12 hour night (top filter)	
10/30	AR 10 FR 12	21:38-9:01 (Middle Filter)	
10/30	AR 10 FR 13	11/1-11/2 (Bottom Filter)	
10/30	AR 10 FR 21	12 hour day (top filter)	
10/30	AR 10 FR 22	9:03-21:37 (Middle Filter)	
10/30	AR 10 FR 23	11/2-11/2 (Bottom Filter)	
10/30	AR 10 FR 31	24 hour day/night (top filter)	
10/30	AR 10 FR 32	21:38-21:37 (Middle Filter)	
10/30	AR 10 FR 33	11/1-11/2 (Bottom Filter)	
10/30	AR 10 FR 41	24 hour Background (top filter)	
10/30	AR 10 FR 42	21:38-21:37 (Middle Filter)	
10/30	AR 10 FR 43	11/1-11/2 (Bottom Filter)	
10/30	AR 10 FR 71	2 min Instack Time Zero	
10/30	AR 10 FR 72	2 min Instack Time Zero	
10/30	AR 10 FR 73	2 min Instack Time Zero	
10/30	AR 10 FR B	Blank	
11/2	AR 11 FR 01	Time zero 40 min Instack (top)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
11/2	AR 11 FR 02	(mid filter)	
11/2	AR 11 FR 03	(bottom filter)	
11/2	AR 11 FR 11	12 hour night (top filter.)	
11/2	AR 11 FR 12	21:37-8:57 (Middle Filter)	
11/2	AR 11 FR 13	11/2-11/3 (Bottom Filter)	
11/2	AR 11 FR 21	12 hour Day (top filter)	
11/2	AR 11 FR 22	8:57-9:30 (Middle Filter)	
11/2	AR 11 FR 23	11/3-11/3 (Bottom Filter)	
11/2	AR 11 FR 31	24 hour day/night (top filter)	
11/2	AR 11 FR 32	9:38-9:30 (Middle Filter)	
11/2	AR 11 FR 33	11/2-11/3 (Bottom Filter)	
11/2	AR 11 FR 41	24 hour Background (top filter)	
11/2	AR 11 FR 42	9:38-9:30 (Middle Filter)	
11/2	AR 11 FR 43	11/2-11/3 (Bottom Filter)	
11/2	AR 11 FR 71	2 min Instack Time zero	
11/2	AR 11 FR 72	2 min Instack Time zero	
11/2	AR 11 FR 73	2 min Instack Time zero	
11/2	AR 11 FR B	Blank Teflon FR filter 11/02	
11/4	AR 12 FR 01	Expose 30 min - Time zero Instack (top f.)	
11/4	AR 12 FR 02	(mid filter)	
11/4	AR 12 FR 03P	(bottom filter) PVC	
11/4	AR 12 FR 11	12 hour night (30 min Instack exp.) (top f.)	
11/4	AR 12 FR 12	21:30-8:56 (Middle Filter)	
11/4	AR 12 FR 13P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 12 FR 21	12 hour Day (30 min Instack exp.) (top f.)	
11/4	AR 12 FR 22	8:58-21:30 (Middle Filter)	
11/4	AR 12 FR 23P	11/5-11/5 (Bottom Filter) PVC	
11/4	AR 12 FR 31	24 hour day/night (30 min instack exp.) (top f.)	
11/4	AR 12 FR 32	8:58-8:56 (Middle Filter)	
11/4	AR 12 FR 33P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 12 FR 41	24 hour Background (30 min instack exp.) (top f.)	
11/4	AR 12 FR 42	8:58-8:56 (Middle Filter)	
11/4	AR 12 FR 43P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 12 FR BP	Blank PVC Lot #5242027	
11/4	AR 12 FR BT	Blank Teflon Lot #2617	
11/4	AR 13 FR 01	Expose 30 min - Time zero Instack (top filter)	
11/4	AR 13 FR 02	(mid filter)	
11/4	AR 13 FR 03P	(bottom filter) PVC	
11/4	AR 13 FR 11	12 hour night (30 min Instack exp.) (top filter)	
11/4	AR 13 FR 12	21:30-8:56 (Middle Filter)	
11/4	AR 13 FR 13P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 13 FR 21	12 hour Day (30 min Instack exp.) (top filter)	

FIELD REACTION SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Sample Time
11/4	AR 13 FR 22	8:58-21:30 (Middle Filter)	
11/4	AR 13 FR 23P	11/5-11/5 (Bottom Filter) PVC	
11/4	AR 13 FR 31	24 hour day/night (30 min instack exp.) (top f.)	
11/4	AR 13 FR 32	8:58-8:56 (Middle Filter)	
11/4	AR 13 FR 33P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 13 FR 41	24 hour Background (30 min instack exp.) (top f.)	
11/4	AR 13 FR 42	8:58-8:56 (Middle Filter)	
11/4	AR 13 FR 43P	11/5-11/6 (Bottom Filter) PVC	
11/4	AR 13 FR BP	Blank PVC Lot #5242027	
11/4	AR 13 FR BT	Blank Teflon Lot #2617	
11/5	AR 14 FR 01	Expose 30 min - Time zero Instack (top filter)	
11/5	AR 14 FR 02	(mid filter)	
11/5	AR 14 FR 03P	(bottom filter) PVC	
11/5	AR 14 FR 11	12 hour night (30 min Instack exp.) (top filter)	
11/5	AR 14 FR 12	20:14-9:30 (Middle Filter)	
11/5	AR 14 FR 13P	11/6-11/7 (Bottom Filter) PVC	
11/5	AR 14 FR 21	12 hour Day (30 min Instack exp.) (top filter)	
11/5	AR 14 FR 22	9:31-20:12 (Middle Filter)	
11/5	AR 14 FR 23P	11/6-11/6 (Bottom Filter) PVC	
11/5	AR 14 FR 31	24 hour day/night (30 min instack exp.) (top f.)	
11/5	AR 14 FR 32	9:31-9:30 (Middle Filter)	
11/5	AR 14 FR 33P	11/6-11/7 (Bottom Filter) PVC	
11/5	AR 14 FR 41	24 hour Background (30 min instack exp.) (top f.)	
11/5	AR 14 FR 42	9:31-9:30 (Middle Filter)	
11/5	AR 14 FR 43P	11/6-11/7 (Bottom Filter) PVC	
11/5	AR 14 FR 71	Instack 2 min sampling	
11/5	AR 14 FR 72	Instack 2 min sampling	
11/5	AR 14 FR 73P	Instack 2 min sampling	
11/5	AR 14 FR BP	Blank PVC Lot #5242027	
11/5	AR 14 FR BT	Blank Teflon Lot #2617	
11/6	AR 15 FR 71	Instack 2 min sampling	
11/6	AR 15 FR 72	Instack 2 min sampling	
11/6	AR 15 FR 73P	Instack 2 min sampling	

APPENDIX B.

