Background Report Reference

AP-42 Section Number: 12.8

Background Chapter: 4

Reference Number: 4

Title: North American Smelting Company - January1981

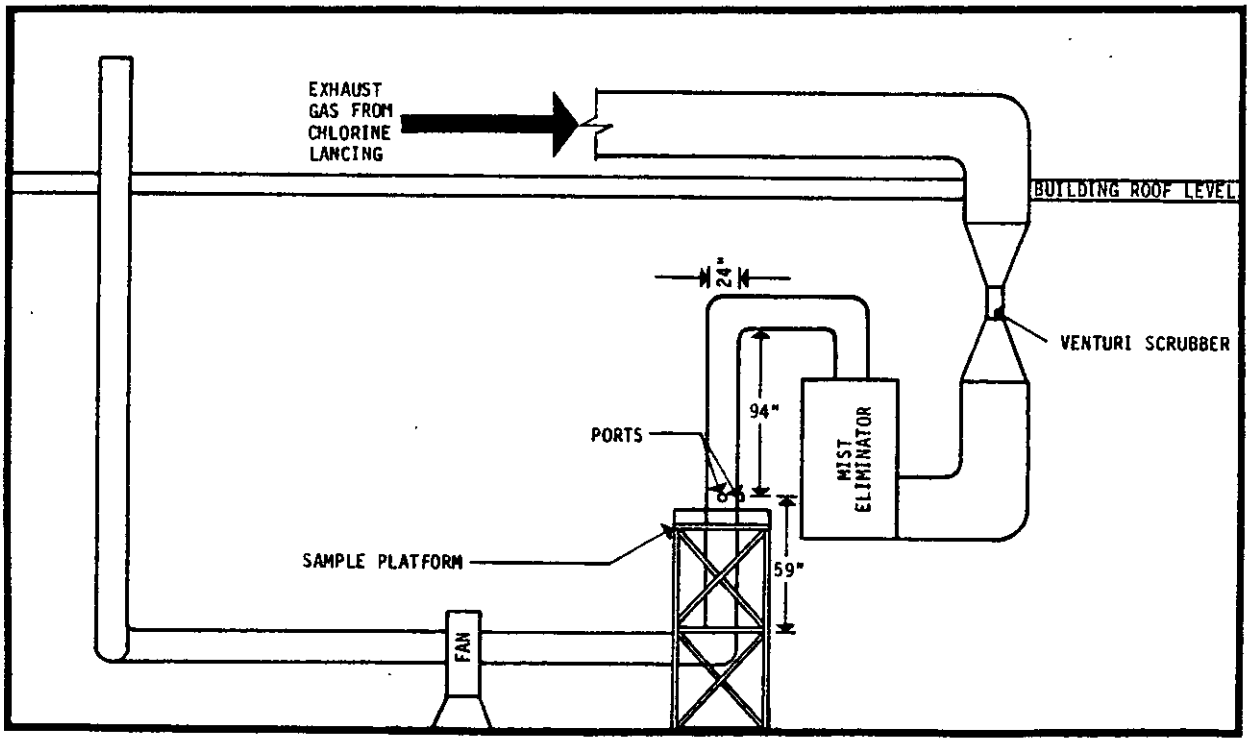
EPA Contract No. 68-02-2815

US EPA

January 1981

7.8

EVALUATION OF STACK SAMPLING TECHNIQUES FOR SECONDARY ALUMINUM INDUSTRY



Prepared for:

U.S. Environmental Protection Agency
Emissions Measurement Branch
Research Triangle Park, North Carolina

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EVALUATION OF STACK SAMPLING TECHNIQUES FOR SECONDARY ALUMINUM INDUSTRY

Contract No. 68-02-2815
Work Assignments 44 and 46

Prepared for

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January 1981
9103.00/41

Submitted by

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CHAPTER 1

INTRODUCTION

The U.S. Environmental Protection Agency may propose new source performance standards for the secondary aluminum industry. Compliance with appropriate emission limiting standards can only be evaluated using reference air sampling techniques. In association with Contract 68-02-2815, Work Assignments 44 and 46 directed Engineering-Science (ES) to develop reliable stack sampling trains necessary to collect accurate samples from certain secondary aluminum process operations.

EPA work assignment requesters identified chlorine compounds and condensable hydrocarbons as the contaminants of particular interest needing investigation. ES and one of its related companies, Harmon Engineering and Testing, reviewed established sample collection and analytical techniques for these contaminants. Specific sample trains and methods of analysis were selected for field evaluation.

During the period December 15 to December 19, ES secured stack emission samples from processes at North American Smelting Company in Wilmington, Delaware. The reverberatory furnace chlorination scrubber was sampled for total particulates, particulate chlorides, chlorine gas, and gas phase hydrochloric acid, with all samples collected at the scrubber outlet. The outlet of the lime coated baghouse controlling emissions from the furnace scrap charging wells was sampled for particulates and condensable and non-condensable hydrocarbons. Some of the sample analyses were completed in the field, whereas the remainder were completed in the McLean and Arcadia laboratories.

This report includes a summary of the collected data and an evaluation of the two sample trains. Operating problems with the sample trains and the associated analytical techniques are discussed. Final recommendations for train assembly and sample analysis are provided.

CHAPTER 2

DESCRIPTION OF TEST LOCATIONS

The methods development test program was centered around operation of the reverberatory furnaces. A hydrocarbons train collected samples from the outlet of equipment used to abate particulates and hydrocarbons in off gases from the furnace charging wells. Particulate and gaseous chlorine compounds contained in furnace chlorination effluent gases were characterized by collecting samples at the outlet of the process scrubber. Each site is discussed in more detail in the remainder of this chapter.

CHLORINE SCRUBBER

At the end of each batch aluminum alloy formulation, excess magnesium is removed by sparging chlorine gas through the melt. The effluent gas proceeds to emissions control equipment for abatement of aluminum chloride particulates, its partial hydrolysis product, hydrochloric acid, and unreacted chlorine.

North American Smelting Company (NASCO) operates a two-stage scrubber for control of atmospheric emissions from chlorine lancing. A high pressure drop venturi scrubber (35" w.c.) collects some particulates and gaseous compounds, and the second stage packed bed scrubber removes more of the relatively difficult to absorb chlorine gas. A baffle-type mist eliminator is located at the top of the packed bed. Sodium hydroxide scrubbing liquor is used on a once-through basis for each stage. A schematic of the scrubbing operation is provided in Figure 2-1.

Test ports located between the scrubber and the fan were used to collect all samples. This location was characterized by a high negative static pressure and a very high loading of scrubbing liquor droplets which penetrated the mist eliminator. In fact, the droplet concentration was so high that sample train cyclones were used to prevent blinding the filter. The high negative pressure required turning the sample pump on prior to insertion of the probe in the stack to prevent pulling the sample filter from its holder.

Simultaneous collection of two samples was accomplished by placing a sample train in each of the two ports. The nozzles were located as close together as possible at the approximate center of the stack.

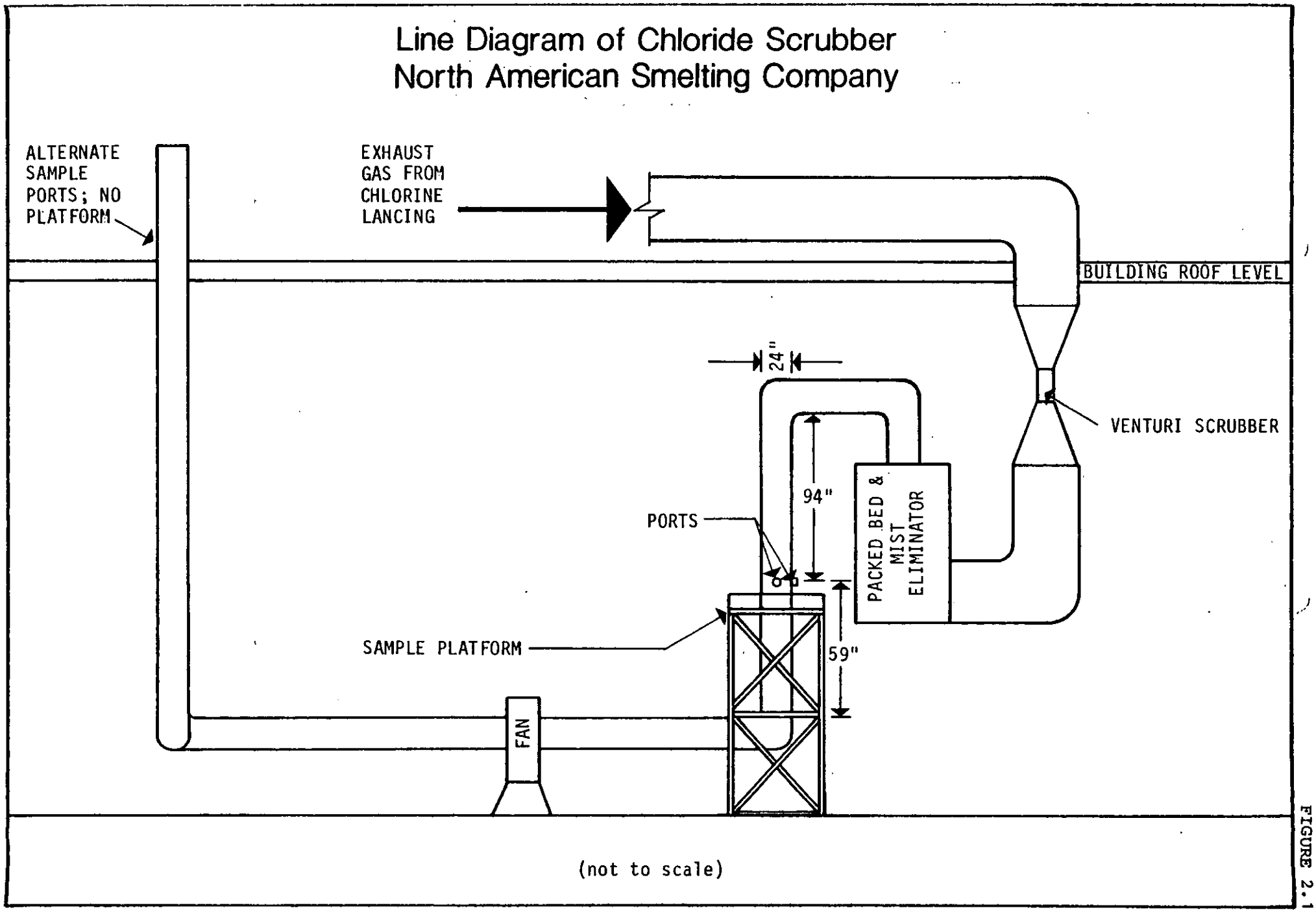


FIGURE 2.1

ENGINEERING-SCIENCE

Chlorination periods varied, depending upon furnace size and magnesium concentration. Emissions tended to increase towards the end of chlorination, and where possible, stack gas samples were collected during the expected maximum emission period.

CHARGING WELL COATED BAGHOUSE

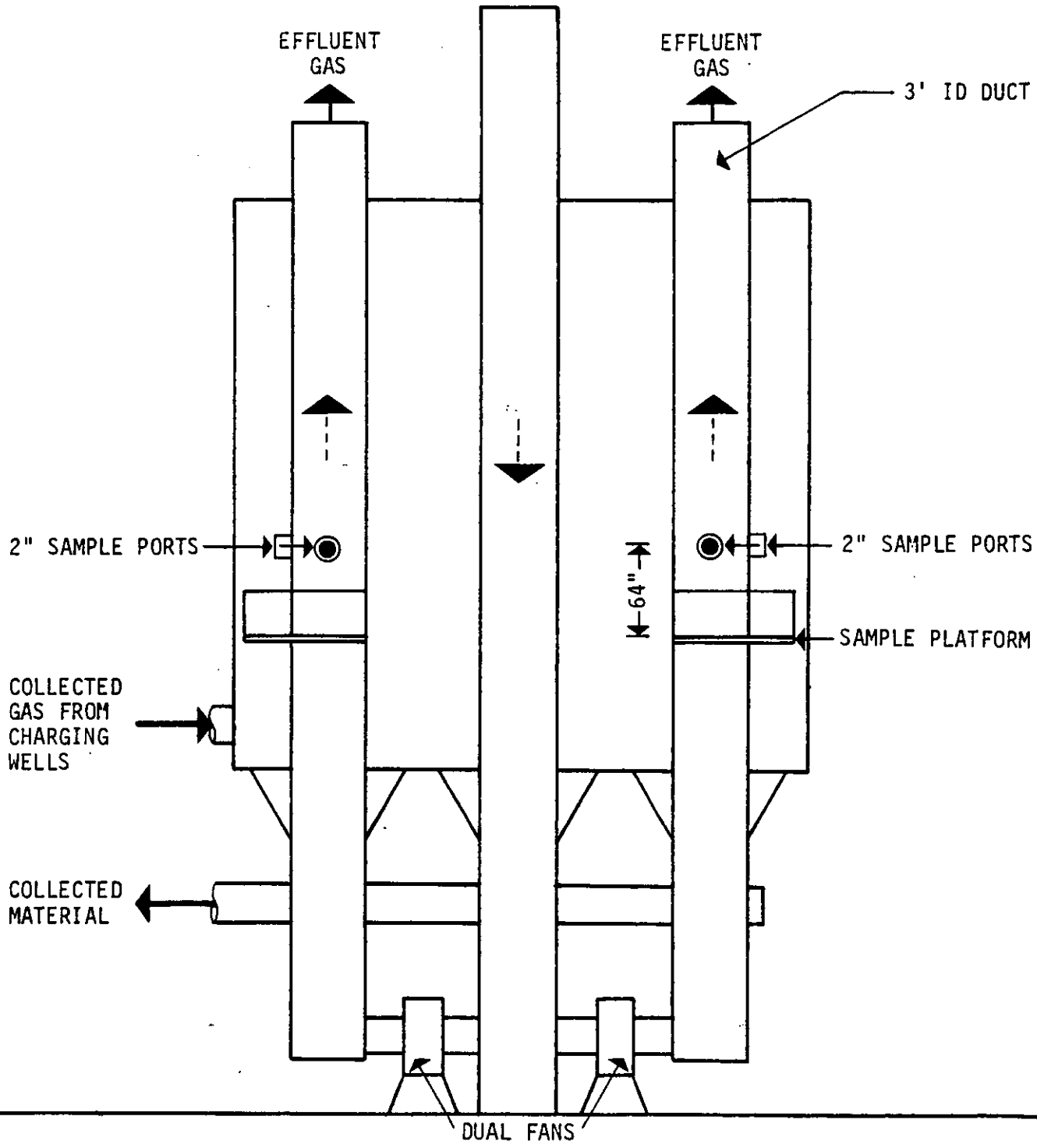
Various types of aluminum alloy scrap, pure alloy components such as silicon, and flux compounds are fed to an open well at one end of each reverberatory furnace. The exact mixture charged for each furnace run depends upon the specific desired alloy formulation and characteristics of available scrap. Exhaust hoods capture volatilized organics and acid compounds, and the resulting mixture of contaminants and room air proceeds to a pre-coat type fabric filter collector.

While operating, the baghouse is not cleaned by regular mechanical shaking or air pulsations. Instead, the bags are initially coated with lime, and when the pressure drop reaches a pre-determined set point value, the bags are cleaned and re-coated. Thus, although charging is essentially continuous from early Monday morning through Friday morning, the bags may be cleaned and re-coated a maximum of twice and possibly not at all during this time span.

A schematic of the baghouse is shown in Figure 2-2. Exhaust gas is split by the two fans and discharged through two separate stacks. All samples were collected from the north stack for the first phase test program.

Pressure drop across the baghouse was approximately 10" w.c. during the sample collection period. This was somewhat above the desired set point and indicated "dirty" bags. NASCO was willing to permit sample collection in this operating mode whereas ordinarily the bags would have been cleaned and re-coated. A sample of the lime recovered after bag cleaning confirmed that the lime collects organic material, as it was colored black and had a definite "oily" odor.

Schematic (end view) of Coated Baghouse North American Smelting Company



CHAPTER 3

DESCRIPTION OF SAMPLE COLLECTION AND ANALYSIS PROCEDURES

The specific air contaminants of interest in this study for the secondary aluminum industry are gaseous and particulate chlorine compounds and condensable hydrocarbons. After a review of expected source emission characteristics and the available characterization methods, specific sample trains, and analytical methods were selected. Details for each of the two types of sample trains are discussed separately below. Copies of all reference procedures are contained in the appendices.