Inventory of Ambient Samples

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Semple Number	Description	Time	Minutes	Cu.Meters
10/21	CC 01 IS LPB	Impinger Train Lab Proof Blank			
10/21	CC 01 IS 01 A	Loc. 1. C train 1st Imp.	13:45-18:00	255	6.0
10/21	CC 01 IS 01 B	Loc. 1. C train 2nd Imp.			
10/21	CC 01 IS 02 A	Loc. 1. B train 1st Imp.	13:45-18:00	255	6.0
10/21	CC 01 IS 02 B	Loc. 1. B train 2nd Imp.			
10/21	CC 01 IS 03 A	Loc. 1. A train 1st Imp.			
10/21	CC 01 IS 03 B	Loc. 1. A train 2nd Imp.	13:45-18:00	255	6.0
10/21	CC 01 NR 04	A,B,C Train Nitric Rinse			
10/21	CC 01 XT 01	Teflon Filter Sample	13:45-18:00	255	4.955
10/22	CC 02 IS 01	Upwind Impinger Train 1	11:30-15:00	210	7.4
10/22	CC 02 IS 02	Upwind Impinger Train 2	11:30-15:00	210	7.4
10/22	CC 02 IS 11	In-stack 3 seconds			0.0035
10/22	CC 02 IS 12	In-stack 10 seconds			0.0116
10/22	CC 02 IS 13	In-stack 30 seconds			0.035
10/22	CC 02 NR 03	Upwind IS 01 + 02 Nitric Rinse			
10/22	CC 02 NR 14	3 + 10 second IS Nitric rinse			
10/22	CC 02 NR 15	30 second IS Nitric rinse			
10/22	CC 02 XT 01	Upwind TEFLON Filter	11:30-15:00	210	4.668
10/22	CC 02 XT 02	Upwind PVC Filter	11:30-15:00	210	4.641
10/22	CC 02 XT 21	Loc. 1 Teflon - Lot 2089	13:18-18:30	312	5.575
10/22	CC 02 XT 22	Loc. 1 PVC - Lot 5288037	12:24-18:30	366	7.010
10/23	CC 03 IS 01	Upwind Impinger Train 1	12:05-15:05	180	4.1
10/23	CC 03 IS 02	Upwind Impinger Train 2	12:05-15:05	180	4.1
10/23	CC 03 IS 11	Pred. Downwind (Loc. 1) Train 1	14:35-18:35	240	8.2
10/23	CC 03 IS 12	Pred. Downwind (Loc. 1) Train 2	14:35-18:35	240	8.2
10/23	CC 03 IS 21	Near Downwind (Loc. 2) Train 1	14:40-18:50	211	4.8
10/23	CC 03 IS 61	Stack 10 sec. time zero Nitric Rinse			
10/23	CC 03 IS 61	Stack 10 sec. time zero			0.0116
10/23	CC 03 IS 62	10 sec stack sample + 3 hr amb.	12:05-15:05	180	4.1
10/23	CC 03 IS 22	Near Downwind (Loc. 2) Train 2	14:40-18:50	211	4.8
10/23	CC 03 IS 23	Near Downwind (Loc. 2) Train 3	14:40-18:50	211	4.8
10/23	CC 03 IS 31	Far Downwind (Loc. 3) Train 1	14:35-18:30	220	5.0
10/23	CC 03 IS 32	Far Downwind (Loc. 3) Train 2	14:35-18:30	220	5.0
10/23	CC 03 IS 33	Far Downwind (Loc. 3) Train 3	14:35-18:30	220	5.0
10/23	CC 03 IS 41	Alt. Downwind (Loc. 4) Trains 1	14:30-18:55	265	6.0
10/23	CC 03 IS 42	Alt. Downwind (Loc. 4) Trains 2	14:30-18:55	265	6.0
10/23	CC 03 IS 43	Alt. Downwind (Loc. 4) Trains 3	14:30-18:55	265	6.0
10/23	CC 03 NR 03	Upwind Train 1 + 2 Nitric Rinse			
10/23	CC 03 NR 62	Time Zero + 3 hr amb. Nitric Rinse			
10/23	CC 03 NR 13	Loc. 1 Train 1 + 2 Nitric Rinse			
10/23	CC 03 NR 24	Loc. 2 Trains 1,2, & 3 Nitric Rinse			
10/23	CC 03 NR 34	Loc. 3 Trains 1,2, & 3 Nitric Rinse			
10/23	CC 03 NR 44	Loc. 4 Trains 1,2, & 3 Nitric Rinse			

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/23	CC 03 XT 01	Upwind Teflon Filter	12:05-15:05	180	3.998
10/23	CC 03 XT 02	Upwind PVC Filter	12:05-15:05	180	3.974
10/23	CC 03 XT 11	Pred. Downwind (Loc. 1) Teflon Filter	15:30-18:30	180	3.217
10/23	CC 03 XT 12	Pred. Downwind (Loc. 1) PVC Filter	14:35-18:35	240	4.584
10/23	CC 03 XT 21	Near Downwind (Loc. 2) Teflon Filter	No Flow		
10/23	CC 03 XT 22	Near Downwind (Loc. 2) PVC Filter	No Flow		
10/23	CC 03 XT 31	Far Downwind (Loc. 3) Teflon Filter	16:15-18:30	135	2.462
10/23	CC 03 XT 32	Far Downwind (Loc. 3) PVC Filter	16:15-18:30	135	2.447
10/23	CC 03 XT 41	Alt. Downwind (Loc. 4) Teflon Filter	14:55-18:55	240	5.348
10/23	CC 03 XT 42	Alt. Downwind (Loc. 4) PVC Filter	14:50-18:50	230	5.043
10/23	CC 03 XT FB 01	XT Teflon Field Blank Ch 1 Loc. 1			
10/23	CC 03 XT FB 02	XT PVC Field Blank Ch 2 Loc. 1			
10/23	CC 03 XT RB 01	Teflon Filter Blank			
10/23	CC 03 XT RB 02	PVC Filter Blank			
10/26	CC 04 IS 11	Loc. 1 48 imp. sample	21:00-21:00	2880	54.015
10/26	CC 04 NR 11	Nitric Rinse Loc. 1 48 imp. sample	11/23-11/25		
10/26	CC 04 XT 11	Loc. 1 48 hours Teflon	21:00-21:00	2880	51.494
10/26	CC 04 XT 12	Loc. 1 48 hours PVC	11/23-11/25	2880	54.551
10/26	CC 05 IS 01	Upwind samp. loc. Train 1	12:48-15:18	150	3.4
10/26	CC 05 IS 02	Upwind samp. loc. Train 2	12:48-15:18	150	3.4
10/26	CC 05 IS 11	Pred. Sam.Loc.(Loc. 1) Train 1	13:50-17:50	240	5.3
10/26	CC 05 IS 12	Pred. Sam.Loc.(Loc. 1) Train 2	13:50-17:50	240	5.3
10/26	CC 05 IS 13	Pred. Sam.Loc.(Loc. 1) Train 3	13:50-17:50	240	5.3
10/26	CC 05 IS 21	Far Downwind (Loc. 2) Train 1	13:45-17:50	240	5.4
10/26	CC 05 IS 22	Far Downwind (Loc. 2) Train 2	13:45-17:50	240	5.4
10/26	CC 05 IS 23a	Far Downwind (Loc. 2) Train 3 Imp 1	13:45-17:50	240	5.4
10/26	CC 05 IS 23b	Efficiency Check Train 3 Imp 2			
10/26	CC 05 IS 31	Loc 3 Scout+Florance Pl. Train 1	13:50-17:50	240	5.7
10/26	CC 05 IS 32a	Loc 3 Train 2 Imp 1	13:50-17:50	240	5.7
10/26	CC 05 IS 32b	Efficiency Check Train 2 Imp 2			
10/26	CC 05 IS 33	Loc 3 Scout+Florance Pl. Train 3	13:50-17:50	240	5.7
10/26	CC 05 IS 41	Loc 4 Suva at Box Co Train 1	13:34-17:34	240	5.5
10/26	CC 05 IS 42	Loc 4 Suva at Box Co Train 2	13:34-17:34	240	5.5
10/26	CC 05 IS 43	Loc 4 Suva at Box Co Train 3	13:34-17:34	240	5.5
10/26	CC 05 IS 61	10 sec. In stack Time zero			0.0116
10/26	CC 05 IS 63	Instack sample+2.5 hr upwind samples	12:48-15:18	150	3.4
10/26	CC 05 NR 03	Nitric Rinse Loc. 0 Trains			
10/26	CC 05 NR 14	Nitric Rinse Trains 1,2,3 Loc1			
10/26	CC 05 NR 24	Nitric Rinse Trains 1,2,3 Loc 2			
10/26	CC 05 NR 34	Nitric Rinse Trains 1,2,3 Loc 3			
10/26	CC 05 NR 44	Nitric Rinse Trains 1,2,3 Loc 4			
10/26	CC 05 NR 62	Nitric Rinse -In stack Time zero			