CHLORINE COMPOUNDS

Sample Collection

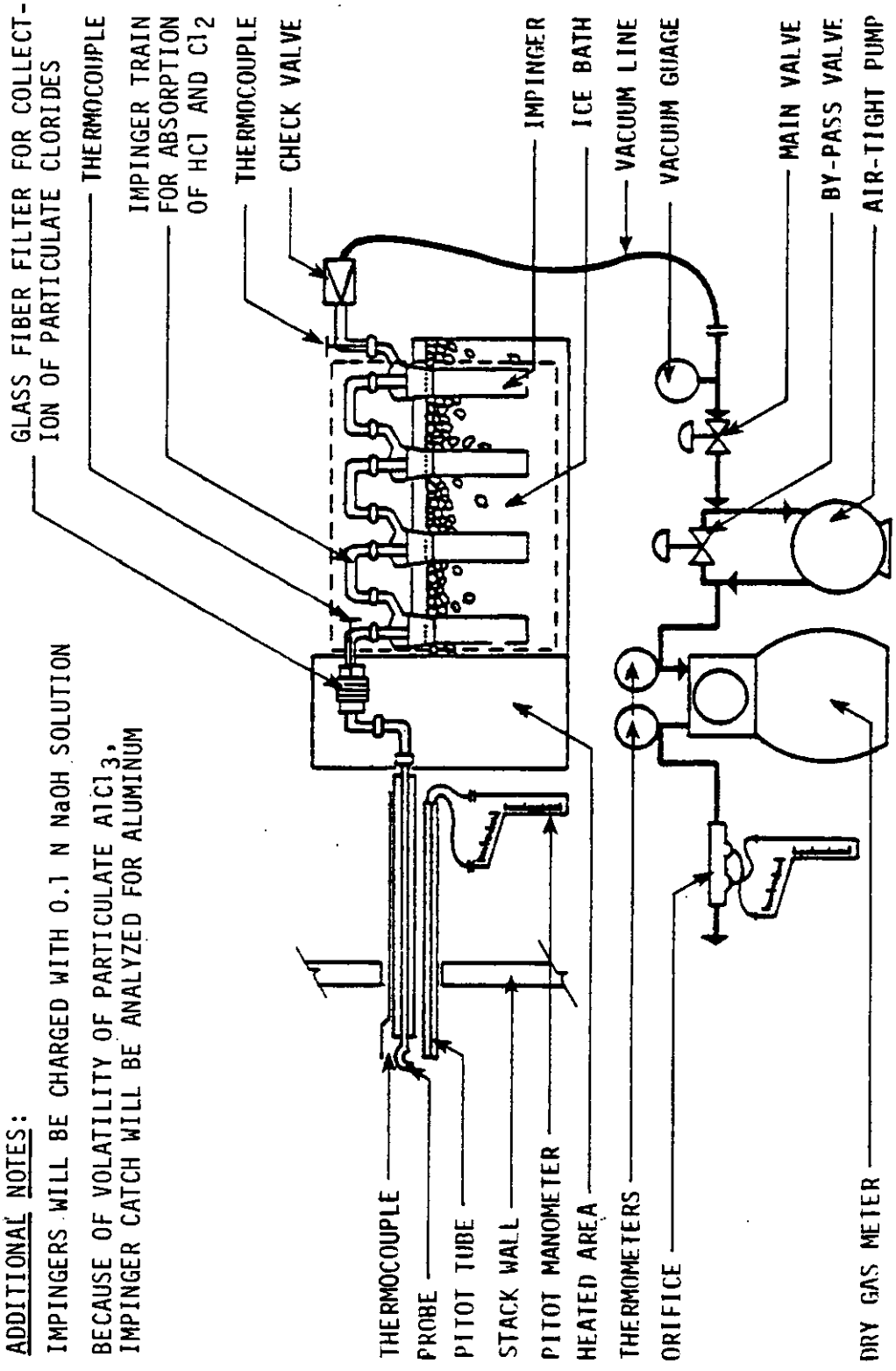
Exhaust gases from the chlorine lancing operation were expected to contain particulte chlorides, chlorine gas, and possibly gas phase hydrochloric acid. Separate characterization for each type of compound was desired.

A standard Method 5 sample train was assembled for this purpose, the only modification involving use of 0.1 normal sodium hydroxide solution instead of water in the impinger. Because of the uncertain absorption and reaction characteristics of low concentration of chlorine gas, three impingers in series were charged with the caustic solution. Tissue quartz filters were used because of their superior chemical compatibility with acidic gases as compared to standard glass fiber media. A schematic of the assembled train is shown in Figure 3-1.

During each chlorination period, simultaneous single point isokinetic samples were collected. Sample train operation, including filter temperature control, was identical to that specified in EPA Method 5. Inclusion of cyclones upstream of the filters was necessary to remove entrained scrubbing liquid droplets.

Normal sample train operation according to EPA Method 5 results in a sample collection rate of approximately 0.75 cfm, meter conditions. The effluent particles from the chlorine scrubber were present at a moderate grain loading, but because of their apparent very fine size, the collected filter cake rapidly produced a high pressure drop. Smaller sample nozzles were used to effect a lower sample collection rate to solve this problem.

Chlorine Compound Sampling Train



ADDITIONAL NOTES:

IMPINGERS WILL BE CHARGED WITH 0.1 N NaOH SOLUTION

BECAUSE OF VOLATILITY OF PARTICULATE $AlCl_3$, IMPINGER CATCH WILL BE ANALYZED FOR ALUMINUM

At the conclusion of each test run, the following separate train fractions were recovered: probe wash, filter, cyclone, first impinger, second impinger, and third impinger. Chlorine analyses were performed immediately after sample collection, whereas the other components were characterized after samples were returned to the laboratory.

Analytical Methods

Specific characterization methods for particulates and gaseous compounds are discussed in separate sections in the remainder of this section. With respect to chlorine compounds, free chlorine was determined first, followed by analysis of total chlorides.

Particulate Chlorides

A standard gravimetric analysis was completed for all filters. After recording the final filter weight, particulte chlorides were determined by extraction of the filter catch with distilled water followed by the mercuric titration procedure. (This procedure is discussed in detail in the subsection for chlorides.)

Additional characterization for aluminum chloride particulate was considered appropriate. It sublimes completely at 29.92" Hg at 352°F, and was, therefore, expected to have a substantial vapor pressure at the Method 5 filtration temperature of 250°F.

In the specific case of NASCO, extracting particulates from a stack environment of approximately 70°F and 27.4" Hg absolute pressure and heating then to 250°F and reducing the absolute pressure even further was expected to result in a phase change of a portion of the aluminum chloride. Thus, each impinger was analyzed for the pressure of aluminum.

Chlorine Gas

In sodium hydroxide solution, chlorine gas reacts as follows:

$$Cl_2 \text{ (gas)} \rightleftharpoons Cl_2 \text{ (aqueous)}$$

$$Cl_2 \text{ (aqueous)} + H_2O \rightleftharpoons HCl + HOCl$$

$$HCl \longrightarrow H^+ + Cl^-$$

$$HOCl \longrightarrow H^+ + OCl^-$$

Thus, analysis of the caustic impinger catch for chlorine actually amounts to analysis for hypochlorous acid or hypochlorite ion, depending upon actual solution pH.

A colorimetric procedure was selected for analysis of free available chlorine, defined as the sum of aqueous chlorine, hypochlorous acid, and hypochlorite ion. The actual method used was 409-D, stabilized neutral orthotolidene, as described in "Standard Methods for Examination of Water and Wastewater." The chlorine-induced color (turquoise) was quantified with a Bausch and Lomb Spectronic 20 single beam spectrophotometer at 625 nanometers.

Prior to field data collection, several preliminary laboratory procedures were necessary. Chlorine demand-free water was prepared for use in all dilutions. Sodium thiosulfate reagent was standardized after the recommended two-week waiting period.

Fundamental to this procedure is the standardization of the stock sodium thiosulfate reagent for its subsequent use in preparing a stock solution of free available chlorine. Standard Methods, Section 409-A describes the titration employed to determine the above mentioned normality. The alternative Dichromate method was used over the primary Biniodate method because of the stability of the stock potassium dichromate reagent used in the former. A sharp, clear end point was reached with diluted sodium thiosulfate (0.025N). A diluted commercial solution of sodium hypochlorite was used to prepare the stock chlorine solution (approximately 50 mg/l). Sodium thiosulfate was then used to determine the true chlorine concentration of this stock solution. A range of concentrations was then made per appropriate dilutions.

The various dilutions, prepared asynchronously, provided the means to develop a standard curve. Each dilution was treated and colorimetrically analyzed as described in the SNORT method. The method requires dilutions to be in the range of 0.01 mg/l and 6.0 mg/l chlorine as defined by detectability and orthotolidine availability, respectively. The same limit applies to sample analysis.

Upon the addition of the orthotolidine and the buffer stabilizer, the diluted standard samples developed a turquoise color and were read on the spectrophotometer at 625 nm. Optical densities (as absorbance or transmittance) were recorded and plotted on a graph. The graph described a line where an increase in concentration results in an increased absorbance. Standard curves were prepared daily in concurrence with sample collection (or audit sample evaluation). Linear regression was used to calculate concentration as a function of absorbance.

Impinger samples were analyzed with the SNORT method immediately following their collection in the field. Dilutions were made to a concentration that indicated 20 to 80% of scale on the spectrophotometer. Where this was not achieved, the extension of the standard curve was necessary to locate the corresponding concentration point. As recommended, the photometer was read within 2 minutes of reagent and sample mixing because of rapid chlorine degradation to chloride. Interferences were compensated for by making a blank with sodium arsenite (reduces available chlorine) and using it as a zero absorbance reference. Due to some observed cloudiness, it was evident that this was necessary. Generally, two dilution aliquots from each sample were analyzed and the average absorbance was used to identify the chlorine concentration.

Total Chlorides

Two titration procedures were selected for analysis of total chloride ion. One method followed the EPA procedure for analysis of hydrochloric acid emissions (mercuric nitrate titration) and the other one was selected from "Standard Methods," Method 408, argentometric analysis (silver nitrate titration). Both methods were evaluated because of reported difficulties with pH control for the mercury titration and with end point detection for the silver titration.

As discussed in the reference mercury titration procedure, some sample aliquots were passed through a cation exchanger to investigate the presence of metal ion interferences.

Total chlorides analysis included contribution by chlorine gas, hydrochloric acid, and particulate chlorides. Chlorine poses a problem for chloride analysis because upon initial absorption it forms an equi-molar mixture of chloride and hypochlorite ions. Hypochlorite gradually decomposes to chloride, so in order to eliminate questions concerning the percentage conversion, all field samples were treated to convert hypochlorite to chloride. This was accomplished through the use of a 3% hydrogen solution added in excess of the molar concentration required to destroy the chlorine, as measured shortly after sample collection and recovery.

The hydrogen peroxide reacts with hypochlorite in a basic solution according to the equation:

$$O\ Cl^- + H_2O_2 \xrightarrow{OH^-} O_2 + Cl^- + H_2O$$

The use of excess hydrogen peroxide has the added advantage of destroying any reducing ions which may be present in the sample and which interfere in the mercuric nitrate titration procedure.

Thus, the total chloride concentration represents the following fractions:

Cl^- total = HCl + 2 Cl_2 + 3 Al Cl_3, expressed as mass equivalents

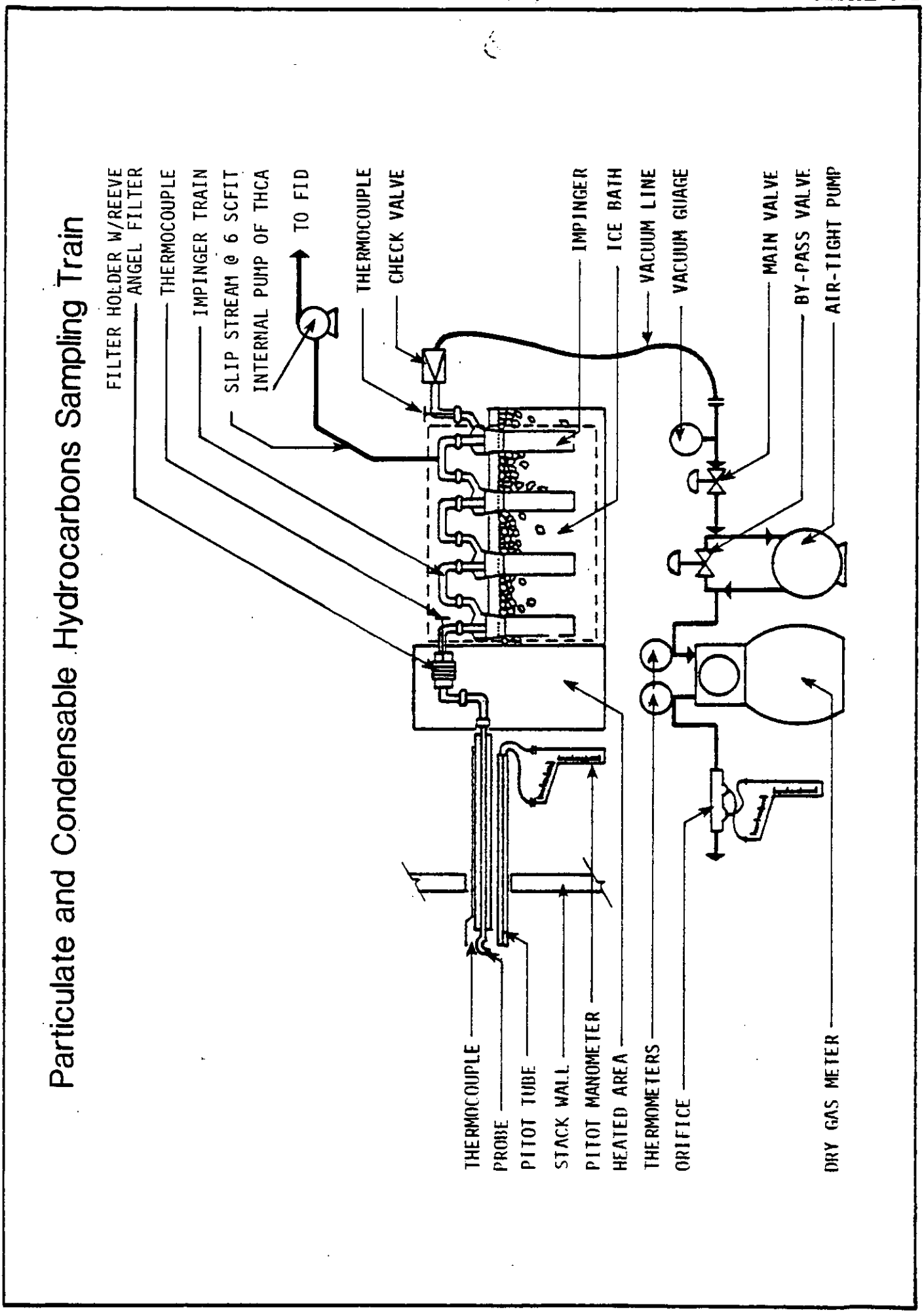
HYDROCARBON COMPOUNDS

Sample Collection

Secondary aluminum smelting operations involve recycling of numerous types of aluminum scrap. Any cutting or lubricating oils, plastic coatings, or plastic components are evolved from furnace charging wells, chip dryers, and sweat furnaces. As a first cut type of analysis, separation of these hydrocarbons into particulate (at 250°F) and condensable (liquid phase between 250°F and 70°F) fractions are desired. Condensable hydrocarbons are of interest because of their formation of droplets when stack gas cools while mixing with ambient air. The noncondensable sample train fraction is unimportant in this case.

A standard Method 5 sample train was selected for hydrocarbons characterization. As indicated in Figure 3-2, a portion of the gas stream was removed from the U tube connecting the empty third impinger and the silica gel impinger, and it was pumped to a flame ionization detector (FID) based total hydrocarbon analyzer (THCA). This fraction of hydrocarbons, defined as "noncondensable," includes any water insoluble organics with a vapor pressure greater than a few ppm by volume at the actual impinger temperature.

The lime coated baghouse at NASCO which abates furnace charging well emissions was selected as the source for evaluation of the hydrocarbons


Particulate and Condensable Hydrocarbons Sampling Train
FILTER HOLDER W/REEVE ANGEL FILTER
THERMOCOUPLE
IMPINGER TRAIN
SLIP STREAM @ 6 SCFIT
INTERNAL PUMP OF THCA
TO FID
THERMOCOUPLE
CHECK VALVE
IMPINGER
ICE BATH
VACUUM LINE
VACUUM GUAGE
MAIN VALVE
BY-PASS VALVE
AIR-TIGHT PUMP
THERMOCOUPLE
PROBE
PITOT TUBE
STACK WALL
PITOT MANOMETER
HEATED AREA
THERMOMETERS
ORIFICE
DRY GAS METER

train. At least one and sometimes two furnaces were being charged during sample collection periods.

Removal of the slipstream to the FID caused a difference between gas volume entering the sample nozzle and volume registered by the dry gas meter, so a correction factor to the desired metering system orifice pressure drop was required to maintain isokinetic sampling at the nozzle. The particular hydrocarbon analyzer used had an internal pump which removed approximately 6 scfh from the Method 5 gas sample. The ΔH correction factor was estimated by noting the actual meter box ΔH when the sampling rate was approximately 0.75 cfm and when it was approximatley 0.65 cfm. The difference was 0.5" w.c., such that nomograph values were decreased by this amount when setting individual traverse point sampling rates.