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/26	CC 05 NR 64	Nitric Rinse Time Zero + 2.5 hr amb			
10/26	CC 05 XT 01	Upwind Teflon	12:48-15:18	150	3.404
10/26	CC 05 XT 02	Upwind PVC	12:48-15:18	150	3.309
10/26	CC 05 XT 11	Pred. Loc. 1 (near downwind) Teflon	13:50-17:50	240	4.293
10/26	CC 05 XT 12	Pred. Loc. 1 (near downwind) PVC	15:50-17:50	120	2.270
10/26	CC 05 XT 21	Far downwind (Loc. 2) Teflon	13:50-17:50	240	4.117
10/26	CC 05 XT 22	Far downwind (Loc. 2) PVC	13:50-17:50	240	4.088
10/26	CC 05 XT 31	Loc 3 (East of source) Teflon	13:50-17:50	240	5.346
10/26	CC 05 XT 32	Loc 3 (East of source) PVC	13:50-17:50	240	5.260
10/26	CC 05 XT 41	Loc 4 (North of source) Teflon	13:34-17:34	240	4.632
10/27	CC 07 IS 01	Imp. sample, Loc 0 Train 1	12:21-15:21	180	4.0
10/27	CC 07 IS 02	Imp. sample, Loc 0 Train 2	12:21-15:21	180	4.0
10/27	CC 07 IS 11	Imp. sample, Loc 1 Train 1	13:00-17:00	240	6.1
10/27	CC 07 IS 12a	Loc 1 Eff. Check Train 2 Imp 1	13:00-17:00	240	6.1
10/27	CC 07 IS 12b	Loc 1 Eff. Check Train 2 Imp 2			
10/27	CC 07 IS 13	Imp. sample, Loc 1 Train 3	13:00-17:00	240	6.1
10/27	CC 07 IS 21	Imp. sample, Loc 2 Train 1	13:10-17:10	240	6.1
10/27	CC 07 IS 22	Imp. sample, Loc 2 Train 2	13:10-17:10	240	6.1
10/27	CC 07 IS 23	Imp. sample, Loc 2 Train 3	13:10-17:10	240	6.1
10/27	CC 07 IS 31	Imp. sample, Loc 3 Train 1	13:05-17:05	240	5.9
10/27	CC 07 IS 32	Loc 3 Eff. Check Train 2 Imp 1	13:05-17:05	240	5.9
10/27	CC 07 IS 33a	Loc 3 Eff. Check Train 2 Imp 2			
10/27	CC 07 IS 33b	Imp. sample, Loc 3	13:05-17:05	240	5.9
10/27	CC 07 IS 41	Imp. sample, Loc 4	13:00-17:00	240	6.2
10/27	CC 07 IS 42	Imp. sample, Loc 4	13:00-17:00	240	6.2
10/27	CC 07 IS 43	Imp. sample, Loc 4	13:00-17:00	240	6.2
10/27	CC 07 IS 61	Time zero, 10 sec. stack sample			0.0116
10/27	CC 07 IS 63	10 sec. Time zero + 3 hr upwind amb	12:21-15:21	180	4.0
10/27	CC 07 IS FB	Field Blank / Acetate			
10/27	CC 07 IS RB	Reagent Blank / Acetate Batch 2			
10/27	CC 07 NR 03	Imp. sample, Loc 0 Nitric Rinse			
10/27	CC 07 NR 12c	Imp. sample, Loc 1 Eff. Check			
10/27	CC 07 NR 14	Imp. sample, Loc 1 Nitric Rinse			
10/27	CC 07 NR 24	Imp. sample, Loc 2 Nitric Rinse			
10/27	CC 07 NR 34	Imp. sample, Loc 3 Nitric Rinse			
10/27	CC 07 NR 44	Imp. sample, Loc 4 Nitric Rinse			
10/27	CC 07 NR 62	Nitric Rinse -In stack Time zero			
10/27	CC 07 NR 64	Nitric Rinse Time Zero + 3 hr amb			
10/27	CC 07 NR RB	Field Blank / 5% Nitric Acid Rinse			
10/27	CC 07 NR RB	Reagent Blank / 5% Nitric Acid			
10/27	CC 07 XT 01	Upwind Teflon	12:21-15:21	180	3.999
10/27	CC 07 XT 02	Upwind PVC	12:21-15:21	180	3.972
10/27	CC 07 XT 11	Pred. Loc. 1 (near downwind) Teflon	13:00-17:00	240	4.361
10/27	CC 07 XT 12	Pred. Loc. 1 (near downwind) PVC	13:00-17:00	240	4.539

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/27	CC 07 XT 21	Far downwind (Loc. 2) Teflon	13:10-17:10	240	5.349
10/27	CC 07 XT 22	Far downwind (Loc. 2) PVC	13:10-17:10	240	5.257
10/27	CC 07 XT 31	Loc 3 (East of source) Teflon	13:05-17:05	240	5.073
10/27	CC 07 XT 32	Loc 3 (East of source) PVC	13:05-17:05	240	5.112
10/27	CC 07 XT 41	Loc 4 (North of source) Teflon	13:00-17:00	240	5.013
10/28	CC 08 IS 01	Imp. sample, Loc 0 Time Zero?	11:25-13:45	140	3.2
10/28	CC 08 IS 02	Imp. sample, Loc 0 Time Zero?	11:25-13:45	140	3.2
10/28	CC 08 IS 03	Imp. sample, Loc 0 Time Zero?	11:25-13:45	140	3.2
10/28	CC 08 IS 11a	Loc 1 Eff. Check Train 1 Imp 1	13:50-17:00	190	4.3
10/28	CC 08 IS 11b	Loc 1 Eff. Check Train 1 Imp 2			
10/28	CC 08 IS 12a	Loc 1 Eff. Check Train 2 Imp 1	13:50-17:00	190	4.3
10/28	CC 08 IS 12b	Loc 1 Eff. Check Train 2 Imp 2			
10/28	CC 08 IS 12c	Loc 1 Eff. Check Train 2 Imp 3			
10/28	CC 08 IS 13	Imp. sample, Loc 1 Train 3	13:50-17:00	190	4.3
10/28	CC 08 IS 21	Imp. sample, Loc 2 Train 1	12:10-17:00	290	6.6
10/28	CC 08 IS 22	Imp. sample, Loc 2 Train 2	12:10-17:00	290	6.6
10/28	CC 08 IS 23	Imp. sample, Loc 2 Train 3	12:10-17:00	290	6.6
10/28	CC 08 IS 31	Imp. sample, Loc 3 Train 1	12:05-17:05	300	6.8
10/28	CC 08 IS 32	Imp. sample, Loc 3 Train 2	12:05-17:05	300	6.8
10/28	CC 08 IS 33	Imp. sample, Loc 3 Train 3	12:05-17:05	300	6.8
10/28	CC 08 IS 41	Imp. sample, Loc 4 Train 1	11:55-16:55	300	6.8
10/28	CC 08 IS 61	Time Zero instack sample 10 seconds			0.0116
10/28	CC 08 NR 04	Imp. sample, Loc 0 Nitric Rinse			
10/28	CC 08 NR 14	Imp. sample, Loc 1 Nitric Rinse			
10/28	CC 08 NR 24	Imp. sample, Loc 2 Nitric Rinse			
10/28	CC 08 NR 34	Imp. sample, Loc 3 Nitric Rinse			
10/28	CC 08 NR 44	Imp. sample, Loc 4 Nitric Rinse			
10/28	CC 08 NR 62	10 sec. Time Zero Nitric Rinse			
10/28	CC 08 XT 01	Upwind Teflon	11:25-15:00	215	4.775
10/28	CC 08 XT 02	Upwind PVC	11:25-15:00	215	4.743
10/28	CC 08 XT 11	Pred. Loc. 1 (near downwind) Teflon	13:50-17:00	190	3.444
10/28	CC 08 XT 12	Pred. Loc. 1 (near downwind) PVC	13:50-17:00	190	3.585
10/28	CC 08 XT 21	Far downwind (Loc. 2) Teflon	12:10-17:00	290	6.459
10/28	CC 08 XT 22	Far downwind (Loc. 2) PVC	12:10-17:00	290	6.352
10/28	CC 08 XT 31	Loc 3 (East of source) Teflon	12:05-17:05	300	6.336
10/28	CC 08 XT 32	Loc 3 (East of source) PVC	12:05-17:05	300	6.386
10/28	CC 08 XT 41	Loc 4 (North of source) Teflon	11:55-16:55	300	5.610
10/29	AR 09 IS 21	Imp. Sample, Loc 2 Downwind	14:54-17:15	141	3.3
10/29	AR 09 IS 22	Imp. Sample, Loc 2 Downwind	14:54-17:15	141	3.3
10/29	AR 09 IS 23	Imp. Sample, Loc 2 Downwind	14:54-17:15	141	3.3
10/29	AR 09 IS 61	Loc 6, Instack 70 min	15:00-16:10	70	2.4
10/29	AR 09 IS 62	Loc 6, Instack 70 min	15:00-16:10	70	2.4
10/29	AR 09 XT 21	Loc 2, Teflon	14:54-17:15	141	3.180

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
10/29	AR 09 XT 22	Loc 2, Teflon	14:54-17:15	141	3.180
10/30	AR 10 IS 01	Upwind (Loc. 0)	14:08-17:58	230	5.2
10/30	AR 10 IS 02	Upwind (Loc. 0)	14:08-17:58	230	5.2
10/30	AR 10 IS 11	Downwind (Loc 1) Train 1	13:38-17:38	240	5.4
10/30	AR 10 IS 12	Downwind (Loc 1) Train 2	13:38-17:38	240	5.4
10/30	AR 10 IS 13	Downwind (Loc 1) Train 3	13:38-17:38	240	5.4
10/30	AR 10 IS 21	Downwind (Loc 2) Train 1	13:22-15:22	230	5.2
10/30	AR 10 IS 22	Downwind (Loc 2) Train 2	13:22-15:22	230	5.2
10/30	AR 10 IS 23	Downwind (Loc 2) Train 3	13:22-15:22	230	5.2
10/30	AR 10 IS 31	Downwind (Loc 3) Train 1	13:54-17:54	233	5.3
10/30	AR 10 IS 32	Downwind (Loc 3) Train 2	13:54-17:54	233	5.3
10/30	AR 10 IS 33	Downwind (Loc 3) Train 3	13:54-17:54	233	5.3
10/30	AR 10 IS 61	30 min instack Time zero	11:00-11:30	30	1.0
10/30	AR 10 IS 62	30 min Time zero + 230 min Loc. 0	14:08-17:58	230	5.2
10/30	AR 10 XT 01	Upwind Teflon	14:08-17:58	230	4.184
10/30	AR 10 XT 02	Upwind NaAc PVC	14:08-17:58	230	4.352
10/30	AR 10 XT 11	Downwind Left (Loc 1) Teflon	13:38-17:38	240	5.072
10/30	AR 10 XT 12	Downwind Left (Loc 1) 1st NaAC PVC	13:38-17:38	240	5.117
10/30	AR 10 XT 31	Downwind Right (Loc 3) Teflon	13:54-17:54	233	5.178
10/30	AR 10 XT 32	Downwind Right (Loc 3) 1st NaAc PVC	13:54-17:54	233	5.144
11/2	AR 11 IS 01	Loc 0 Upwind Train 1	13:20-17:10	230	5.2
11/2	AR 11 IS 02	Loc 0 Upwind Train 2	13:20-17:10	230	5.2
11/2	AR 11 IS 11a	Loc 1 Downwind Train 1 1st imp	13:10-17:10	240	4.6
11/2	AR 11 IS 11b	Loc 1 Downwind Train 1 2nd imp			
11/2	AR 11 IS 12a	Loc 1 Downwind Train 2 1st imp	13:10-17:10	240	4.6
11/2	AR 11 IS 12b	Loc 1 Downwind Train 2 2nd imp			
11/2	AR 11 IS 13	Loc 1 Downwind Train 3	13:10-17:10	240	4.6
11/2	AR 11 IS 21	Loc 2 Downwind Train 1	13:58-15:56	118	2.6
11/2	AR 11 IS 22	Loc 2 Downwind Train 2	13:58-15:56	118	2.6
11/2	AR 11 IS 23	Loc 2 Downwind Train 3	13:58-15:56	118	2.6
11/2	AR 11 IS 31	Loc 3 Downwind Train 1	13:20-17:20	240	5.4
11/2	AR 11 IS 32	Loc 3 Downwind Train 2	13:20-17:20	240	5.4
11/2	AR 11 IS 33	Loc 3 Downwind Train 3	13:20-17:20	240	5.4
11/2	AR 11 IS 41	Loc 4 Far Downwind Train 1	13:40-17:44	244	6.0
11/2	AR 11 IS 42	Loc 4 Far Downwind Train 2	13:40-17:44	244	6.0
11/2	AR 11 IS 43	Loc 4 Far Downwind Train 3	13:40-17:44	244	6.0
11/2	AR 11 IS 61	30 min Instack Time Zero	11:00-11:30	30	1.1
11/2	AR 11 IS 62	Instack Time Zero + 230 min amb	13:20-17:10	230	5.2
11/2	AR 11 IS FB	Sample Train Field Blank			
11/2	AR 11 IS RB	NaAcetate Reagent Blank Batch 3			
11/2	AR 11 XT 01	Upwind (Loc 0) Teflon	13:10-17:10	240	4.365
11/2	AR 11 XT 02	Upwind (Loc 0) 1st NaAc PVC	13:10-17:10	240	4.542
11/2	AR 11 XT 11	Downwind Left (Loc 1) Teflon	13:00-17:30	270	5.713

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
11/2	AR 11 XT 12	Downwind Left (Loc 1) 1st NaAC PVC	13:00-17:30	270	5.772
11/2	AR 11 XT 21	Downwind (Loc 2) Teflon	13:58-15:56	118	2.436
11/2	AR 11 XT 22	Downwind (Loc 2) 1st NaAc PVC	13:58-15:56	118	4.005
11/2	AR 11 XT 31	Downwind Right (Loc 3) Teflon	13:20-17:20	240	5.333
11/2	AR 11 XT 32	Downwind Right (Loc 3) 1st NaAc PVC	13:20-17:20	240	5.292
11/2	AR 11 XT 41	Far Downwind (Loc. 4) Teflon	13:41-17:44	243	2.220
11/2	AR 11 XT B	1st Batch Blank Na Acetate Filter			
11/3	AR 12 IS 01	Loc 0, Upwind Train 1	12:45-17:45	293	7.4
11/3	AR 12 IS 02	Loc 0, Upwind Train 2	12:45-17:45	293	7.4
11/3	AR 12 IS 11	Loc 1, East of CT 9 Train 1	11:50-18:00	370	8.2
11/3	AR 12 IS 12	Loc 1, East of CT 9 Train 2	11:50-18:00	370	8.2
11/3	AR 12 IS 13	Loc 1, East of CT 9 Train 3	11:50-18:00	370	8.2
11/3	AR 12 IS 21	Loc 2, In Tank Farm Train 1	12:52-17:52	<300	<7.0
11/3	AR 12 IS 22	Loc 2, In Tank Farm Train 2	12:52-17:52	<300	<7.0
11/3	AR 12 IS 23	Loc 2, In Tank Farm Train 3	12:52-17:52	<300	<7.0
11/3	AR 12 IS 31	Loc 3N, NW corner of Lot Train 1	13:05-18:05	300	8.0
11/3	AR 12 IS 32	Loc 3N, NW corner of Lot Train 2	13:05-18:05	300	8.0
11/3	AR 12 IS 33	Loc 3N, NW corner of Lot Train 3	13:05-18:05	300	8.0
11/3	AR 12 IS 41	Loc 4, Far Downwind Train 1	11:44-17:06	322	7.2
11/3	AR 12 IS 42	Loc 4, Far Downwind Train 2	11:44-17:06	322	7.2
11/3	AR 12 IS 43	Loc 4, Far Downwind Train 3	11:44-17:06	322	7.2
11/3	AR 12 IS 61	Instack Time zero, (30 min)			1.1
11/3	AR 12 IS 62	Time zero + 293 min at Loc 0	12:45-17:45	293	7.4
11/3	AR 12 XT 01	Upwind (Loc 0) Teflon	12:45-17:45	293	5.309
11/3	AR 12 XT 02	Upwind (Loc 0) 2nd NaAc Filter	12:45-17:45	293	5.529
11/3	AR 12 XT 11	Loc 1, East of CT 9 Teflon	11:50-17:50	360	7.616
11/3	AR 12 XT 12	Loc 1, East of CT 9 2nd NaAc Filter	11:50-17:50	360	7.678
11/3	AR 12 XT 21	Loc 2, In Tank Farm Teflon	12:52-17:52	300	5.819
11/3	AR 12 XT 22	Loc 2, In Tank Farm 2nd NaAc Filter	12:52-17:52	300	5.323
11/3	AR 12 XT 31 N	Loc 3N, NW corner of Lot Teflon	13:05-18:05	300	6.664
11/3	AR 12 XT 32 N	Loc 3N, NW corner 2nd NaAc Filter	13:05-18:05	300	6.63
11/3	AR 12 XT 41	Loc 4, Far Downwind Teflon	11:44-17:06	322	3.108
11/3	AR 12 XT BGF	Blank Na Acetate Filter 2nd Batch			
11/3	AR 12 XT BT	Blank Filter Teflon Lot #2089			
11/4	AR 13 IS 01	Loc 0, Upwind Train 1	12:30-18:00	330	8.3
11/4	AR 13 IS 02	Loc 0, Upwind Train 2	12:30-18:00	330	8.3
11/4	AR 13 IS 11	Loc 1, West of CT 9 Train 1	12:00-18:00	360	9.5
11/4	AR 13 IS 12	Loc 1, West of CT 9 Train 2	12:00-18:00	360	9.5
11/4	AR 13 IS 13	Loc 1, West of CT 9 Train 3	12:00-18:00	360	9.5
11/4	AR 13 IS 21	Loc 2, In Tank Farm Train 1	12:36-17:22	286	6.5
11/4	AR 13 IS 22	Loc 2, In Tank Farm Train 2	12:36-17:22	286	6.5
11/4	AR 13 IS 23	Loc 2, In Tank Farm Train 3	12:36-17:22	286	6.5
11/4	AR 13 IS 31a	Loc 3N, Train 1, Imp 1	12:40-17:40	292	7.4