The magnitude of the ΔH correction factor was high enough for some sample points that it represented 1/2 of the desired ΔH. For example, a certain sample point velocity head was such that the orifice pressure drip was 1" w.c., or 0.5" w.c. with the correction factor deducted. A sample nozzle larger than normal was used to lower the % deduction due to the FID slipstream.

Prior to charging the train, all glassware was cleaned with chromic acid solution, as specified in Method 5A. Sample train operation for sample collection was identical to that described in the reference procedure.

At the conclusion of each run, the following separate fractions were recovered: probe wash, filter, back half rinse including filter holder, and combined impingers. The probe wash and initial back half rinse were completed with acetone, and a second back half rinse was performed with trichloroethylene. U tube connections were wiped with trichloroethylene prior to back half recovery to control collection of silicone grease.

Analytical Methods

Total Particulates

A standard gravimetric analysis was completed for the sample train quartz filters and acetone probe wash.

Condensable Organics

Dual back half rinses were performed because of the unknown recovery characteristics of acetone. A standard gravimetric analysis was completed for the acetone and 1,1,1 trichloroethane back half rinses.

The chloroform-ether extraction procedure described in Method 5A was followed for the combined impinger catch. For each run, the initial solution pH was approximately 2, such that neutralization with caustic was necessary prior to the initial extraction. Because some organics are more completely extracted at low pH that at neutral pH, a second stage extraction was completed after readjusting to a pH of 1 with hydrochloric acid. A standard gravimetric analysis was completed for all chloroform/ether extracts.

Noncondensable Organics

Hydrocarbons that were not successfully collected in the impinger train were determined by diverting part of the "back half" Method 5 gas stream to a flame ionization detector (FID) in a total hydrocarbon analyzer (THCA).

A Scott Model 215 THCA was utilized in the field. It was located and operated on the ground beneath the sampling ports. Data were recorded on a Linear Model 555 flat bed recorder.

The THCA was zeroed with zero air (THC <0.1 ppm) and calibrated with methane span gases. Span gas calibrations should be made in a concentration range that will approximate test emissions. Therefore, methane span gases of 31.6 ppm and 81.7 ppm were used in this test anticipating low hydrocarbon loadings.

Unfortunately, span gas calibration gases, even at full range adjustments, failed to respond to their true value. Methane span gases of 31.6 ppm and 81.7 ppm corresponded to 27.1 and 70.3% chart responses on a 0-100 range. The most probable cause of this anomaly was operating below the recommended ambient temperature limit of the instrument. Scott THCA Model 215 operating manual specifications indicate an operation range between 32°F and 130°F. Field test conditions remained around 25°F. Later, at the ES McLean office, under room conditions, THCA span gas calibrations yielded accurate linear responses.

The low span gas values in the field did not discount THC concentration responses, however, even though the actual concentration was not indicated, the span gases retained linearity. Thus, a simple correction was made for true hydrocarbon emissions by multiplying observed responses by the ratio of the true span value and the observed span response (e.g., $\frac{31.6 \text{ ppm } CH_4}{27.1 \text{ ppm } CH_4} = 1.17$).

Prior to sample collection, a leak check was conducted through the teflon line and analyzer by capping off the sample inlet adjacent to the U-tube assembly. With the pump on, the bypass flow meter dropped down to zero, indicating a leak tight sample line and instrument.

To insure simultaneous sampling with the Method 5 run, it was necessary to turn off the pump while connecting the sample line to the U-tube assembly. Consequently, earlier leak test procedures excluded the sample line/U-tube assembly connection. Problems with simultaneous leak checks (i.e. meter box pump override of the THCA pump) justified this particular procedure.

The THCA and Method 5 train started sampling simultaneously. The flow rate of the gas stream diverted to the THCA was controlled by an internal sample pressure regulator (i.e. only accessible by removing the top panel) and monitored by a bypass flow meter. The bypass flow typically registered 5 to 7 scfh, rotameter scale. From this gas stream, approximately 6 ml/min was directed to the FID.

Sample pressures of 1.0 psi and bypass flow rates of 6 scfh approximated starting conditions. However, particulate loading on the filter in the Method 5 sample box produced a proportional vacuum. Hence, without a compensating

adjustment to the THCA sample pressure, the actual sample diversion slowly dropped to about 4 scfh by the termination of the tests.

At the conclusion of each test run, the piece of unheated teflon connecting the THCA to the Method 5 sample box was purged with ambient air to insure constant background sampling conditions.

CHAPTER 4

TABULAR SUMMARY OF RESULTS

During the period of December 15 through December 19, a total of six chlorine compound and two hydrocarbon compound samples were collected using minor modifications of the EPA Method 5 manual stack sampling train. The two complete hydrocarbon samples were supplemented with a brief experiment involving impinger collection efficiency. Results of all field samples are summarized in tabular form in this chapter.

On December 16, EPA representatives delivered quality assurance samples for chlorine and chlorides. Initial chlorine analyses were completed on site, and chloride samples were titrated at a later date. Results of these analyses are also included in this chapter.

Separate tables are presented where possible, but because of the relationship between chlorine and chloride analyses, some combined tables are noted.

CHLORINE AND CHLORIDES (SCRUBBER TESTS)

Results for EPA audit samples are listed in Tables 4-1 and 4-2. The EPA reference values for chlorine are not included pending re-analysis of some of the samples.

For the total of six chlorine compound runs, three repetitions each with the two simultaneously operating trains, overall results are provided in Table 4-3. This table includes total filter weight and extractable chlorides from the filter as well as separate chlorine and chloride analyses for the probe wash, cyclone, and first, second, and third impingers. A comparison of impinger catches only is provided in Table 4-4.

Evaluations of individual impinger chlorine collection efficiency and of particulate vs. gaseous chloride fractionation are provided in Tables 4-5 and 4-6.

Calculated values for particulate and gaseous loadings in terms of concentration and mass emission rate are contained in Table 4-7. Values for hydrochloric acid emissions were not calculated because of uncertainty in the analysis for aluminum in the impinger catch, as discussed more completely in Chapter 5.

TABLE 4-1

AUDIT SAMPLE CHLORINE CONCENTRATIONS (mg/l)

Sample #	Date Analyzed					Total* Cl^-
	12/16	12/18	12/19	1/7	1/9	
2256	98.5	--	136.8	124.6	--	617
2285	88.4	--	--	116.7	127.0	--
3071	188.2	--	287.2	224.4	--	824
3087	170.4	--	--	263.8	218.4	--
4050	--	292.6	--	366.5	292.1	--

* Determined by mercury titration procedure. For chlorine samples only, chloride concentration should be exactly twice the chlorine concentration.

TABLE 4-2

AUDIT SAMPLE CHLORIDE CONCENTRATIONS (mg/l)

Sample #	Concentration by Mercury Method	Concentration by Silver Method	EPA Value	Relative Accuracy by Mercury Method, %	Relative Accuracy by Silver Method, %
2210	3042	2902	3000	+1.40	-3.27
3021	5107	4793	5000	+2.14	-4.14
4020	7103	6770	7000	+1.47	-3.29
5231	9145	8727	9000	+1.61	-3.03
Overall Average Accuracy:		Mercury		+1.66%	
		Silver		-3.43%	

TABLE 4-3

SUMMARY OF CHLORINE COMPOUND TRAIN FRACTIONS[a,b]

Run	Filter		Probe	Cyclone		1st Impinger		2nd Impinger		3rd Impinger		Totals[c]	
	mg(Tot)	$mgCl^-$	$mgCl^-$	$mgCl_2$	$mgCl^-$	$mgCl_2$	$mgCl^-$	$mgCl_2$	$mgCl^-$	$mgCl_2$	$mgCl^-$	$mgCl_2$	$mgCl^-$
2A	470.9	62.0	1.0	1.0	36.3	267.0	312.0	45.0	46.9	2.7	2.6	314.7	423.5
2B	193.2	15.8	1.2	1.5	19.6	305.4	446.0	169.8	119.5	16.0	8.3	491.2	589.6
3A	166.7	11.5	0.2	1.1	10.4	21.3	45.8	1.7	4.0	ND[d]	3.6	23.0	64.9
3B	160.5	11.2	0.3	1.4	17.3	14.6	29.8	0.9	1.5	ND	0.4	15.5	42.9
4A[e]	512.6	49.6	0.7	0.3	15.4	99.8	234.9	5.6	9.3	ND	0.7	105.4	294.5
4B	499.0	55.8	0.6	ND	18.1	101.2	216.2	7.0	7.9	ND	0.6	108.2	280.5

[a] All weights in milligrams.

[b] Chlorine reported in atomic form, equivalent weight 35.45.

[c] Cyclone and probe wash fractions not included in totals.

[d] ND means less than 0.1 milligram.

[e] The final test run incorporated two separate furnace clorinations.

TABLE 4-4

TABULAR SUMMARY OF CHLORINE AND CHLORIDE ANALYSES
IMPINGER TOTALS ONLY

Test Run	Total Milligrams Chlorine	Total Milligrams Chloride
2A	314.7	361.5
2B	491.2	573.8
3A	23.0	53.4
3B	15.5	31.7
4A	105.4	244.9
4B	108.2	224.7

Note: Chlorine reported in atomic form, equivalent weight 35.45.

TABLE 4-5

STAGED COLLECTION EFFICIENCY OF IMPINGERS

Run	Total Chlorine (mg)	% Collected of Total		
		First Impinger	Second Impinger	Third Impinger
2A	314.7	84.8	14.3	0.9
2B	491.2	62.2	34.6	3.2
3A	23.0	92.6	7.4	0
3B	15.5	94.2	5.8	0
4A	105.4	94.7	5.3	0
4B	108.2	93.5	6.5	0

TABLE 4-6

CHLORIDE TRAIN FRACTIONS AS % OF TOTAL

Run	Total Chloride (mg)	% Contribution			
		Filter	First Impinger	Second Impinger	Third Impinger
2A	423.5	14.6	73.7	11.1	0.6
2B	589.6	2.7	75.6	20.3	1.4
3A	64.9	17.7	70.6	6.2	5.5
3B	42.9	26.1	69.5	3.5	0.9
4A	294.5	16.8	79.8	3.2	0.2
4B	280.5	19.9	77.1	2.8	0.2

TABLE 4-7

CHLORINE COMPOUND EMISSION DATA

Run Number	Total Particulates Emission Rate (lb/hr)	Total Particulates Grain Loading (gr/dscf)	Chloride Particulates Emission Rate (lb/hr)	Chloride Particulates Grain Loading (gr/dscf)	Chlorine Gas Emission Rate (lb/hr)	Conc. (ppm)
2A	18.0	0.238	2.4	0.031	12.1	247
2B	7.3	0.097	0.6	0.008	18.7	383
3A	8.6	0.103	0.6	0.007	1.2	22
3B	7.7	0.092	0.5	0.006	0.7	14
4A	27.4	0.315	2.6	0.030	5.7	101
4B	25.6	0.305	2.9	0.034	5.6	103

HYDROCARBONS AND PARTICULATES (BAGHOUSE TESTS)

Back half extraction and rinse data are summarized in Table 4-8. Sample filter weight gains were less than 0.1 milligram and are not reported. Acetone probe rinse catches for the two runs were 3.7 and 22.6 milligrams, respectively.

Hydrocarbon analyzer data indicated widely varying concentrations. Typically, there was a certain background concentration, and spikes above ground were observed soon after a batch of scrap was charged. A portion of a strip chart containing one peak is reproduced as Figure 4-1.

Strip chart data reduction was based on a manual calculation of ten-minute averages. Overall test period concentrations were then calculated from the ten-minute averages. Results of these calculations are provided in Tables 4-9 and 4-10. In order to compare average concentrations to calculated versus actual observed values, some typical concentration ranges and peak values are listed in Table 4-11. Copies of the strip charts are provided in the appendices.

Completion of the two normal test runs confirmed that some hydrocarbons were not collected by the impingers. A brief experiment was devised to evaluate impinger collection efficiency at this relatively low hydrocarbon concentration. The results are provided in Table 4-12 and Figure 4-2.

Calculated results for the front half and back half emissions are listed in Table 4-13.

TABLE 4-8

CONDENSABLE ORGANICS BACK HALF DATA
(ALL WEIGHTS IN MILLIGRAMS)

	Run 1	Run 2
Acetone Rinse	14.3	7.3
Trichloroethylene Rinse	4.3	10.4
Neutral Extraction	2.7	--
Acid Extraction	--	1.1
TOTAL	21.3	18.8

TABLE 4-9

BAGHOUSE TOTAL HYDROCARBON EMISSIONS SUMMARY:
CORRECTED OVERALL AND PERIODIC AVERAGES
OF TEST 1 THCA DATA

Test #1 (12/17/80)

	Period (Test Minutes)	Average (ppm)
Port A	0-10	41.6
	10-20	19.9
	20-30	13.5
	30-39	22.8
Overall Port A	0-39	24.5
Port B	0-10	33.3
	10-20	16.5
	20-30	11.7
	30-35	12.3
Overall Port B	0-35	16.7
Overall Test Average	0-74	22.0

TABLE 4-10

BAGHOUSE TOTAL HYDROCARBON EMISSIONS SUMMARY:
CORRECTED OVERALL AND PERIODIC AVERAGES
FOR TEST 2 THCA DATA

Test #2

	Period (Test Minutes)	Average (ppm)
Port B	0-12	84.9
	12-22	127.0
	22-32	106.9
	32-36	69.2
Overall Port B	0-36	101.0
Port A	0-10	49.5
	10-20	57.2
	20-30	72.5
	30-36	46.5
Port A Average	0-36	57.5
Overall Test Average	0-72	79.2

TABLE 4-11

TOTAL HYDROCARBON CONCENTRATION RANGES
AND PEAKS FOR FIELD TESTS ON 12/17/80

Time	Run	Port	Range (ppm)	Peaks (ppm)
1005	1	A	11.2 to >104.4*	31.2, 47.7, >104.4*
1100	1	B	10.2 to 52.9	52.8, 46.0, 15.3
1501	2	B	66.2 to 157.3	>104.4*, 82.0, 129.5
1613	2	A	5.8 to 103.0	99.6, 73.8, 75.6, 81.5, 147.0

* Peak went off scale, 104.4 represents the minimum corrected concentration.

TABLE 4-12

HYDROCARBON PENETRATION THROUGH IMPINGERS

Time	Mode[a]	Range (ppm)[b]	Average (ppm)
1047	B	12.8 to 16.2	15.1
1050	I	19.2 to 20.2	19.9
1053	B	31.0 to 57.2	52.5
1056	I	14.0 to 27.4	23.4
1059	B	14.5 to 23.6	20.1
1102	I	14.5 to 24.1	18.4
1105	B	12.3 to 13.6	12.7
1108	I	10.9 to 16.8	13.3

[a] B denotes bypass of impingers or stack gas concentration whereas I denotes hydrocarbon concentration after sample was pulled through two impingers.

[b] Total hydrocarbon concentration as methane.