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
11/4	AR 13 IS 31b	Loc 3N, Train 1, Imp 2			
11/4	AR 13 IS 32a	Loc 3N, Train 2, Imp 1	12:40-17:40	292	7.4
11/4	AR 13 IS 32b	Loc 3N, Train 2, Imp 2			
11/4	AR 13 IS 33	Loc 3, NW corner of lot, Train 3	12:40-17:40	292	7.4
11/4	AR 13 IS 41	Loc 4, Far downwind Train 1	12:00-17:15	315	7.5
11/4	AR 13 IS 42	Loc 4, Far downwind Train 2	12:00-17:15	315	7.5
11/4	AR 13 IS 43	Loc 4, Far downwind Train 3	12:00-17:15	315	7.5
11/4	AR 13 IS 61	Instack Time zero,(30 min CT-9,FC 13)	10:39-11:09	30	1.1
11/4	AR 13 IS 62	Time Zero + 330 min. amb. at Loc. 0	12:30-18:00	330	8.3
11/4	AR 13 XT 01	Loc 0, Teflon Filter	12:30-18:00	330	5.999
11/4	AR 13 XT 02	Loc 0, NaAcetate Filter 2nd Batch	12:30-18:00	330	6.241
11/4	AR 13 XT 11	Loc 1, Teflon Filter	12:00-18:00	360	7.615
11/4	AR 13 XT 12	Loc 1, NaAcetate Filter 2nd Batch	12:00-18:00	360	7.679
11/4	AR 13 XT 21	Loc 2, Teflon Filter	12:36-17:22	286	6.066
11/4	AR 13 XT 22	Loc 2, NaAcetate Filter 2nd Batch	12:36-17:22	286	5.525
11/4	AR 13 XT 31	Loc 3, Teflon Filter	12:40-17:40	292	6.488
11/4	AR 13 XT 32	Loc 3, NaAcetate Filter 2nd Batch	12:40-17:40	292	6.441
11/4	AR 13 XT 41	Loc 4, Teflon Filter	12:00-17:15	315	2.991
11/5	AR 14 IS 01	Loc. 0 Previous Upwind Train 1	12:50-17:55	305	7.9
11/5	AR 14 IS 02	Loc. 0 Previous Upwind Train 1	12:50-17:55	305	7.9
11/5	AR 14 IS 03	Loc. 0 Previous Upwind Train 1	12:50-17:55	305	7.9
11/5	AR 14 IS 11	Loc. 1 W of CT 9 Train 1	12:10-17:05	295	6.3
11/5	AR 14 IS 12	Loc. 1 W of CT 9 Train 2	12:10-17:05	295	6.3
11/5	AR 14 IS 13	Loc. 1 W of CT 9 Train 3	12:10-17:05	295	6.3
11/5	AR 14 IS 21	Loc 2N Int. Truck Park. lot, Train 1	13:06-16:36	210	5.0
11/5	AR 14 IS 22	Loc 2N Int. Truck Park. lot, Train 2	13:06-16:36	210	5.0
11/5	AR 14 IS 23	Loc 2N Int. Truck Park. lot, Train 3	13:06-16:36	210	5.0
11/5	AR 14 IS 31a	Loc 3N, Train 1 1st Imp	12:25-17:22	298	6.7
11/5	AR 14 IS 31b	Loc 3N, Train 1 2nd Imp			
11/5	AR 14 IS 32a	Loc 3N, Train 2 1st Imp	12:25-17:22	298	6.7
11/5	AR 14 IS 32b	Loc 3N, Train 2 2nd Imp			
11/5	AR 14 IS 33	Loc 3N, NW corner of lot Train 3	12:25-17:22	298	6.7
11/5	AR 14 IS 41	Loc 4 Prev. Far Downwind Train	12:30-17:13	283	7.2
11/5	AR 14 IS 42	Loc 4 Prev. Far Downwind Train	12:30-17:13	283	7.2
11/5	AR 14 IS 61	30 min Instack Time Zero (CT 9,FC 13)	10:56-11:26	30	1.1
11/5	AR 14 IS 62	Time Zero + 283 min. amb. at Loc 4	12:30-17:13	283	7.2
11/5	AR 14 IS RB	NaAc Reagent blank Batch 4			
11/5	AR 14 XT 01	Loc 0 Previous upwind Teflon	12:50-17:55	305	5.549
11/5	AR 14 XT 02	Loc 0 NaAcetate Filter 2nd Batch	12:50-17:55	305	5.773
11/5	AR 14 XT 11	Loc 1, Teflon Filter	12:10-17:05	295	6.239
11/5	AR 14 XT 12	Loc 1, NaAcetate Filter 2nd Batch	12:10-17:05	295	6.290
11/5	AR 14 XT 21	Loc 2N, Teflon Filter	13:06-16:36	210	3.785
11/5	AR 14 XT 22	Loc 2N, NaAcetate Filter 2nd Batch	13:06-16:36	210	4.006
11/5	AR 14 XT 31N	Loc 3N, Teflon Filter	12:25-17:22	298	6.625

AMBIENT SAMPLES FOR THE FATE OF HEXAVALENT CHROMIUM Los Angeles, California

Date	Sample Number	Description	Time	Minutes	Cu.Meters
11/5	AR 14 XT 32N	Loc 3N, NaAcetate Filter 2nd Batch	12:25-17:22	298	6.588
11/5	AR 14 XT 41	Loc 4, Teflon Filter	12:30-17:13	283	2.649
11/5	AR 14 XT RB 2	2nd Batch NaAcetate Filter Blank			
11/5	AR 14 XT RB 1	Teflon Filter Blank Lot #2089			
11/6	AR 15 IS 01	Loc 0, Original Upwind Train 1	13:42-17:42	240	4.9
11/6	AR 15 IS 02	Loc 0, Original Upwind Train 2	13:42-17:42	240	4.9
11/6	AR 15 IS 11	Loc 1, W of CT 9 Train 1	12:10-18:02	354	7.3
11/6	AR 15 IS 12	Loc 1, W of CT 9 Train 2	12:10-18:02	354	7.3
11/6	AR 15 IS 13	Loc 1, W of CT 9 Train 3	12:10-18:02	354	7.3
11/6	AR 15 IS 21	Loc 2, Tank Farm Train 1	13:30-17:55	265	6.1
11/6	AR 15 IS 22	Loc 2, Tank Farm Train 2	13:30-17:55	265	6.1
11/6	AR 15 IS 23	Loc 2, Tank Farm Train 3	13:30-17:55	265	6.1
11/6	AR 15 IS 31	Mobile DW 13:22 to 15:40 NE corner	13:22-18:15	290	7.2
11/6	AR 15 IS 32	of lot (Loc. 3N), from 15:43 to 18:15	13:22-18:15	290	7.2
11/6	AR 15 IS 33	at roadway corner (Loc. 3)	13:22-18:15	290	7.2
11/6	AR 15 IS 41	Far downwind of Loc 2 Train 1	13:29-18:07	278	6.5
11/6	AR 15 IS 42	Far downwind of Loc 2 Train 1	13:29-18:07	278	6.5
11/6	AR 15 IS 61	30 min. Instack Time zero (CT9,FC13)	11:00-11:30	30	1.3
11/6	AR 15 IS 62	Time zero + 240 min. amb. at Loc 0	13:42-17:42	240	4.9
11/6	AR 15 XT 01	Loc 0, Teflon Filter	13:42-17:42	240	4.364
11/6	AR 15 XT 02	Loc 0, NaAcetate Filter 3rd Batch	13:42-17:42	240	4.614
11/6	AR 15 XT 11	Loc 1, Teflon Filter	12:10-18:02	354	7.474
11/6	AR 15 XT 12	Loc 1, NaAcetate Filter 3rd Batch	12:10-18:02	354	7.548
11/6	AR 15 XT 21	Loc 2, Teflon Filter	13:30-17:55	265	5.888
11/6	AR 15 XT 22	Loc 2, NaAcetate Filter 3rd Batch	13:30-17:55	265	5.937
11/6	AR 15 XT 31	Loc 3N and 3, Teflon Filter	13:22-18:15	290	5.485
11/6	AR 15 XT 32	Loc 3N and 3, NaAc Filter 3rd Batch	13:22-18:15	290	5.483
11/6	AR 15 XT 41	Loc 4, Teflon Filter	13:29-18:07	278	2.502
11/6	AR 15 XT RB 2	3rd Batch NaAcetate Filter			