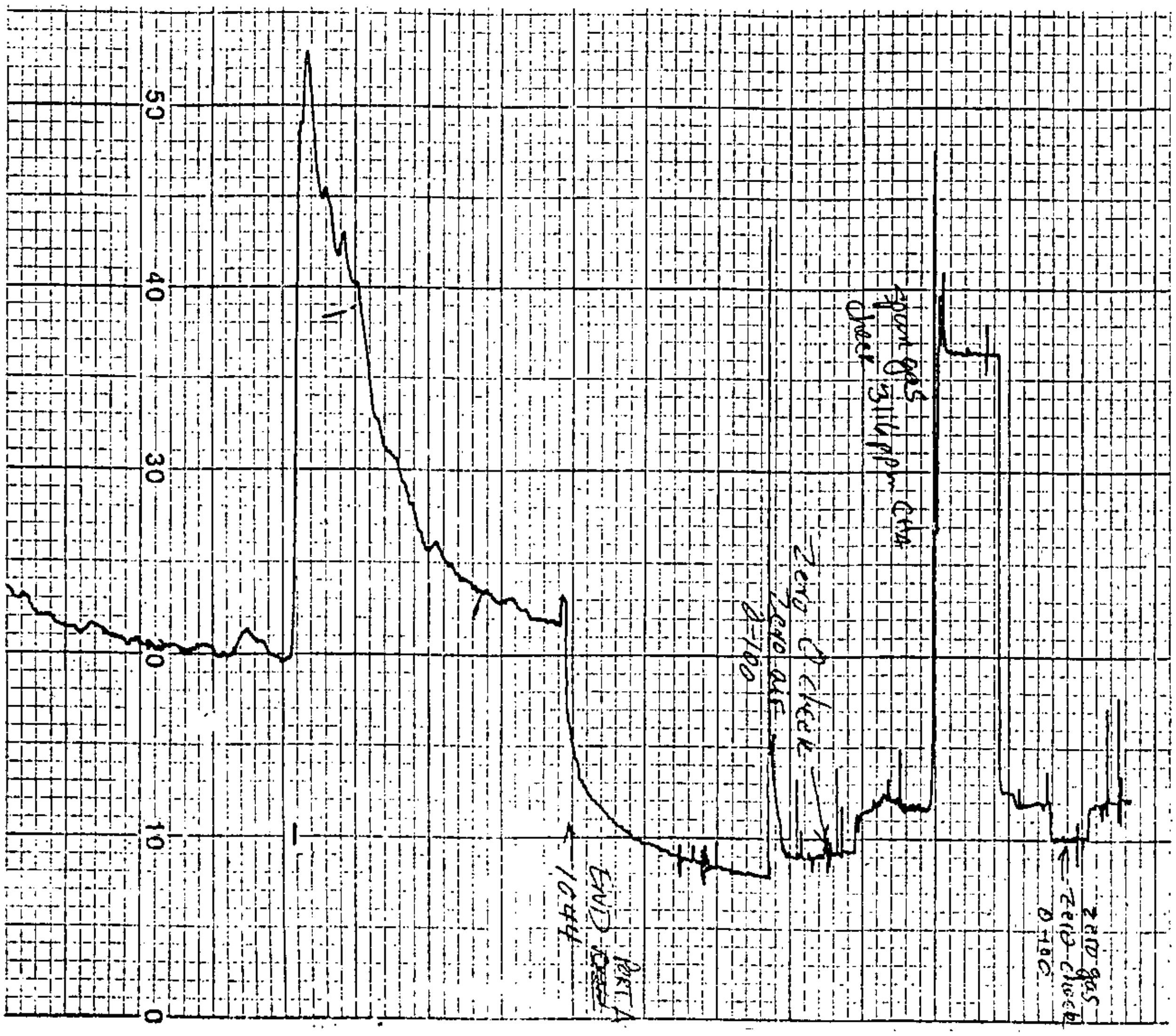
Overall average concentration with impingers: 18.8
Overall average concentration without impingers: 25.1
Impinger collection efficiency: 25%

TABLE 4-13

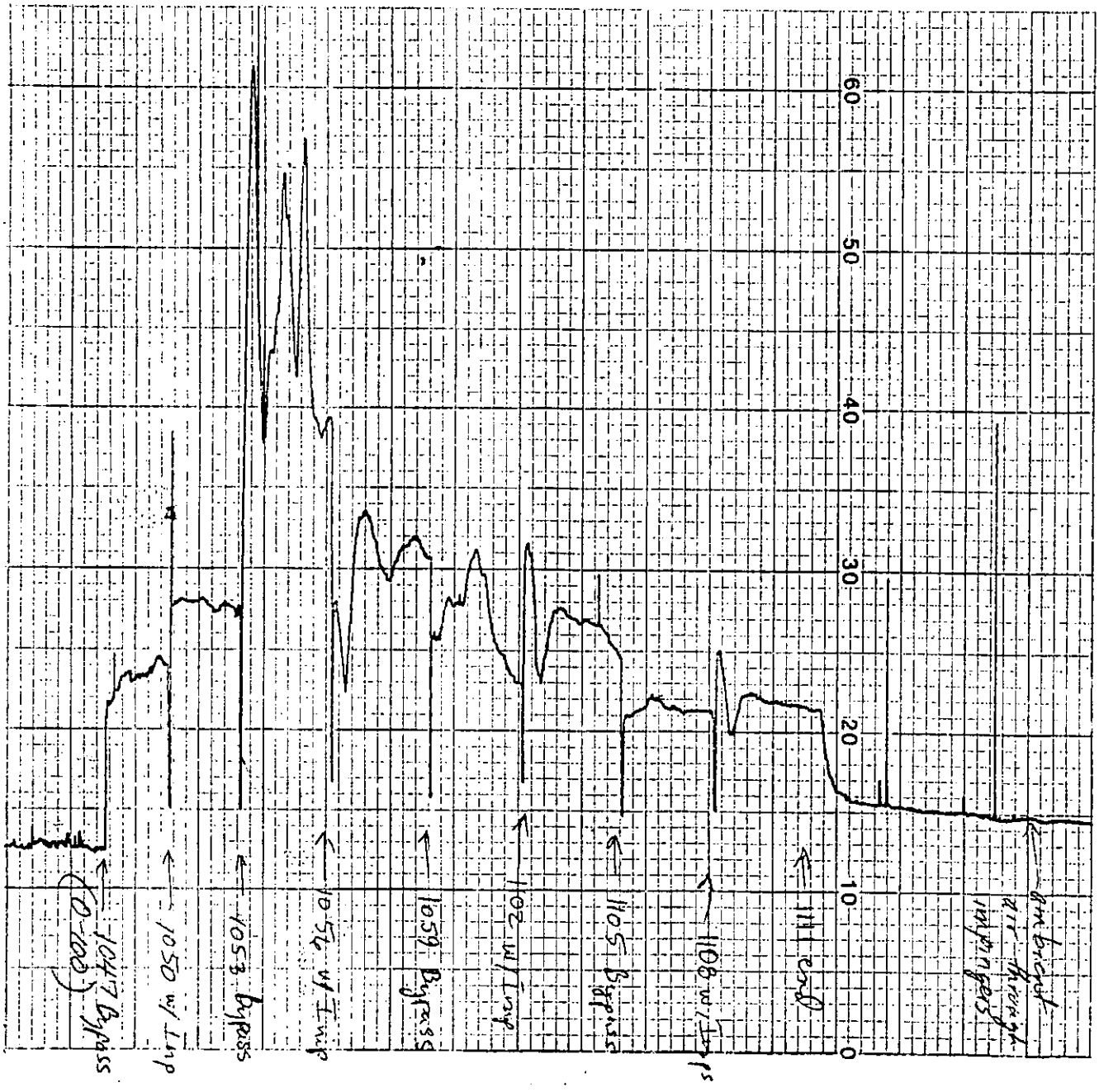
HYDROCARBON COMPOUND EMISSION DATA

	Run Number 1	Run Number 2
Front Half Emission Rate (lb/hr)	0.06	0.54
Front Half Loading (gr/dscf)	0.0006	0.005
Back Half Emission Rate (lb/hr)	0.35	0.45
Back Half Loading (gr/dscf)	0.003	0.004

Non-Condensable Hydrocarbon Peak



Impinger Collection Efficiency Experiment



CHAPTER 5

CRITICAL DISCUSSION OF EXPERIMENTAL RESULTS

Some problems were experienced with both sample collection and analytical procedures used for the Wilmington tests. There is every indication, however, that conventional stack sampling trains and routine laboratory procedures can be used for satisfactory characterization of chlorine and hydrocarbon compound emissions. Prior to recommending the final procedures, problems with the developmental procedures are discussed using NASCO test data.

ANALYSIS OF FREE CHLORINE

As indicated in Table 4-1, repeated analyses for the same quality assurance samples contained an unacceptable degree of imprecision. Also, some of the individual impinger analyses reported in Table 4-2 do not indicate the minimum expected chloride to chlorine ratio of 2:1. Specific reasons for the analytical errors are currently unknown.

The fact that chlorine analyses by 409-D relies on the intermediate spectrophotometer calibration curve places crucial importance on that curve. As shown in Figure 5-1 and Table 5-1, the calibration curve was not constant from day to day. It is true that some inherent scatter is present for all chlorine analyses (published results by American Public Health Association attribute a relative accuracy of 12.8% and relative standard deviation of 34.7% for results of 15 different laboratory analyses for 0.8 mg/l Cl_2 by 409-D), but a standard, repeatable calibration curve as developed by the same individual is essential. Our observed scatter in the calibration curve no doubt was responsible for the largest portion of the differences in the three reported concentrations for each audit sample.

Substantial dilution of commercial sodium hypochlorite solution was required to produce a low enough concentration for calibration curve development, and usually, dilutions of 20:1 to 1000:1 were necessary fo sample adjustment. Errors introduced during dilution, including use of dirty glassware, may well have contributed to variations in the analyses. Chlorine demand free water, prepared as directed in 409-D, was used for all dilutions.

The instability of the turquoise color also introduces variations due to individual field technician analysis. A slight difference in analysis speed could introduce significant error considering the deterioration of chlorine.

The standardizations and standard curve preparation require a significant allotment of time. The deterioration of chlorine in the standard

Daily Standard Curves
C1 Concentration vs. Absorbance

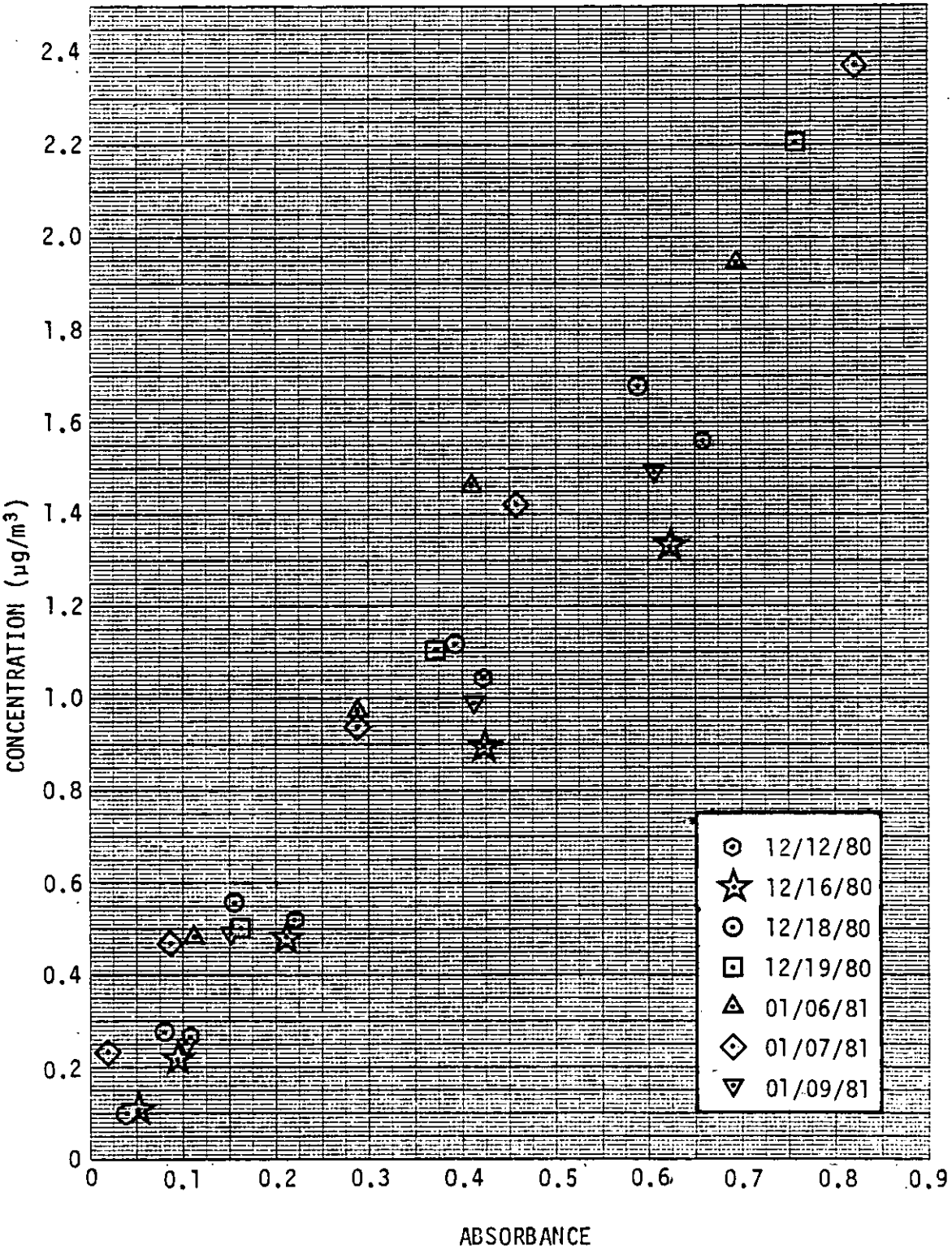


TABLE 5-1

REGRESSION CONSTANTS FOR CHLORINE CALIBRATION CURVES

Date	Number of Points on Line	a_1 [1]	a_o [1]	r^2 [2]
12/12	5	2.379	0.0160	0.999
12/16	5	2.098	0.0154	0.999
12/18	4	2.667	0.0988	0.996
12/19	3	2.8483	0.0447	1.000
1/7	5	2.625	0.211	0.999
1/9	4	2.467	-0.003	0.996

[1] These are constants for the linear correlation.
$C = a_o + a_1 A$
C = chlorine concentration, mg per liter, expressed as Cl
A = absorbance (optical density) of sample as determined by spectrophotometer

[2] r^2 is the coefficient of determination.

dilutions requires that new dilutions be prepared either during or between sample runs rather than relying on the original. Also, as mentioned earlier, dilutions have to be made and analyzed one at a time and, therefore, delegate the method to a tedious slow pace. Overall, the time requirement of this method seems to limit its field application.

Initially, it was supposed that variations in spectrophotometer operations caused at least some of the analytical problems. Subsequently, daily checks with stock cobalt chloride solutions indicated steady instrument operation.

DISCUSSION OF RELATIONSHIP BETWEEN CHLORINE AND CHLORIDE

Inspection of results in Table 4-2 from the standpoint of chlorine vs. chloride indicates some expected trends and some unexpected. Based on our accurate, precise analysis of EPA quality assurance samples for chlorides, a relatively high degree of confidence is placed on the chloride numbers. The expected minimum ratio $Cl^-:Cl_2$ of 2:1 was observed only for the first impingers of Runs 3A, 3B, 4A, and 4B, and for the second impinger of Run 3A. Discrepancies are attributed to errors in the chlorine analysis.

Operating problems were experienced during Runs 2 and 3. During Run 2, at a normal sampling flow rate, a high pressure drop across the filter caused the screen type filter supports to detach from the filter holder, permitting some particulate to proceed directly to the impingers. The post-test leak check for Run 3B was very poor. These problems would certainly negate use of the samples for compliance purposes, but A vs. B results should compare better for Runs 2 and 3. (Particulates, both total and chloride fractions, compared very well for 3A and 3B in spite of the leak, but the gaseous components do not compare.) Only for Test Runs 4A and 4B were both particulate and gaseous results comparable.

Probe wash and cyclone fractions were not included in the reported results because they represented mainly entrained scrubbing liquid droplets. The high ratio of $Cl^-:Cl_2$ for the cyclone fraction could possibly be due to thermal decomposition of hypochlorite ion in the cyclone flask contained in the heated front half compartment.

Although problems were apparent with the chlorine analyses, a definite statement can be made concerning the number of impingers, based on results contained in Table 4-5. If a nozzle size is selected to sample at about 0.75 cfm, three impingers must be charged with absorbing solution. If the next smaller standard nozzle size is used, two impingers will suffice. The latter case would, of course, extend the sampling period required to collect a minimum gas volume, so for routine sampling three impingers should be used. Each impinger should be analyzed separately to prevent excessive dilution of the first impinger, which should always capture at least 60% of the total chlorine.

CHLORIDE TITRATIONS

Both the mercuric nitrate and silver nitrate titration procedures were evaluated. These procedures were initially investigaged by ES using EPA audit samples (Table 4-2). The mercuric nitrate procedure was consistently more accurate, but no problems were experienced with either method. The mercury method was used for analysis of all field samples.

As a general rule, no difficulty was experienced in use of the mercuric nitrate titration procedure. Concerns were expressed in the Work Plan regrading the final pH of the sample prior to titration. Several samples were checked for pH prior to analysis using narrow range pH paper, and all were found to fall within the required range. Sample pH adjustments were accomplished as described in the method.

Several sample aliquots were passed through an ion exchange column of Rexyn 101H as a check for metal ion interference. For the specific case of secondary aluminum reverberatory furnace exhaust gas sampling, the use of this ion exchange column was not required, since passage of a sample appeared to have no effect on the results.

Note that the criterion for establishing the presence of metal ion interference, as explained in the modified method presented in the appendix, was to pass a sample aliquot through the ion exchange column, and compare the titration results with an untreated sample's results. If these results differ by more than 1%, the sample is said to contain interferring ions. This is too stringent a criterion, since it is difficult to obtain that degree of reproducibility with a standard sodium chloride solution. Perhaps a more realistic value for titration differences would be 3%. Differences of this magnitude would definitely indicate possible interferences and not just variations inherent to the analytical procedure.

In summary, both the silver and mercury titration procedures produced accurate analyses. The silver procedure was actually less complicated because it involved fewer steps, but the mercury method was more accurate. It should be noted, however, that the end point for the $AgNO_3$ titration was not difficult to detect, contrary to comments received by ES regarding this procedure.

PARTICULATE CHLORIDES

The most surprising result of the scrubber sample filter analyses was that chlorine, reported as chloride, contributed only about 15-20% of the total filter weight. Aluminum chloride must have been the predominant particulate compound (one method for production of aluminum chloride for use as a catalyst is similar to that by which it is formed during demagging), but it has a chloride weight fraction of 80% in anhydrous form. Handbook data indicates $AlCl_3$ to be very soluble in water, however, the filter extractions produced a colloidal material that required filtering prior to titration. It is unknown whether this contributed to the low chloride fraction.