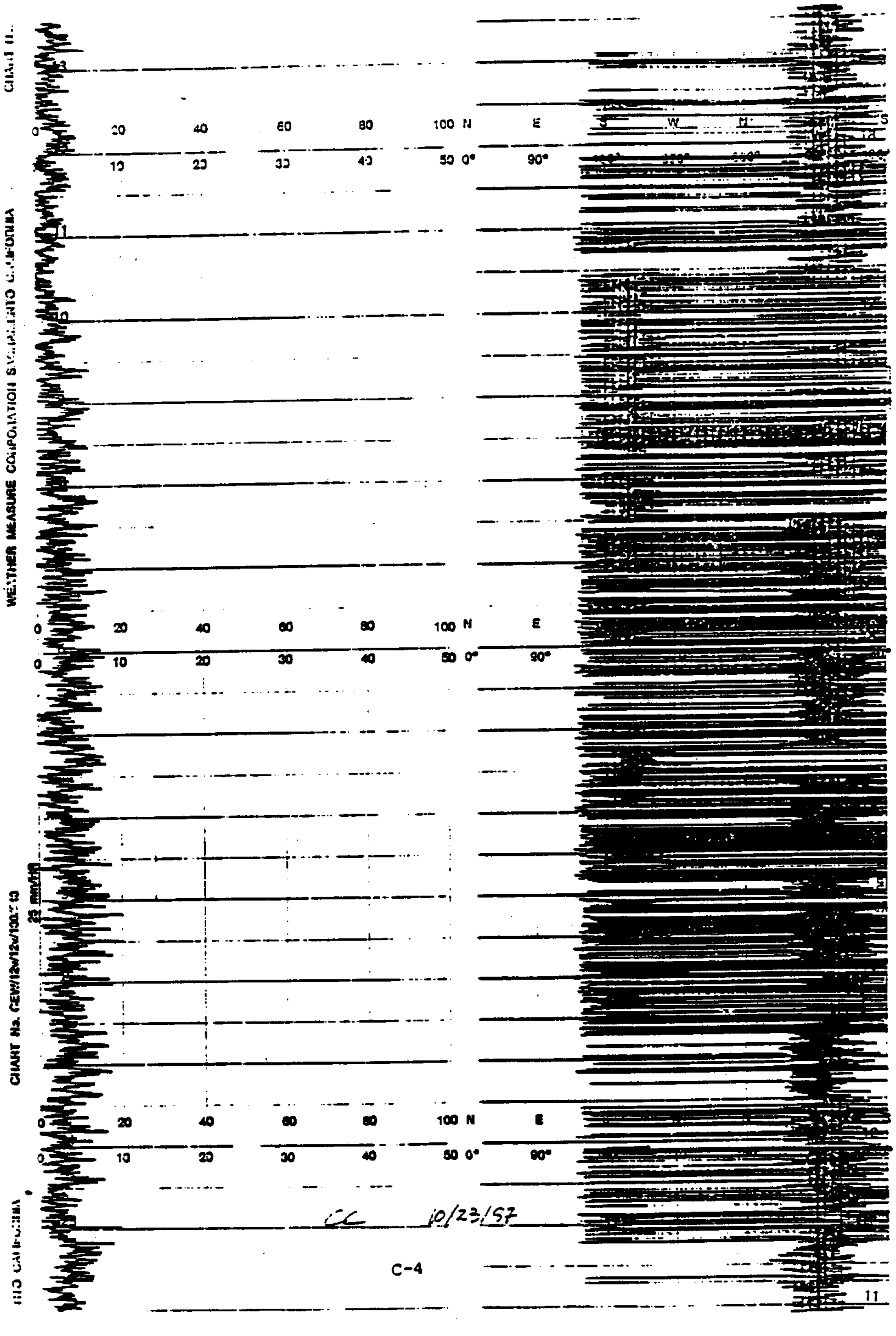
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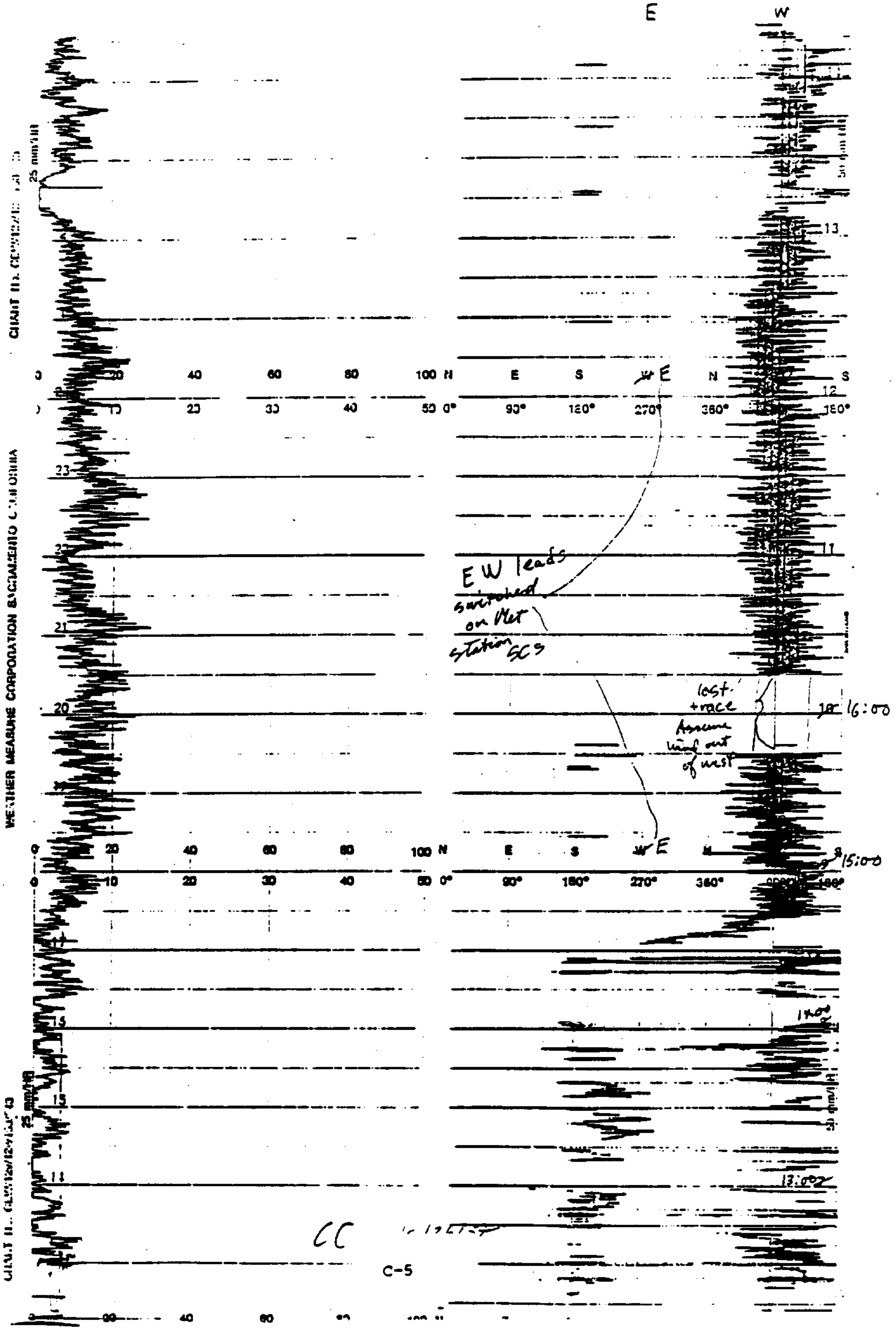
CHART No. CEW/12v/12v/130:10
25 mm/HR
0
20
40
60
80
100
N
E
S
W
N
0
10
20
30
40
50
0°
90°
180°
270°
360°
11
10

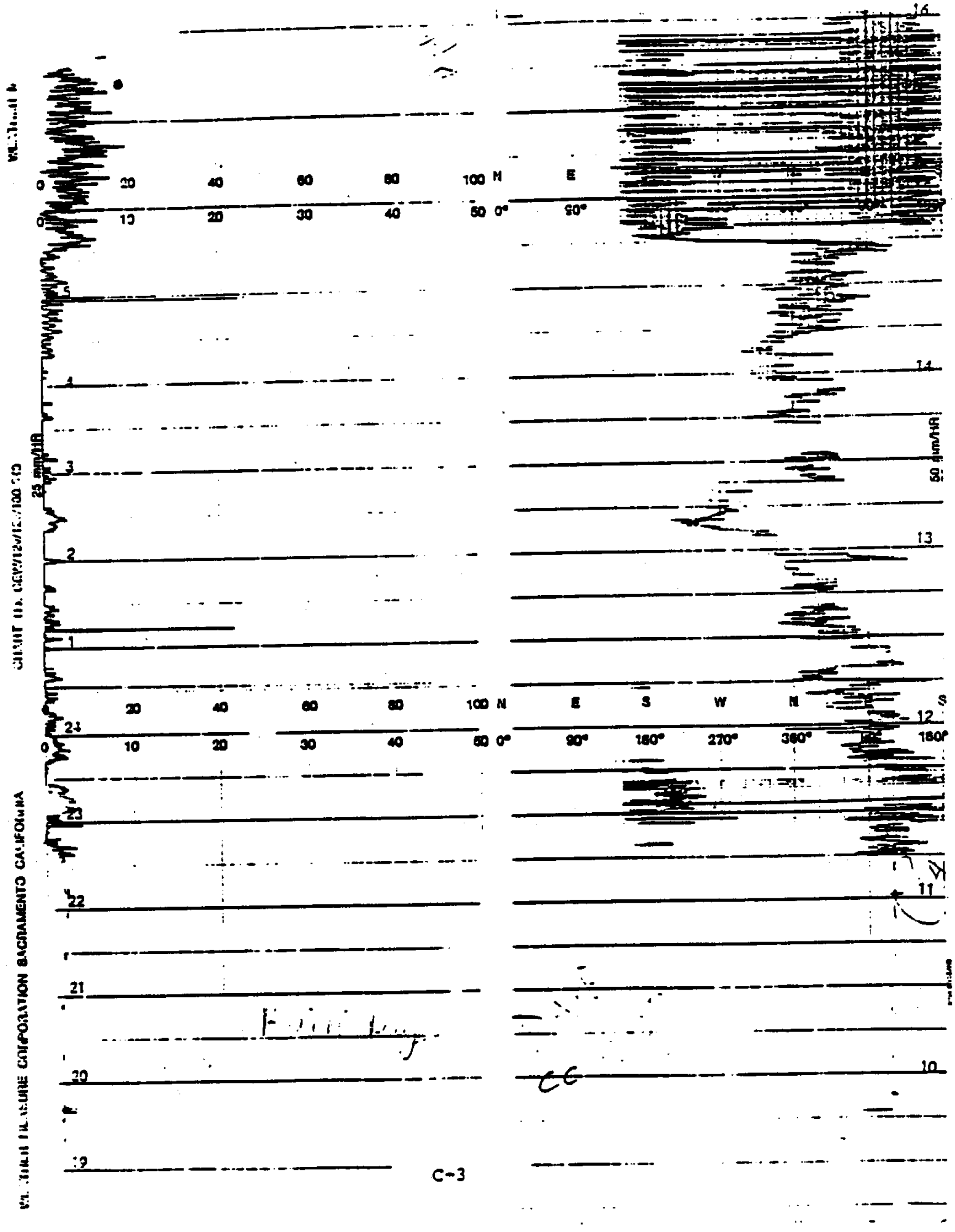
CC 10/23/97

C-4


E
W
CHART NO. CENTERLINE 1:1 25 mm/HR
WEATHER MEASURE CORPORATION SACRAMENTO CALIFORNIA
0 20 40 60 80 100
0 10 20 30 40 50
N E S W N E S
0° 90° 180° 270° 360° 90° 180°
13
12
11
10 16:00
9 15:00
14:00
13:00
EW leads switched on Met station SCS
lost trace
Assume wind out of west
W E
CC
C-5

APPENDIX C.

Meteorological Data Station Strip Charts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25 mm/HR
50 mm/HR
0
20
40
60
80
100
0
10
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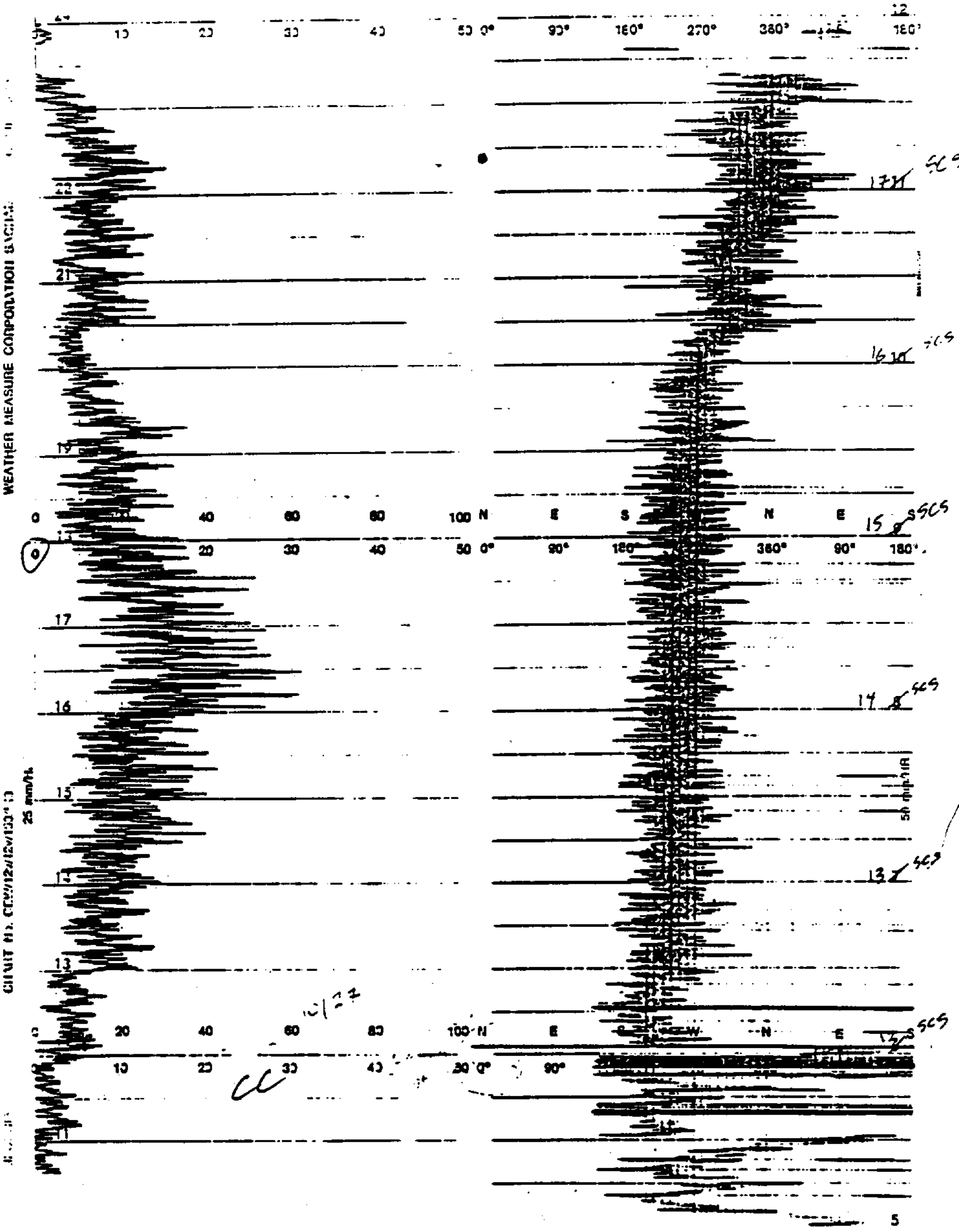
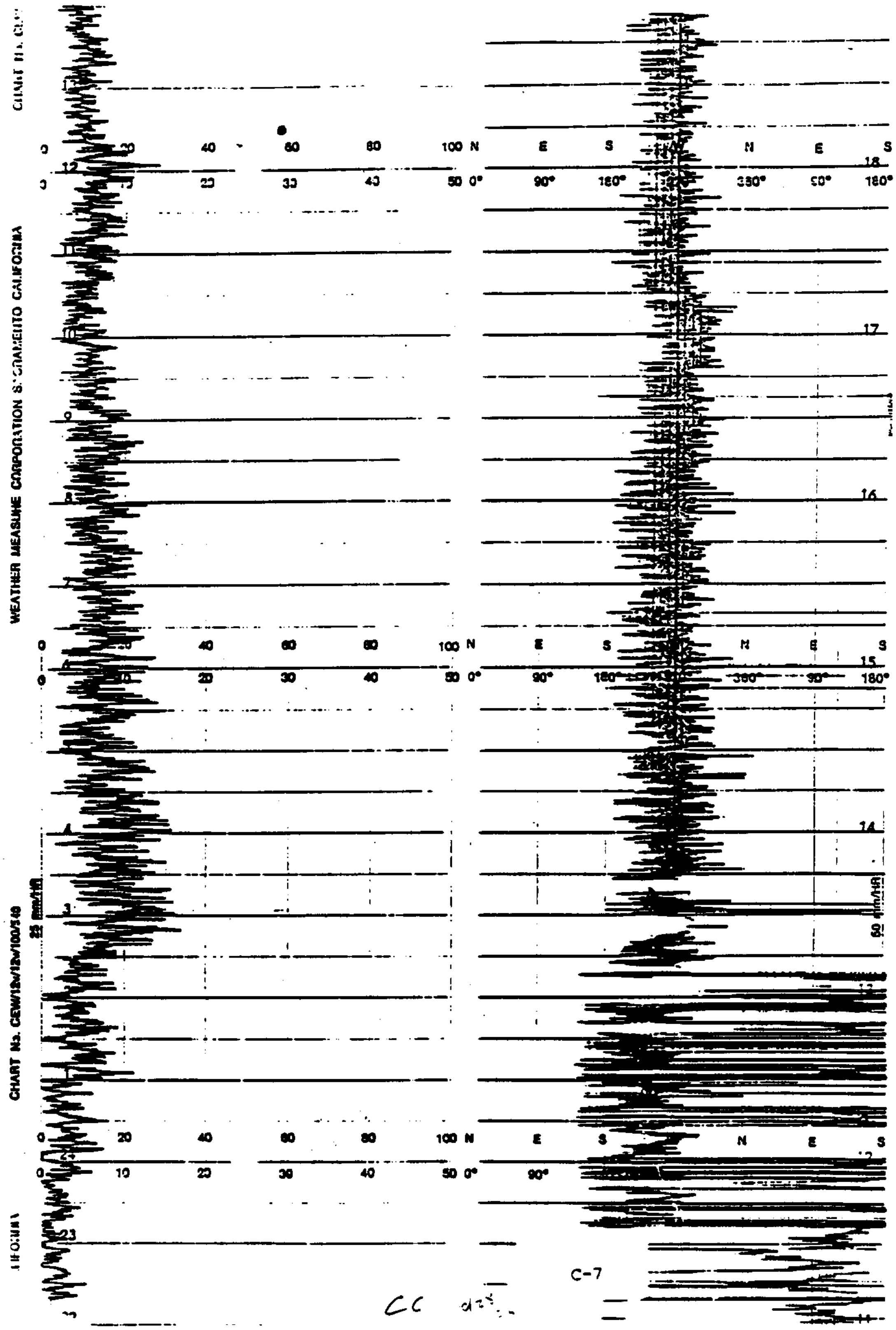
50
N
E
S
W
N
S
0°
90°
180°
270°
360°
180°
16
15
14
13
12
11
10
5
4
3
2
1
24
23
22
21
20
19
CC