The collected particles were white and appeared to have a very fine size. Some alloy compound chlorides like copper and manganese are non-volatile at

the temperature of molten aluminum (greater than about 1,220°F). Only zinc and silicon chlorides among common alloy constituents are volatile under these conditions, and they should be present in far lower concentrations than aluminum chlorides. All of these metal chlorides are white solids. At this time, it is impossible to state the exact chemical composition of the particulate effluent. The only firm characterization is that approximately 15 to 20% are water soluble chlorides.

Chlorine compound impinger catches were analyzed for the presence of aluminum because of the anticipated decomposition of $Al\ Cl_3$. Atomic absorption was the selected analytical techniques for undiluted aliquot samples from each impinger. Aluminum has a relatively high concentration threshold for AA analysis, and our results were typically very close to our detectability limit of 15 milligrams per liter. Qualitatively, it can be stated that aluminum was present in at least some of the impingers for all test runs. Quantitatively, it can only be stated that as much as a few milligrams were present in some of the impingers.

Some of the impingers appeared slightly cloudy immediately after sample collection, but many later developed a definite white precipitate. This was probably due to initial formation of aluminate ion in the caustic solution followed by gradual conversion to insoluble aluminum hydroxide. Certainly these precipitates contributed to the low aluminum concentration in solution.

Aliquots of the filter extract were also analyzed by AA. Again, the results were inconclusive. The highest reported value was only about 6% of the total filter weight.

Although the impinger catch aluminum analyses were semi-quantitative, they did confirm the presence of aluminum. The quartz filters used (Pall Corporation Type QAST) met the Method 5 filtration efficiency specification, and it would not have been possible for any particle size to penetrate the filter in milligram quantities during the course of a typical sample run. The aluminum must have reached the impingers in vapor form, meaning that partial decomposition of collected material occurred on the heated filter.

Operation of the sample train filter at the standard Method 5 temperature of about 250°F thus biases the reported mass loading towards lower values. Careful temperature control high enough only to prevent water condensation should be used for more accurate particulate matter characterization.

HYDROCARBONS TRAIN FRONT HALF

Quartz filters for the two baghouse runs had a negative weight change. No doubt this was due to the poor mechanical properties of the selected media. The filters were very difficult to handle at the end of a test, and some pieces were separated from the main filters. They had developed an electrostatic charge, and some small pieces were impossible to recover.

There was no apparent particle loading on the filters. During the course of both sample runs, the baghouse stacks were optically clear, so it is speculated that the filter loading would have been very low in any case.

Substantial acetone probe wash weights were recorded for the two complete test runs. The particulate matter appeared to have included relatively large lime dust particles which must have seeped thru the bags. Some oily material was also present.

CONDENSABLE HYDROCARBONS

When inspecting the back half data listed in Table 4-8, it is noted that the glassware rinses produced a higher mass loading than the impinger extractions. This was probably due to the fact that the condensed organics were very insoluble in water and preferentially adhered to the glass walls. Collection of silicone grease is a possibility, but all connecting joints were wiped off with trichloroethylene prior to back half recovery.

It is not surprising that TCE recovery was more complete than acetone. A chlorinated hydrocarbon would be expected to have a higher solubility for many hydrocarbons than would the relatively polar acetone. Of course, the chlorinated hydrocarbons have undesirable properties, and probably should not be recommended for routine field use. Use of acetone only will cause incomplete recovery of some hydrocarbons.

With respect to the extraction procedure, firm conclusions are difficult because there was only a very small mass loading to work with. It does seem that both neutral and acid extractions are necessary. This comment is specific to the NASCO charging well hydrocarbons, the exact composition of which are unknown, and other hydrocarbon classifications could well respond differently.

NONCONDENSABLE HYDROCARBONS

When interpeting THCA data, it is important to remember that the FID reports responses equivalent to methane. Thus, 10 ppm of n-octane would have a response roughly equivalent to 80 ppm methane. The following discussion contains references to concentrations greater than 100 ppm, but without knowing exact chemical composition and individual response factors, the true hydrocarbon concentration cannot be determined.

During test runs, insignificant zero and span gas drifts occurred from post-test checks. Concentration values were corrected for a temperature related reduction in instrument response, as discussed in the previous chapter. Ambient background concentrations ranged from 2.3 to 5.5 ppm, and were typically low compared to the FID results.

The second run maintained a running higher concentration level throughout the duration of the test. NASCO had indicated that their "dirtiest" scrap was processed during that general period of time.

As indicated in Chapter 4, there were periods during both test runs where the FID peaks were greater than 100 ppm. Overall, both tests indicated an average hydrocarbon concentration less than 100 ppm. Whether or not this is significant depends on the source classification and the levels of interest. These low concentrations are irrelevant in terms of formation of detached particulate matter plumes.

A brief experiment was completed using a modified impinger and a regular Greenburg-Smith impinger. Absorption and condensation conditions were much better than during a regular Method 5 run because of the lower sample flow rate (0.1 cfm using the internal THCA pump only). Even so, the impinger collection efficiency was only about 25%. Ordinarily, though, these concentrations would not be of interest.

It was discovered later that the impinger water from the method 5A samples had experienced a reduction of their pH's to 2. Therefore, the acidity may have retarded the ability of the water to remove condensable hydrocarbons. In light of this, representative collection of condensable hydrocarbons may be more successfully retained by a caustic or strong buffer solution.

The mass of noncondensable hydrocarbons as methane was highest for Run 2, and was approximately 130 milligrams. This was much higher than the condensable hydrocarbons weight of about 20 milligrams. Strict comparison of the two mass fractions is impossible because of the unknown composition of the hydrocarbons.

CHAPTER 6

RECOMMENDATIONS FOR EVALUATION PROCEDURES

Our experience to date with chlorine and hydrocarbon compound evaluation techniques does not yet provide a firm data base for potential reference procedures. Analysis of the NASCO test data does, in fact, answer some important questions concerning sample train configuration and collected sample analytical procedures; however, some aspects must be viewed as developmental. The particular area of concern at this point is the analysis of chlorine. A recommendation for future studies for this analysis and all others of interest for the secondary aluminum industry are discussed in this chapter.

CHLORINE COMPOUNDS - SAMPLE COLLECTION

Complete recovery of chlorine concentrations as low as approximately 20 ppm can be achieved by using three impingers in series charged with 100 ml of 0.1N sodium hydroxide solution. At relatively low sample flow rates, all chlorine is recovered by the first two impingers. A third impinger in series provides a safety factor when low flow rate sampling ($\approx$0.3 cfm) is impractical. Although hydrochloric acid was not absolutely identified at NASCO, complete recovery with two impingers should be expected, regardless of flow rate up to about 1 cfm.

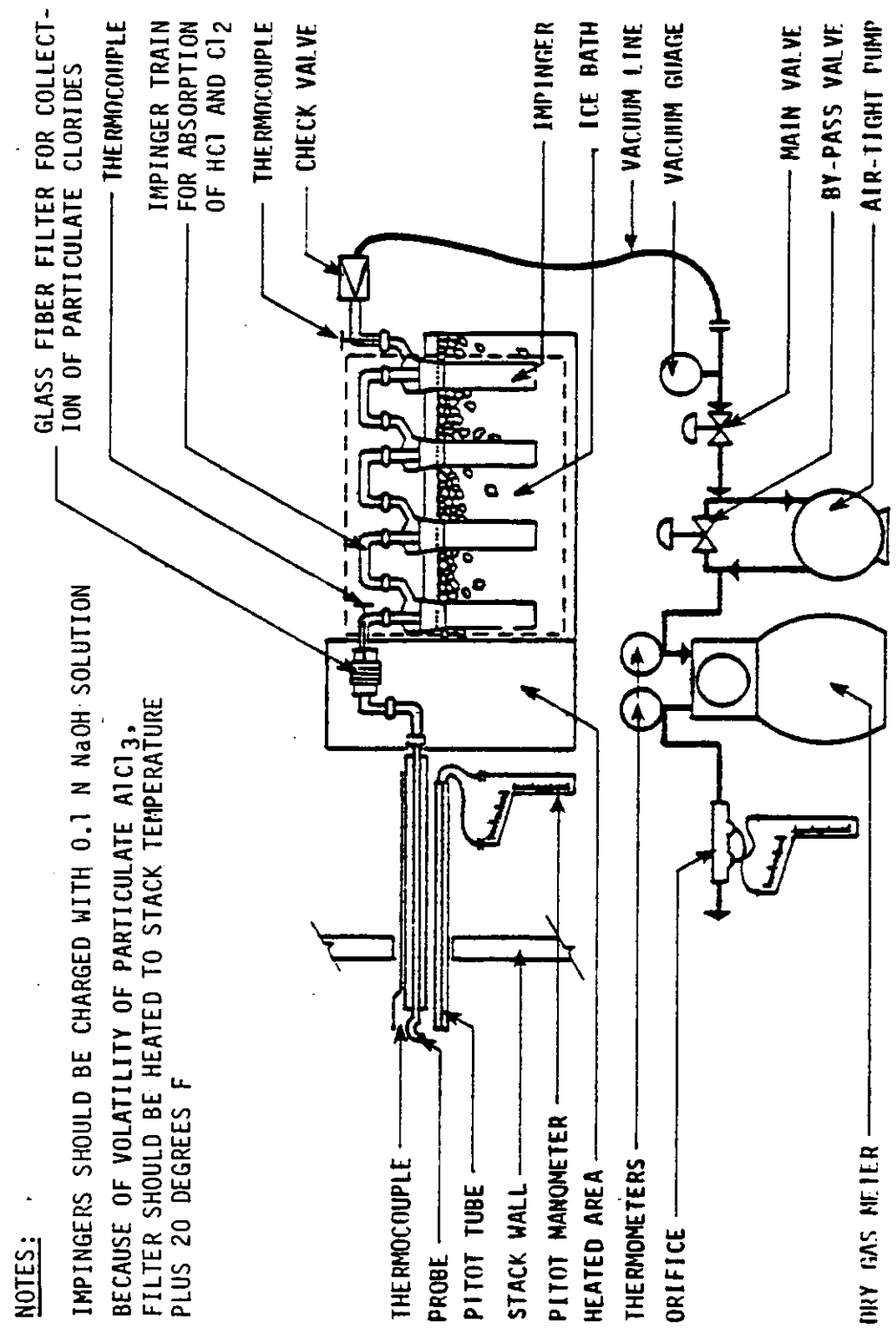
Particulate chlorides are retained on the sample filter only as long as high temperature does not cause sublimation or decomposition. The standard Method 5 temperature of 250°F is too high for accurate characterization of aluminum chloride. Based upon a preliminary pre-test stack temperature measurement, the sample filter should be heated only about 20°F above stack temperature. This should be high enough to prevent both moisture condensation and significant sample deterioration.

Quartz filters have superior chemical properties, but their mechanical properties leave much to be desired. Standard Reeve-Angel glass fiber filters should be used for all future samples.

Anticipating some instances of low gaseous chlorine compounds at the scrubber outlet, glass frit filter supports should not be used. Use of stainless steel screen filter supports is recommended.

The recommended sample train is diagrammed in Figure 6-1. Operation is identical to EPA Method 5, except that filter temperature control is based on actual stack temperature instead of the conventional value of 250°F.

Chlorine Compound Sampling Train



NOTES:

IMPINGERS SHOULD BE CHARGED WITH 0.1 N NaOH SOLUTION

BECAUSE OF VOLATILITY OF PARTICULATE $AlCl_3$, FILTER SHOULD BE HEATED TO STACK TEMPERATURE PLUS 20 DEGREES F

CHLORINE COMPOUND ANALYSES

Chlorine Method 409-D, and all other methods designed for evaluation of potable or wastewater, should be rejected for stack sampling application because they were designed for very low chlorine concentration and are time consuming. Extensive dilution is normally required to lower impinger sample concentration to the range of 1 mg/l. Much higher dilutions would be necessary for samples collected at control device inlets. Errors are possible in dilution, and once the chlorine concentration has been reduced, sample stability is a problem. A more rugged technique suitable for routine field use is desired.

The alkaline arsenite procedure (included in the appendices) was initially considered and rejected as being too insensitive. This technique can be used for simultaneous evaluation of chlorine, hydrochloric acid, and particulate chlorides. The reported lower limit for application was 10 ppm by volume of Cl_2 or HCl, which is equivalent to a chlorine or chloride concentration of about 40 mg/l.

Briefly, the arsenite technique is used to convert chlorine to chloride. Chlorine gas is absorbed in the impinger solution of sodium hydroxide and sodium arsenite and is immediately reduced. A back titration of spent absorbing solution determines the amount of arsenic consumed which indicates how much chlorine reacted. The difference in total chlorides (titrated using the mercury procedure) from the amount attributable to chlorine conversion provides the analysis for hydrochloric acid or other chloride compounds. Only titration procedures are required, and sample dilution is unnecessary. In fact, the techniques should be more accurate at higher concentrations.

One method of extending the useful lower range of the arsenite procedure below 40 mg/l is to use lower normality titrating solutions. This and other improvements will be considered prior to the next field test program.

Analysis of chlorine samples should be completed in the field within two hours after sample collection. Samples should be kept on ice until analysis. Impingers should be recovered and analyzed separately, as mixing the contents would result in dilution of the first impinger catch.

Based upon the NASCO samples, the predominant gaseous chlorine compound is molecular chlorine and not hydrogen chloride.

TOTAL CHLORIDES IN SOLUTION

The mercuric nitrate titration procedure is recommended. Our experience confirmed it to have been reliable and accurate. Narrow range pH paper is a satisfactory indicator for the pH dependent titration end point detection.

Sample aliquot volumes should be selected so as to result in a minimum titration volume on the order of one milliliter.

Accurate determination of total chlorides is dependent upon conversion of chlorine in hypochlorous form to chloride ion. A direct, simple approach

is to add a stoichiometric excess of hydrogen peroxide. Solution pH must be at a pH greatr than 7. After the chlorine concentrations have been determined, the amount of peroxide necessary for a 10 to 20% excess may be calculated.

Chlorination Scrubber Effluent Particulates

A certain percentage of the filter catch is water soluble chlorides, but the largest portion is not. Both total filter weight and chloride fraction should be reported.

HYDROCARBON COMPOUNDS - SAMPLE COLLECTION

The recommended layout for the hydrocarbons sample train is pictured in Figure 6-2. Operation is identical to the standard Method 5 train.

Similar to the scrubber train, Reeve-Angel filters should be used. Quartz filters would be suitable if only particulate chloride analysis instead of total weight were desired.

Impingers should be charged with 0.1N potassium or sodium hydroxide instead of distilled water. Some organics are more soluble at high pH, and use of a caustic impinger solution would promote sample recovery and would prevent a large portion of organics adhering to the impinger walls. Use of a caustic solution would also help prevent formation of an acidic medium due to absorption of acid gases and would, therefore, again result in more complete recovery.

Use of a hydrocarbon analyzer should not be necessary. The amount of material recoverable by physical condensation is proportional to the difference in hydrocarbon compound partial pressure at about 250°F and about 70°F. If the material does not condense out at the impinger temperature, it may cause some type of hydrocarbon emission problem, but it should not result in formation of a particulate matter plume at the stack exit.