C-3



wrong time scale selected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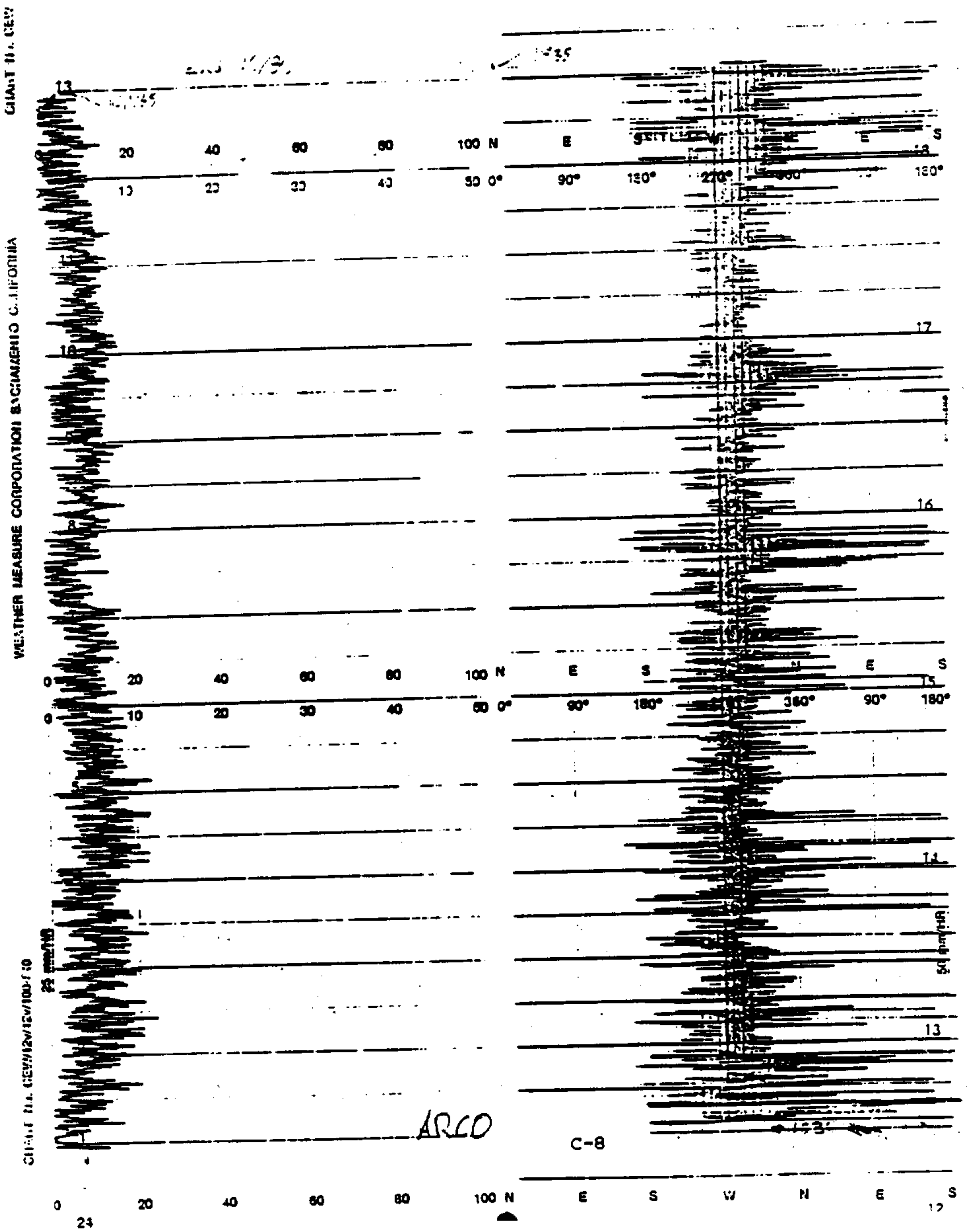
20
40
60
80
100
10
30
50
N
E
S
0°
90°
180°
360°
C-7

CC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0 10 20 30 40 50 0° 90° 180° 270° 360° 90° 180°
25 mm/HR
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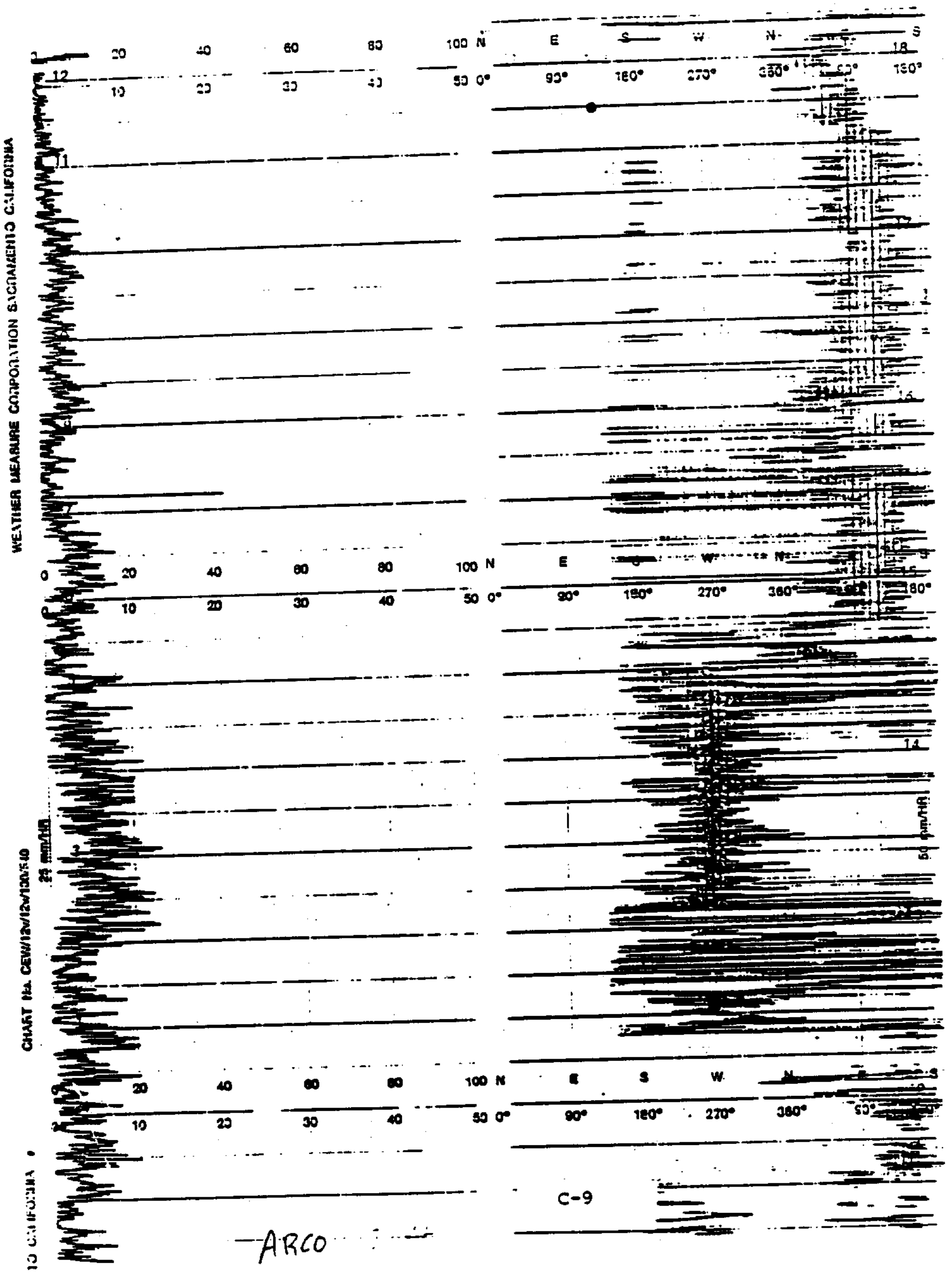
13
24
ARCO
C-8


WEATHER MEASURE CORPORATION SACRAMENTO CALIFORNIA
CHART No. CEW/12v/12v/130/540
25 mm/HR
50 mm/HR
0 20 40 60 80 100
0 10 20 30 40 50
N E S W N E S
0° 90° 180° 270° 360° 90° 180°
12
11
18
17
16
15
14

C-9

ARCO