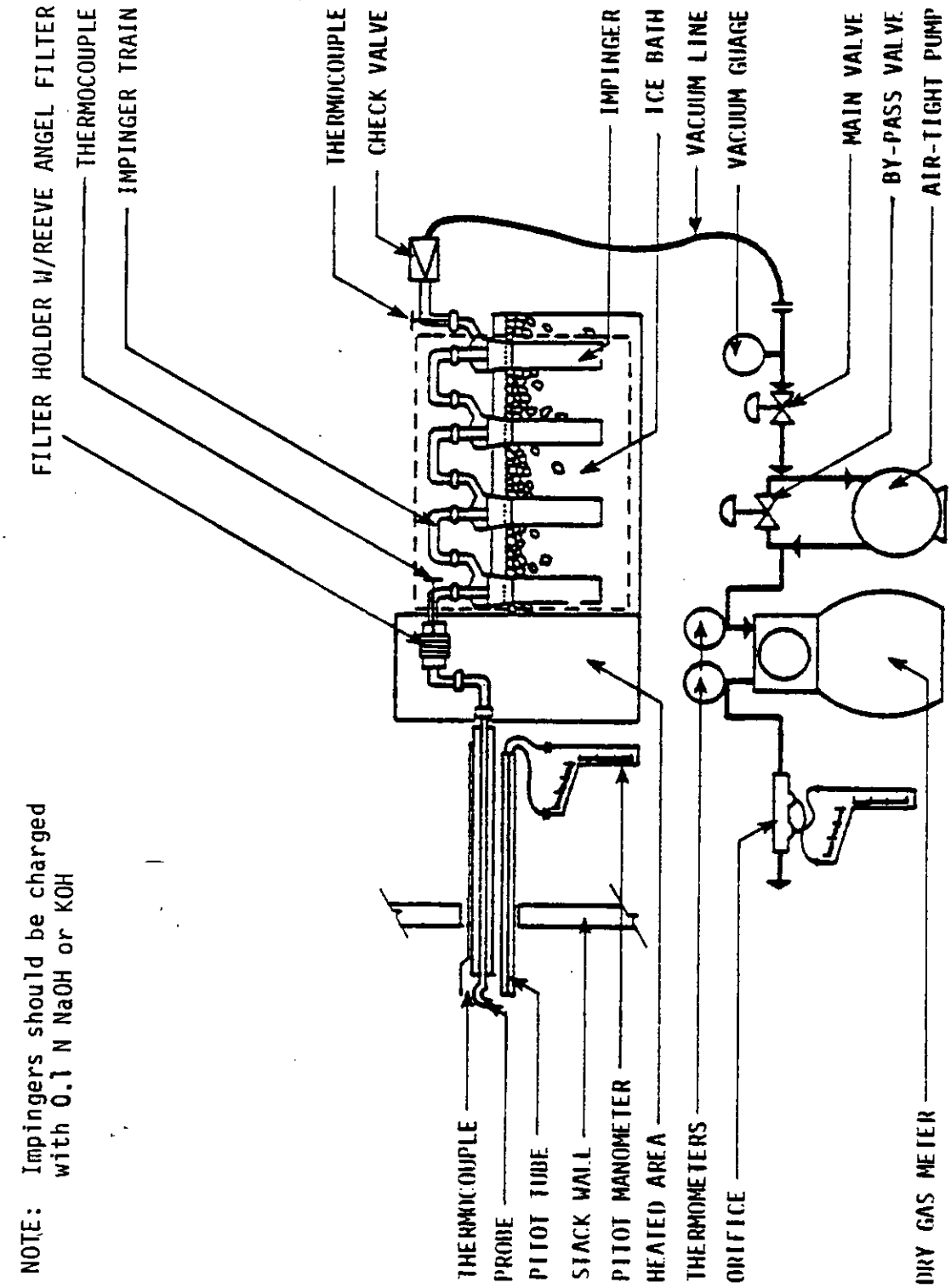
CLEAN UP AND RECOVERY OF BACK HALF HYDROCARBONS

Use of all conventional hydrocarbon solvents in the field involves potential exposure to hazardous conditions. Rinsing the probe and impinger glassware in a laboratory hood would be much safer, but would be totally impractical. Thus, desirable solvents such as chloroform (or any of the chlorinated or fluorinated hydrocarbons), ethyl ether, and benzene are eliminated from consideration. Presently, acetone seems to be an acceptable compromise. Some organics adhering to the probe liner or other glass surfaces will not be completely recovered by acetone, but acetone is currently believed to have fewer hazardous properties than other suitable solvents.

Some hydrocarbon compounds are not completely recoverable from a neutral solution. Impinger contents should be acidified to a pH less than 2 with hydrochloric acid prior to extraction. The necessity of using an acid extraction vs. a neutral extraction could be determined on a case-by-case basis for

Particulate and Condensable Hydrocarbons Sampling Train

NOTE: Impingers should be charged with 0.1 N NaOH or KOH



each source/control equipment classification, but it is more straightforward to rely upon the acid extraction for general application. Impinger contents should be acidified to a pH less than 2 with hydrochloric acid prior to extraction.

APPENDIX A

CHLORINE PROCEDURES

Standard Methods
For the Examination of Water and Wastewater

FOURTEENTH EDITION

Prepared and published jointly by:
AMERICAN PUBLIC HEALTH ASSOCIATION
AMERICAN WATER WORKS ASSOCIATION
WATER POLLUTION CONTROL FEDERATION

Publication Office:
American Public Health Association
1015 Eighteenth Street NW
Washington, DC 20036

The chlorination of water supplies and polluted waters serves primarily to destroy or deactivate disease-producing microorganisms. A secondary benefit is the overall improvement in water quality resulting from the reaction of chlorine with ammonia, iron, manganese, sulfide, and some organic substances.

Chlorination may produce adverse effects by intensifying the taste and odor characteristics of phenols and other organic compounds present in a water supply. Combined chlorine formed on chlorination of ammonia- or amine-bearing waters affects some forms of aquatic life adversely. To promote the primary purpose of chlorination and to minimize any adverse effects, it is essential that proper testing procedures be used with a fore-knowledge of the limitations of the analytical determination.

Chlorine applied to water in its elemental or hypochlorite form initially undergoes hydrolysis to form free available chlorine consisting of aqueous molecular chlorine, hypochlorous acid, and hypochlorite ion. The relative proportion of these free chlorine forms is pH-dependent, and at the pH of most waters the hypochlorous acid and hypochlorite ion will predominate.

Free chlorine reacts readily with ammonia and certain nitrogenous compounds to form combined available chlorine. With ammonia, chlorine reacts to form the chloramines: monochloramine, dichloramine, and nitrogen trichloride. The presence and concentrations of these combined forms depend on many conditions, chiefly pH, temperature, and the initial chlorine-to-nitrogen ratio. Both free and combined chlorine may be present simultaneously. Combined chlorine in water supplies may be formed in the treatment of raw waters containing ammonia, by the addition of ammonium salts in pre-chlorination, or by producing a combined chlorine residual in the distribution system. Chlorinated wastewater effluents, as well as certain chlorinated industrial effluents, normally contain only combined chlorine forms. Historically, the principal analytical problem has been to distinguish between free and combined forms.

In two separate but related studies, designated Study No. 1 and 2, respectively, samples were prepared and distributed to participating laboratories for the purpose of evaluating the residual chlorine methods.

In Study No. 1, three solid synthetic unknowns were prepared: One powdered unknown was compounded of 70% calcium hypochlorite* and NaCl filler to yield a free available chlorine concentration of 800 µg/l upon dissolution in chlorine-demand-free distilled water; the second was compounded of 70% calcium hypochlorite* and NaCl filler to yield a total available chlorine concentration of 640 µg/l upon dissolution and mixing with an aqueous ammonium buffer solution in chlorine-demand-free distilled water; and the third was prepared from Halazone,† p-(N,N-dichlorosulfamyl) benzoic acid, to yield a total available chlorine concentration of 1,830 µg/l upon dissolution in chlorine-demand-free distilled water. The results obtained by the participating laboratories are summarized in Table 409:I.

In Study No. 2, each participating laboratory received four sealed glass ampoules of concentrated solution (three hypochlorite solutions of different concentrations and one ammonium chloride borate buffer solution) which, when diluted according to instructions, provided two samples containing free chlorine and one containing combined chlorine. Sample No. 1 contained 440 μg/l free chlorine, a concentration likely to be encountered in analysis of treated potable water. Sample No. 2 contained 980 μg/l free chlorine, the maximum concentration likely to be encountered in analysis of treated potable water. Sample No. 3 contained only combined chlorine at a concentration of 660 μg/l to simulate an insufficiently chlorinated water having no free chlorine residual. To facilitate statistical computations, a value of 50 μg/l free chlorine was selected as the "true" value rather than the theoretical 0.0 μg/l. In Study No. 2, the data were treated statistically according to a total error term defined as

$$\text{Total error} = 100 \times \frac{\text{Absolute value of mean error} + 2\,(\text{Std. Dev.})}{\text{True value}}$$

The results obtained by the participating laboratories are summarized in Tables 409:II through IV. In the last column of these tables all data on Sample No. 1 are omitted because of sample instability, and therefore the results can be used only for comparative purposes and not as a measure of the overall precision or accuracy. Free chlorine data also were omitted in Column 3 because the stated free chlorine content is an artifact and actually was zero.

Because of poor accuracy and precision and a high overall (average) total error in comparison with other available methods, the orthotolidine procedures that have been so widely used have been deleted as standard methods. The methyl orange technic also has been deleted because of the poor precision (lack of reproducibility) inherent in a bleaching technic in which operator skill and environmental factors such as temperature are critical.

The results presented in Tables 409:I through IV are valuable only for comparison of the methods tested. Many factors, such as analytical skill, recognition of known interferences, and inherent limitations, determine the reliability of any given method.

Some oxidizing agents, including free halogens other than chlorine, will appear quantitatively as free chlorine; this is also true of chlorine dioxide. Some nitrogen trichloride may be measured as free chlorine. The actions of interfering substances should be familiar to the analyst because they affect a particular method.

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* Olin Matheson Chemical Corp., HTH (granular).

† Abbott Laboratories.

TABLE 409:I. PRECISION AND ACCURACY DATA FOR RESIDUAL CHLORINE METHODS IN STUDY NO. 1

Method	Residual Chlorine Concentration		Number of Laboratories	Relative Standard Deviation %	Relative Error %
	Free µg/l	Total µg/l			
Titrimetric (iodine)		840	32	27.0	23.6
		640	30	32.4	18.5
		1,830	32	23.6	16.7
Amperometric	800		23	42.3	25.0
		640	24	24.8	8.5
		1,830	24	12.5	8.8
Orthotolidine	800		15	64.6	42.5
		640	17	37.3	20.2
		1,830	18	31.9	41.4
Orthotolidine-arsenite	800		20	52.4	42.3
		640	21	28.0	14.2
		1,830	23	35.0	49.6
Stabilized neutral orthotolidine	800		15	34.7	12.8
		640	16	8.0	2.0
		1,830	17	26.1	12.4
Ferrous DPD	800		19	39.8	19.8
		640	19	19.2	8.1
		1,830	19	9.4	4.3
DPD Colorimetric	980		26	20.7	15.6
		660	25	27.6	15.6
Leuco crystal violet	800		17	32.7	7.1
		640	17	34.4	0.9
		1,830	18	32.4	18.6
Methyl orange	800		26	43.0	22.0
		640	26	30.1	14.2
		1,830	26	19.9	7.2

TABLE 409:II. SUMMARY OF OVERALL ACCURACY IN STUDY NO. 2 (AVERAGE MEAN ERROR IN MG/L)

Method	Sample 1		Sample 2		Sample 3		Overall Average	Omitting all Data on Sample 1 and Free on Sample 3
	Free	Total	Free	Total	Free	Total		
Methyl orange	-0.219	-0.171	-0.044	-0.006	-0.006	+0.029	0.079	0.026
Leuco crystal violet	-0.250	-0.209	-0.085	-0.070	-0.050	-0.007	0.112	0.054
SNORT	-0.241	-0.198	-0.113	-0.107	-0.048	-0.032	0.123	0.084
DPD-titrimetric	-0.259	-0.198	-0.192	-0.059	-0.038	-0.031	0.130	0.094
DPD-colorimetric	-0.263	-0.213	-0.153	-0.097	-0.014	+0.103	0.140	0.117
Amperometric	-0.241	-0.189	-0.230	-0.119	-0.012	-0.108	0.150	0.152
OTA	-0.282	-0.253	-0.198	-0.102	+0.114	-0.092	0.174	0.130

TABLE 409:III. SUMMARY OF OVERALL PRECISION IN STUDY NO. 2 (AVERAGE STANDARD DEVIATION IN MG/L)

Method	Sample 1		Sample 2		Sample 3		Overall Average	Omitting all Data on Sample 1 and Free on Sample 3
	Free	Total	Free	Total	Free	Total		
Leuco crystal violet	0.085	0.055	0.042	0.015	0.000	0.089	0.048	0.049
SNORT	0.093	0.092	0.120	0.142	0.004	0.110	0.094	0.124
Amperometric	0.106	0.072	0.206	0.137	0.040	0.171	0.122	0.171
DPD-colorimetric	0.102	0.100	0.171	0.152	0.057	0.210	0.132	0.177
DPD-titrimetric	0.110	0.103	0.298	0.205	0.019	0.121	0.143	0.208
Methyl orange	0.143	0.162	0.315	0.301	0.055	0.143	0.187	0.253
OTA	0.090	0.098	0.335	0.325	0.195	0.218	0.210	0.293

TABLE 409:IV. SUMMARY OF OVERALL (AVERAGE) TOTAL ERROR IN STUDY NO. 2

Method	Sample 1		Sample 2		Sample 3		Overall Average	Omitting all Data on Sample 1 and Free on Sample 3
	Free	Total	Free	Total	Free	Total		
Leuco crystal violet	95.31	72.59	17.24	10.20	100.00	28.00	53.90	18.52
SNORT	97.04	87.00	35.95	39.97	112.40	38.15	68.42	38.02
DPD-titrimetric	108.86	91.77	80.51	47.89	153.40	41.33	87.29	56.64
Amperometric	102.95	75.63	65.46	40.14	182.80	68.21	89.20	57.94
DPD-colorimetric	106.18	94.00	50.57	40.83	256.40	79.33	104.55	56.90
Methyl orange	114.86	112.59	68.83	62.12	232.00	47.75	106.36	59.56
OTA	104.95	101.90	88.57	76.81	1007.80	79.93	243.33	81.77

1. Selection of Method

a. Natural and treated waters: The iodometric methods (A and B) are suitable for measuring chlorine concentrations greater than 1 mg/l, but are not accurate at lower concentrations or in the presence of interferences.

The amperometric titration method (C) is a standard of comparison for the determination of free or combined chlorine. It is affected little by common oxidizing agents, temperature variations, turbidity, and color. The method is not as simple as the colorimetric methods and requires greater operator skill to obtain the best reliability.

The ferrous DPD method (E) provides a titrimetric procedure for determining free available chlorine and for estimating free and combined chlorine fractions present together.

The stabilized neutral orthotolidine (SNORT) and the DPD colorimetric methods (Methods D and F, respectively) are applicable to the determination of free available chlorine. Procedures are given for estimating the combined fractions. Increasing concentrations of monochloramine are likely to produce an increased interference with the free chlorine determination. In addition, the SNORT and DPD methods are subject to interference by oxidized forms of manganese.

The leuco crystal violet (LCV) method (G) makes possible the determination of free available chlorine, total chlorine, and combined chlorine by difference. The LCV method exhibits a relatively minimal interference as monochloramine concentrations are increased in the determination of free available chlorine; however, nitrite and monochloramine in combination, as well as oxidized forms of manganese, will produce interference in determining free available chlorine.

The amperometric, LCV, DPD, and SNORT methods are unaffected by dichloramine concentrations in the range of 0 to 9 mg/l (as Cl_2) in the determination of free chlorine. Nitrogen trichloride, if present, reacts partially as free available chlorine in the amperometric, DPD, and SNORT methods. Nitrogen trichloride does not interfere with the LCV procedure for free chlorine.

The free available chlorine test, syringaldazine (Method H, Tentative) was developed as a procedure specific for free available chlorine. It is unaffected by significant concentrations of monochloramine, dichloramine, nitrate, nitrite, and oxidized forms of manganese.

Sample color and turbidity may interfere in all colorimetric procedures unless they are compensated for.

Organic contaminants may produce a false free chlorine reading in most colorimetric methods (see ¶ 1*b* below).

b. Polluted waters: The determination of residual chlorine in samples containing organic matter presents special problems. Because of the presence of organic compounds, particularly organic nitrogen, the residual chlorine exists in a combined state. A considerable residual may exist in this form, but at the same time there may be appreciable unsatisfied chlorine demand. The addition of the reagents in the determination may change these relationships so that residual chlorine is lost during the analysis. In wastewater, the differentiation between free available chlorine and combined available chlorine is not ordinarily made because wastewater chlorination is seldom carried far enough to produce free available chlorine.

The determination of residual chlorine in industrial wastes is similar to that in sewage when the waste contains organic matter, but may be similar to the determination in water when the waste is low in organic matter.

Although the methods given below are useful for the determination of residual chlorine in wastewaters and treated effluents, selection in accordance with the composition of the sample being tested is necessary. Some industrial wastes, or mixtures of wastes with domestic wastewater, may require special precautions and modifications to obtain satisfactory results.

Free chlorine in a wastewater can be determined by any of the methods presented in Sections 409 A through 409 H, provided that known interfering substances are absent or compensated for. The amperometric method (C) is the method of choice because it is not subject to interference from color, turbidity, iron, manganese, or nitrite nitrogen. The DPD and SNORT methods are subject to interference from high concentrations of monochloramine unless these are compensated for by addition of arsenite immediately after reagent addition. The LCV method (G) is significantly less affected by high monochloramine concentrations and an arsenite addition will produce a minimum interference. The presence of oxidized forms of manganese will interfere in most colorimetric procedures and, in addition, the combination of monochloramine and nitrite will seriously interfere with the LCV procedure.

The tentative syringaldazine method (H) is unaffected by concentrations of monochloramine, dichloramine, nitrite, nitrogen, iron, manganese, and other interfering compounds normally found in domestic wastewaters.

For total available chlorine in samples containing significant amounts of organic matter, the iodometric back titration method (B) should be used to prevent contact between the full concentration of liberated iodine and the sample. Either the amperometric or the starch-iodide end point may be used. In the absence of the interference, the two modifications give concordant results. The amperometric end point is inherently more accurate and is free of interference from color and turbidity, which can cause difficulty with the starch-iodide end point. On the other hand, certain metals and complex anions in some industrial wastes interfere in the amperometric titration and indicate the use of another method for such wastewaters. Silver in the form of soluble silver cyanide complex, in concentrations as low as 1.0 mg/l silver, poisons the cell at pH 4.0 but not at 7.0. The silver ion, in the absence of the cyanide complex, gives extensive response in the current at pH 4.0 and gradually poisons the cell at all pH levels. Cuprous copper in the soluble copper cyanide ion, in concentrations as low as 5 mg/l copper or less, poisons the cell at pH 4.0 and 7.0. Although manganese, iron, and nitrite may interfere with this method, the interference is minimized by buffering to pH 4.0 before addition of KI. An unusually high content of organic matter may cause some uncertainty in the end point. Whenever manganese, iron, and nitrites are definitely absent, this uncertainty can be reduced and precision improved by buffering below pH 4.0—even as low as pH 3.0.

Regardless of the method of endpoint detection, either phenylarsine oxide or thiosulfate may be used as the standard reducing reagent. The former is more stable and is preferred.

The SNORT colorimetric, DPD titrimetric and colorimetric, and the LCV

methods (D, E, F, and G, respectively) are applicable to the determination of total available chlorine in polluted waters. In addition, both DPD procedures and the amperometric titration and SNORT methods allow for the estimation of the monochloramine and dichloramine fractions. Since these methods depend on the stoichiometric production of iodine, polluted waters containing iodine-reducing substances may not be analyzed accurately by these methods.

In all of the colorimetric procedures, compensate for color and turbidity by use of color and turbidity "blanks" in visual or spectrophotometric determinations.

2. Sampling and Storage

Chlorine in aqueous solution is not stable, and the chlorine content of samples or solutions, particularly weak solutions, will decrease rapidly. Exposure to sunlight or other strong light or agitation will accelerate the reduction of chlorine. Therefore, start chlorine determinations immediately after sampling, avoiding excessive light and agitation. Do not store samples to be analyzed for chlorine.

409 D. Stabilized Neutral Orthotolidine (SNORT) Method

1. General Discussion

a. Principle: Orthotolidine is quite stable in the reduced form when stored in brown bottles in the presence of hydrochloric acid. However, the stability of oxidized orthotolidine decreases as the pH increases. For this reason, orthotolidine usually has been used at a pH of 1.3 or less. As the pH increases, the rate of reaction of orthotolidine with combined chlorine, iron, and nitrite becomes slower and their interference essentially disappears at pH 7. Anionic surface-active agents stabilize the color developed by free chlorine and orthotolidine at pH 7.0. "Aerosol OT,"* sodium di(2-ethyl-hexyl) sulfosuccinate, is the best stabilizing reagent. The optimum concentration of stabilizer is 40 mg for each 100 ml of sample plus reagents.

* A trademark of the American Cyanamid Co.

The ratio by weight of orthotolidine dihydrochloride to chlorine must be at least 8 to 1. With the concentration of orthotolidine recommended in the procedure, the chlorine concentration must not exceed 6 mg/l.

The pH of the final solution must be between 6.5 and 7.5 to minimize low-pH interference and high-pH fading. If the pH of the sample is less than 5 or greater than 9, and the alkalinity is greater than 150 or the acidity greater than 200 mg/l, check the final pH of the solution. If the alkalinity is high and the final pH does not lie within the range of 6.5 to 7.5, adjust the sample pH to this range before analysis.

To insure correct color development, minimum interference, a pH of 6.5 to 7.5, and a ratio of orthotolidine to free chlorine of at least 8 to 1, the sample must be added to the reagents.

The reaction time and temperature are much less important in this method than in other colorimetric methods for chlorine determination. Nevertheless, for extremely large combined chlorine to free chlorine ratios, high temperature and long waiting times are undesirable. At 35 C a 1-mg/l monochloramine solution produces a false free chlorine residual of 0.01 mg/l per min. At high temperature and for long waiting times, color fading may become important, especially at levels below 0.1 mg/l of free chlorine. A 1-mg/l solution of free chlorine fades at the rate of 0.005 mg/l per min at 35 C.

Iodide can be added in neutral solution to measure monochloramine and in acidic solution to measure dichloramine. The reaction of iodide and chloramine yields a concentration of iodine equivalent to the chloramine. In the colorimetric procedure, orthotolidine is present with the chloramine when iodide is added and the iodine produced by the chloramine is immediately reduced back to iodide and acts as a catalyst in generating an amount of blue orthotolidine equivalent to the original chloramine present. Because of this catalytic effect, lesser amounts of iodide are required than in amperometric titration; this improves the separation of the monochloramine and dichloramine fractions.

b. Interference: When orthotolidine or any other chromogenic reagent is used to measure residual chlorine, strong oxidizing agents of any kind interfere. Such interferences include bromine, chlorine dioxide, iodine, manganic compounds, and ozone. However, the reduced forms of these compounds—bromide, chloride, iodide, manganous ion, and oxygen—do not interfere. Reducing agents such as ferrous compounds, hydrogen sulfide, and oxidizable organic matter do *not* interfere in the analytical method but may interfere in maintaining chlorine residuals by reducing the chlorine residual by reaction with the chlorine to produce chloride ion, that is, acting simply as chlorine demand.

Turbidity and color also interfere unless the background turbidity or color is compensated for by using a blank. Concentrations of 55 mg/l iron, 92 mg/l nitrite, and 6,000 mg/l chloride do not interfere. The interference of combined chlorine is insignificant in the determination of free chlorine except (as noted before) at high temperature and long waiting times. Manganic compounds produce up to stoichiometric interference but can be compensated for by

using a blank. In the presence of more than 10 μg/l manganic manganese, a blank is prepared by adding 5 ml sodium arsenite to a 100-ml sample. This sample is added to the reagents, as usual, and this blank is used as a reference in measuring the free chlorine present, either by zeroing the photometer with this blank or by using the blank as a reference when making color comparison.

If nitrogen trichloride is present, half reacts as free available chlorine but the remainder does not interfere in the monochloramine and dichloramine measurements. Many different organic chloramines are possible. The extent to which these organic chloramines interfere in the monochloramine or dichloramine steps depends on the nature of the organic compound; they may appear in either or both fractions.

c. Minimum detectable concentration: Approximately 10 μg/l free chlorine.

2. Apparatus

Colorimetric equipment: One of the following is required:

a. Filter photometer, providing a light path of 1 cm or longer for ≤1 mg/l free chlorine residual, or a light path from 1 to 10 mm for free chlorine residual >1.5; also equipped with a red filter having maximum transmission in the range of 600 to 650 nm.

b. Spectrophotometer, for use at 625 nm, providing a light path noted in the paragraph above.

3. Reagents

a. Chlorine-demand-free distilled water: Add sufficient chlorine to distilled water to destroy the ammonia and nitrite. The amount of chlorine required will be about 10 times the amount of ammonia nitrogen present; produce an initial residual of more than 1.0 mg/l free chlorine. Let the chlorinated distilled water stand overnight or longer; then expose to direct sunlight until all residual chlorine is discharged.

b. Neutral orthotolidine reagent: Add 5 ml conc HCl to 100 ml chlorine-demand-free distilled water. Add 10 ml of this acid solution, 20 mg mercuric chloride, $HgCl_2$, 30 mg disodium ethylenediamine tetraacetate dihydrate, also called (ethylenedinitrilo)-tetraacetic acid sodium salt, and 1.5 g orthotolidine dihydrochloride to chlorine-demand-free distilled water and dilute to 1 l. Store in a brown bottle or in the dark at room temperature. Protect at all times from direct sunlight. Use no longer than 6 months. Avoid contact with rubber. Do not let the temperature fall below 0 C because the resulting crystallization of orthotolidine can lead to deficient subsequent color development.

CAUTION: *Handle this chemical with extreme care. Never use a mouth pipet for dispensing this reagent, but rely on an automatic dropping or safety pipet to measure the necessary volumes. Avoid inhalation or exposure to the skin.*

c. Buffer-stabilizer reagent: Dissolve 34.4 g dipotassium hydrogen phosphate, K_2HPO_4, 12.6 g potassium dihydrogen phosphate, KH_2PO_4, and 8.0 g "Aerosol OT," 100% solid di(2-ethylhexyl)sulfosuccinate, in a solution of 500 ml chlorine-demand-free water and 200 ml diethylene glycol monobutyl ether. Dilute to 1 l with chlorine-demand-free water.

d. Potassium iodide solution: Dissolve

in the photometer tube or a 250-ml beaker on a magnetic stirrer. Mix the reagent slightly and add the sample to the reagents with gentle stirring. Measure the percent transmittance and convert to absorbance at 625 nm. The value obtained (*A*) from the calibration curve represents the free chlorine residual. To minimize possible interference from high concentrations of combined chlorine and high-temperature fading, complete mixing of the sample with the reagents and reading on the photometer within approximately 2 min.

c. Monochloramine: Return any portion used for measuring free chlorine in ¶4*b* to the sample. Add, with stirring, 0.5 ml KI solution to each 100-ml sample, or a similar ratio for other sample volumes. Again measure the transmittance of the residual free chlorine plus the monochloramine and obtain the value (*B*) from the calibration curve.

d. Dichloramine: Return any portion used for measuring the monochloramine in ¶4*c* to the sample. Add, with stirring, 1 ml H_2SO_4 solution to each 100-ml sample, or a similar ratio for other sample volumes. After 30 sec for color development add 1 ml sodium carbonate solution slowly with stirring or until a pure blue solution returns. Measure the transmittance of the total residual chlorine—free chlorine, monochloramine, and dichloramine—and obtain the value (*C*) from the calibration curve with a slight dilution correction.

e. Compensation for interferences: Compensate for the presence of natural color or turbidity as well as manganic compounds by adding 5 ml arsenite to 100 ml sample. Add this blank sample to the reagents as above. Use the color of

0.4 g KI in chlorine-demand-free distilled water and dilute to 100 ml. Store in a brown glass-stoppered bottle, preferably in a refrigerator. Discard when a yellow color develops.

e. Sulfuric acid solution: Cautiously add 4 ml conc H_2SO_4 to chlorine-demand-free distilled water and dilute to 100 ml.

f. Sodium carbonate solution: Dissolve 5 g Na_2CO_3 in chlorine-demand-free distilled water and dilute to 100 ml.

g. Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water and dilute to 1 l. (CAUTION: *Toxic—take care to avoid ingestion.*)

4. Procedure

a. Calibration of photometer: Construct a calibration curve by making dilutions of standardized hypochlorite solution prepared as directed under Chlorine Demand, Section 410A.3*a*. Take special precautions when diluting to low concentrations because of possible consumption of small amounts of chlorine by trace impurities. Use chlorine-demand-free water in making the dilutions. Expose all glassware to be used in the dilutions to water containing at least 10 mg/l of chlorine and leave it in contact for a few hours. Rinse with chlorine-demand-free water. Develop and measure the colors as described below for the sample.

b. Color development of free chlorine: Use 0.5 ml neutral orthotolidine and 0.5 ml stabilizer-buffer reagent with 10-ml samples; 5 ml neutral orthotolidine and 5 ml stabilizer-buffer reagent with 100 ml; and the same ratio for other volumes. Place the neutral orthotolidine and stabilizer-buffer mixture

the blank to set 100% transmittance or zero absorbance on the photometer. Measure all samples in relation to this blank. Read from the calibration curve the concentrations of chlorine present in the sample.

5. Calculation

mg/l free residual chlorine
$= A$, including ½ trichloramine if present

mg/l monochloramine $= B - A$, as mg/l Cl
mg/l dichloramine $= 1.03\ C - B$, as mg/l Cl
mg/l total chlorine $= 1.03\ C$, as mg/l Cl

6. Precision and Accuracy

See Tables 4509: I through IV preceding and the general introduction to Section 4509.

409 A. Iodometric Method I

1. General Discussion

a. Principle: Chlorine will liberate free iodine from potassium iodide solutions at pH 8 or less. The liberated iodine is titrated with a standard sol tion of sodium thiosulfate, with starch as the indicator. The reaction is preferably carried out at pH 3 to 4.

b. Interference: Although the neutral titration minimizes the interfering effect of ferric, manganic, and nitrite ions, the acid titration is preferred; it is most accurate for determination of total available residual chlorine. Use acetic acid for the acid titration; use sulfuric acid only when interfering substances are absent; *never use hydrochloric acid.*

c. Minimum detectable concentration: The minimum detectable concentration approximates 40 µg/l Cl if 0.01*N* sodium thiosulfate is used with a 500-ml sample.

2. Reagents

a. Acetic acid, conc (glacial).

b. Potassium iodide, KI, crystals.

c. Standard sodium thiosulfate, 0.1*N*: Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in 1 l freshly boiled distilled water and standardize the solution against potassium biniodate or potassium dichromate after at least 2 wk storage. Use boiled distilled water and add a few milliliters $CHCl_3$ to minimize bacterial decomposition of the thiosulfate solution.

Standardize the 0.1*N* sodium thiosulfate by one of the following procedures:

1) Biniodate method—Dissolve 3.249 g anhydrous potassium biniodate, $KH(IO_3)_2$, of primary standard quality,* in distilled water and dilute to 1,000 ml to yield a 0.1000*N* solution. Store in a glass-stoppered bottle.

To 80 ml distilled water, add, with constant stirring, 1 ml conc H_2SO_4, 10.00 ml 0.1000*N* $KH(IO_3)_2$ and 1 g KI. Titrate immediately with 0.1*N* $Na_2S_2O_3$ titrant until the yellow color of the liberated iodine is almost discharged. Add 1 ml starch indicator solution and continue titrating until the blue color disappears.

2) Dichromate method—Dissolve 4.904 g anhydrous potassium dichromate, $K_2Cr_2O_7$, of primary standard quality, in distilled water and dilute to 1,000 ml to yield a 0.1000*N* solution. Store in a glass-stoppered bottle.

Proceed as in the biniodate method, with the following exceptions: Substitute 10.00 ml 0.1000*N* $K_2Cr_2O_7$ for the $KH(IO_3)_2$ and let the reaction mixture stand 6 min in the dark before titrating with the 0.1*N* $Na_2S_2O_3$ titrant.

$$\text{Normality } Na_2S_2O_3 = \frac{1}{\text{ml } Na_2S_2O_3 \text{ consumed}}$$

d. Standard sodium thiosulfate titrant, 0.01*N* or 0.025*N*: Improve the stability of 0.01*N* or 0.025*N* $Na_2S_2O_3$ by diluting an aged 0.1*N* solution, made as directed above, with freshly boiled distilled water. Add a few milliliters $CHCl_3$ or 0.4 g sodium borate and 10 mg mercuric iodide/l solution. For accurate work, standardize this solution daily in accordance with the directions given above, using 0.01*N* or 0.025*N* $KH(IO_3)_2$ or $K_2Cr_2O_7$. To speed up

* G. F. Smith Chemical Company, Columbus, Ohio, or equivalent.

operations where many samples must be titrated use an automatic buret of a type in which rubber does not come in contact with the solution. Standard sodium thiosulfate titrants, 0.0100*N* and 0.0250*N*, are equivalent, respectively, to 354.5 μg and 886.3 μg available Cl/1.00 ml.

e. Starch indicator solution: To 5 g starch (potato, arrowroot, or soluble), add a little cold water and grind in a mortar to a thin paste. Pour into 1 l of boiling distilled water, stir, and let settle overnight. Use the clear supernate. Preserve with 1.25 g salicylic acid, 4 g zinc chloride, or a combination of 4 g sodium propionate and 2 g sodium azide/l starch solution. Some commercial starch substitutes are satisfactory.

f. Standard iodine, 0.1N: Refer to Method C, ¶3*a*2).

g. Dilute standard iodine, 0.0282N: Refer to Method C, ¶3*a*3).

3. Procedure

a. Volume of sample: Select a sample volume that will require no more than 20 ml 0.01*N* $Na_2S_2O_3$. Thus, for residual chlorine concentrations of 1 mg/l or less, take a 1,000-ml sample; for a chlorine range of 1 to 10 mg/l, a 500-ml sample; and above 10 mg/l, proportionately less sample.

b. Preparation for titration: Place 5 ml acetic acid, or enough to reduce the pH to between 3.0 and 4.0, in a flask or white porcelain casserole. Add about 1 g KI estimated on a spatula. Pour in the sample and mix with a stirring rod. Add chlorine-demand-free distilled water if a larger volume is preferred for titration.

c. Titration: Titrate away from direct sunlight. Add 0.025*N* or 0.01*N* thiosulfate from a buret until the yellow color of the liberated iodine is almost discharged. Add 1 ml starch solution and titrate until the blue color is discharged.

If the titration is made with 0.025*N* thiosulfate instead of 0.01, then, with a 1-l sample, 1 drop is equivalent to about 50 μg/l. It is not possible to discern the end point with greater accuracy. If a 500-ml sample is titrated, 1 drop will correspond to about 100 μg/l, which is within the limit of sensitivity. Hence, use of 0.025*N* solution is acceptable. Many laboratories have this on hand.

d. Blank titration: Correct the result of the sample titration by determining the blank contributed by such reagent impurities as: (*a*) the free iodine or iodate in the potassium iodide that liberates extra iodine; or (*b*) the traces of reducing agents that might reduce some of the iodine liberated.

Take a volume of distilled water corresponding to the sample used for titration in ¶s 3*a-c*, add 5 ml acetic acid, 1 g KI, and 1 ml starch solution. Perform either Blank Titration A or B, whichever applies.

1) Blank titration A—If a blue color develops, titrate with 0.01*N* or 0.025*N* sodium thiosulfate to the disappearance of the blue and record the result.

2) Blank Titration B—If no blue color occurs, titrate with 0.0282*N* iodine solution until a blue color appears. Back-titrate with 0.01*N* or 0.025*N* sodium thiosulfate and record the difference as Titration B.

Before calculating the chlorine, subtract Blank Titration A from the sample titration; or, if necessary, add the net equivalent value of Blank Titration B.

ATMOSPHERIC EMISSIONS FROM HYDROCHLORIC ACID MANUFACTURING PROCESSES

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and
Public Health Service

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APPENDIX A. SAMPLING AND ANALYTICAL TECHNIQUES

DETERMINATION OF HYDROGEN CHLORIDE AND CHLORINE IN STACK GAS.

The method discussed herein is used to determine the presence of hydrogen chloride in the stack gases from hydrochloric acid manufacturing processes. Samples are collected from the gas stream in either midget impingers or a grab-sampling bottle containing sodium hydroxide, and hydrogen chloride is determined by the Volhard titration.[9] If chlorine is suspected to be present in the stack emission, another sample is collected in a similar manner, except that a known quantity of alkaline arsenite absorbing reagent is substituted for sodium hydroxide. Chlorine is reduced to chloride by arsenite, and is measured by titration of the unconsumed arsenite with standard iodine solution. Total chloride content of the sample is determined by the Volhard titration. Hydrogen chloride concentration is calculated by subtraction of the chlorine concentration from total chloride concentration. This method is applicable in determining hydrogen chloride and chlorine concentrations ranging from 10 ppm to percentage quantities.

Reagents

All chemicals must be ACS analytical reagent-grade.

Water

Deionized or distilled water.

Absorbing Reagents:

1. Sodium hydroxide (1 N) – Dissolve 40 g of sodium hydroxide in water and dilute to 1 liter. This reagent is used when the stack gas concentration of hydrogen chloride is suspected to be less than 1,000 ppm.
2. Sodium hydroxide (2.5 N) – Dissolve 100 g of sodium hydroxide in water and dilute to 1 liter. This reagent is used when the stack gas concentration of hydrogen chloride is suspected to be greater than 1,000 ppm.
3. Alkaline arsenite (1 N NaOH and 0.1 N $NaAsO_2$) Dissolve 40 g of NaOH and 6.5 g of sodium arsenite ($NaAsO_2$) in water and dilute to 1 liter in a volumetric flask. This reagent is used when the stack gas concentration of hydrogen chloride and Cl_2 is suspected to be less than 1,000 ppm.
4. Alkaline arsenite (2.5 N NaOH and 0.5 N $NaAsO_2$) Dissolve 100 g of NaOH and 32.5 g of $NaAsO_2$ in water and dilute to 1 liter in a volumetric flask. This reagent is used when the stack gas concentration of hydrogen chloride and Cl_2 is suspected to be greater than 1,000 ppm.

Ferric Alum Indicator

Dissolve 28.0 g of ferric ammonium sulfate $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 70 ml of hot water. Cool, filter, add 10 ml of concentrated nitric acid (HNO_3), and dilute to 100 ml in a volumetric flask.

Nitric Acid (8N)

Prepare NO_X-free nitric acid by adding 100 ml of HNO_3 to 100 ml of water and boiling in a flask until the solution is colorless. Store in a glass reagent bottle.

Nitrobenzene

Reagent grade.

Sodium Chloride (Primary Standards)

1. NaCl (0.1 N) – Dissolve 5.846 g of dried sodium chloride (NaCl) in water and dilute to 1 liter in a volumetric flask.
2. NaCl (0.01 N) – Dissolve 0.5846 g of dried NaCl in water and dilute to 1 liter in a volumetric flask, or dilute 100 ml of 0.1 N NaCl to 1 liter.

Ammonium Thiocyanate

1. NH_4CNS (0.1 N) – Dissolve 8 g of NH_4CNS in water and dilute to 1 liter in a volumetric flask.
2. NH_4CNS (0.01 N) – Dilute 100 ml of 0.1 N NH_4CNS to 1 liter in a volumetric flask, or dissolve 0.8 g NH_4CNS in 1 liter of distilled water.

Silver Nitrate

1. $AgNO_3$ (0.1 N) – Dissolve 17.0 g of silver nitrate ($AgNO_3$) in water and dilute to 1 liter in a volumetric flask. Transfer to an amber reagent bottle. Standardize this solution against 0.1 N NaCl solution, according to the Volhard titration.[9]
2. $AgNO_3$ (0.01 N) – Dissolve 1.7 g of $AgNO_3$ in water and dilute to 1 liter in a volumetric flask. Transfer to an amber reagent bottle. Standardize this solution against standard 0.01 N NaCl solution, according to the Volhard titration.

Starch Solution (Iodine Indicator), 1.0%

Make a thin paste of 1 g of soluble starch in cold water and pour into 100 ml of boiling water while stirring. Boil for a few minutes. Store in a glass-stoppered bottle.

Standard Iodine Solution (0.1 N)

Dissolve 12.69 g of resublimed iodine (I_2) in 25 ml of a solution containing 15 g of iodate-free potassium iodine (KI); dilute to 1 liter in a volumetric flask. Standardize this solution against a standard thiosulfate solution using starch as an indicator. This solution should be stored in an amber reagent bottle and refrigerated when not in use.

Apparatus

(See Figures A-1 and A-2)

Sampling Probe

10-mm Pyrex® glass tubing of any convenient length.

Filter

A small fiberglass filter may be fitted to the probe inlet when particulate matter is present in the gas stream being sampled.

Heating Tape

Used to heat probe.

Variable Voltage Regulator

Used to regulate probe heating.

Dry Gas Meter

Readable to the nearest 0.01 cubic foot.

Vacuum Pump

A diaphragm-type pump rated at 15 liters per minute.

Absorbers

1. Midget impinger -- An all-glass midget impinger sampling train capable of removing hydrogen chloride and chlorine from a gas sample may be used when sampling stack gas suspected of containing less than 0.1 percent hydrogen chloride or chlorine.

   The sampling train should consist of a probe, four midget impingers, a gas drying tube, a vacuum pump, and a flow meter, as illustrated in Figure A-1.

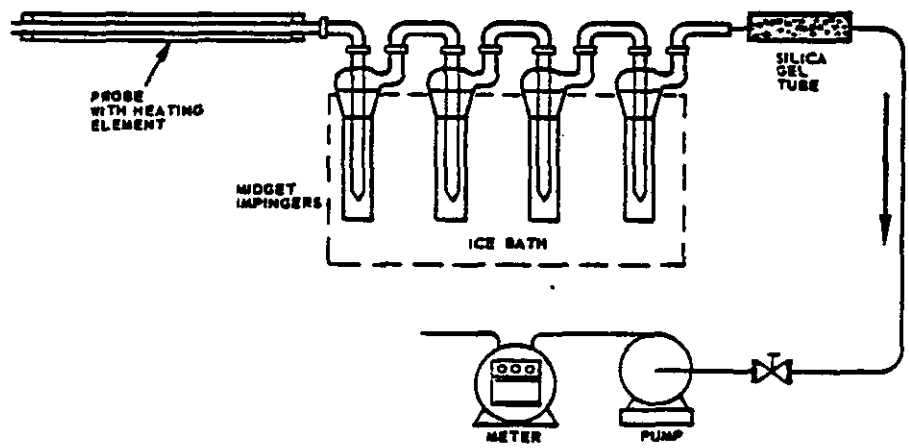


Figure A-1. Impinger gas sampling train.

A Pyrex® glass tube serves as the probe. It should have a ball joint on the outlet to which other glassware can be easily connected. The probe should be wrapped with nickel-chromium heating wire, insulated with glass wool and installed into a protective 1-inch-diameter stainless steel

tube. During sampling, the heating wire is connected to a calibrated, variable transformer to maintain a temperature of up to 250° F on the probe wall. A heating tape may also be used to heat the probe.

Four midget glass impingers are connected in series to the probe outlet with glass ball joints. The first three impingers each contain 15 ml of absorbing reagent. The fourth impinger is left dry to catch any material that is carried over from the other impingers. All four impingers are cooled in an icewater bath.

Gases leaving the impingers are dried as they pass through a tube of silica gel. They then are pumped to the airtight vacuum pump and gas meter. Sampling rates are regulated by using a valve to adjust the flow through the pump.

2. Grab-sampling bottle — An accurately calibrated 2-liter glass bottle equipped with Teflon® stopcocks (Figure A-2) should be used when sampling percentage quantities of hydrogen chloride or chlorine. Absorbing reagent is added to the grab-sample bottle after the sample has been collected.

Figure A-2. Grab sample bottle.

Dispenser (Absorbing Reagent)

A 100-milliliter round-bottom flask, modified with a Teflon® stopcock and ball joint extension (see Figure A-3) is used as a dispenser for absorbing reagent. It is used to add reagent to the grab-sampling bottle after the sample has been collected.

Analytical Procedure

Collection of Samples

1. Midget impinger train:
   Pipet 15 ml of absorbing reagent into each of the three midget impingers. Heat probe to prevent moisture condensation. Start pump and sample at a rate of 1 to 3 liters per minute for at least 60 minutes.
2. Grab sampling:
   Flush probe and draw about 20 liters of gas through the sample bottle. Pipet 25 ml of absorbing reagent into the dispenser and add to the grab-sample bottle following collection of the sample. Shake bottle thoroughly for about 2 minutes to insure complete absorption.
3. Transfer the contents of the impingers or grab-sampling bottle to a sample container, such as a polyethylene bottle, containing deionized or distilled water.

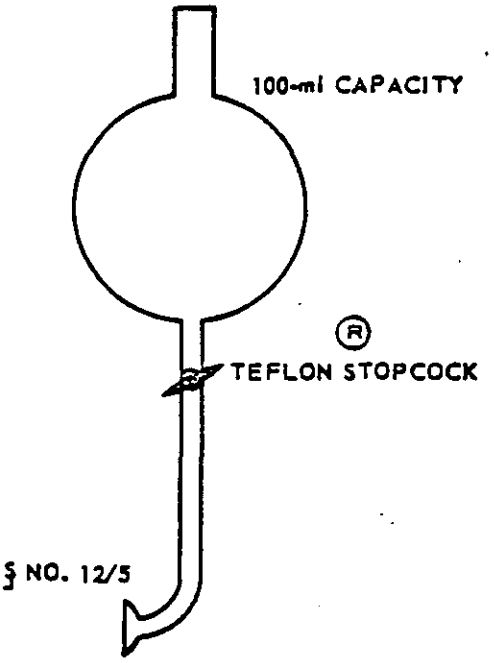


Figure A-3. Burette for adding absorbing reagent.

Sample Preparation

Measure the actual volume of the liquid sample or adjust to a known volume using a graduated cylinder or volumetric flask.

Procedure A

Analysis of Hydrogen Chloride

Pipet an aliquot of the sample into a 250-ml Erlenmeyer flask. Add 25 ml of water, 5 ml of nitric acid and swirl to mix. Depending on chloride content, add 0.1 N or 0.01 N silver nitrate from a buret until the silver chloride formed begins to coagulate. When coagulation occurs, add an additional 5 ml of silver nitrate. Add 3 ml of nitrobenzene and 2 ml of ferric indicator, then back-titrate with 0.1 N or 0.01 N ammonium thiocyanate until the first appearance of the reddish-brown $Fe(CNS)_6^{-3}$ complex. A blank determination for chloride in the absorbing reagent should be run simultaneously and subtracted from the sample results. From the titer of NH_4CNS solution, as determined previously by titration against standard $AgNO_3$ solution using ferric alum as an indicator, calculate the net volume of $AgNO_3$ required for precipitation of the chloride.

Calculations

Compute the number of milligrams of hydrogen chloride present in the sample by the following equation:

$$C = HCl, mg = \text{net ml } AgNO_3 \times T \times F$$

T = hydrogen chloride equivalent of standard $AgNO_3$

(T = 3.65 mg HCl/ml for 0.1 N $AgNO_3$)

(T = 0.365 mg HCl/ml for 0.01 N $AgNO_3$)

$$F = \frac{\text{sample volume, ml}}{\text{aliquot volume, ml}}$$

Convert the volume of gas sampled to the volume at standard conditions of 70° F and 29.92 in. Hg.

$$V_s = V \times \frac{P}{29.92} \times \frac{530^\circ R}{(t + 460^\circ R)}$$

V = volume of gas sampled, as measured on dry gas meter or equal to volume of grab sample bottle—liters
P = barometric pressure (in. Hg) or absolute pressure at gas meter
t = average temperature of gas sampled, ° R

Determine the concentration of hydrogen chloride in the gas sample by the following formula:

$$\text{ppm HCl} = \frac{(662)\ (C)}{V_s}$$

662 = μl/mg of HCl at 70° F and 29.92 in. Hg
C = concentration of HCl, mg
V_s = volume of gas sampled in liters at 70° F and 29.92 in. Hg

Procedure B

Analysis of Hydrogen Chloride in the Presence of Chlorine

Pipet an aliquot of the sample into a 250-ml Erlenmeyer flask and proceed with the Volhard titration for total chlorides as described under Procedure A. A blank determination for chloride in the absorbing reagent (alkaline-arsenite reagent) should be run simultaneously and subtracted from the sample results.

Pipet another aliquot of the sample into a 250-ml Erlenmeyer flask. Add a few drops of phenolphthalein indicator, neutralize carefully with concentrated hydrochloric acid, and cool. Add sufficient solid sodium bicarbonate ($NaHCO_3$) to neutralize any excess hydrochloric acid, then add 2 to 3 g more. Add 2 ml of starch indicator and titrate with 0.1 N iodine solution to the blue endpoint. For the reagent blank, determine the number of ml of 0.1 N I_2 required to titrate 25 ml of alkaline-arsenite absorbing reagent, as described above.

Calculations

Determine the number of milliliters of 0.1 N I_2 required to titrate the entire sample by the following formula:

$$\text{Sample (ml 0.1 N } I_2\text{)} = \text{(ml of 0.1 N } I_2 \text{ for aliquot)} \times F$$

$$F = \frac{\text{volume of sample, ml}}{\text{volume of aliquot, ml}}$$

$$Cl_2, \text{ mg} = \text{Blank (ml 0.1 N } I_2\text{)} - \text{Sample (ml 0.1 N } I_2\text{)} \times 3.546$$

3.546 = chlorine equivalent of 0.1 N I_2, mg

Convert the volume of gas sampled at standard conditions of 70° F, 29.92 in. Hg, using the formula in Procedure A. Calculate the concentration of Cl_2 in the sample using the following formula:

$$\text{ppm } Cl_2 \text{ by volume} = \frac{(340)(C)}{V_s}$$

340 = 1/mg of Cl_2 at 70° F and 29.92 in. Hg

C = concentration of Cl_2, mg
V_s = volume of gas sampled at standard conditions, liters

Determine the number of milligrams of hydrogen chloride present in the sample by subtracting the number of milligrams of chlorine present, as determined by the iodine titration, from the total number of milligrams of chloride present as determined by the Volhard titration. Calculate the concentration of hydrogen chloride in parts per million using the formula in Procedure A.

Total stack gas volume must also be measured in order to determine the emissions on a weight basis. This may be done by measuring the gas velocity with a pitot tube.

The following equations are used to determine gas velocity and gas volume:

$$V_S = 172\,(F)\,(\sqrt{\Delta P \text{ avg}})\left[\sqrt{T_S} \times \frac{29.92}{P_S} \times \frac{29.0}{M_S}\right]$$

V_S = velocity in feet per minute at stack conditions
F = pitot tube–correction factor (0.85 for type S)
M_S = molecular weight of stack gas
T_S = average stack gas temperature ° R
P_S = average stack gas pressure, in. Hg
ΔP = pitot tube manometer reading, in. water

The total stack gas volume is then:

$$Q_s = (V_S)(A)\left[\frac{P_S}{T_S}\right] \quad (17.4)$$

A = stack area, sq ft
Q_s = gas volume, ft^3/min at 70° F and 29.92 in. Hg

The emissions on a weight per hour basis may then be determined by the following equation:

$$W = ppm \times 10^{-6} \times Q_s \times 60 \times \frac{\text{mol wt}}{387}$$

W = emissions, lb/hr
ppm = parts per million by volume of contaminant
Q_s = stack gas flow rate, scfm
mol wt = molecular weight of contaminant
Cl_2 = 70.92 HCl = 36.46
387 = volume (ft^3) occupied by 1 lb mol at 70° F and 29.92 in. Hg

Discussion of Procedure:

The estimated error for the combined sampling and analytical procedure is ±10 percent. The precision of the analytical methods is ±2 percent on standard samples containing NaCl and $NaAsO_2$.

The usual volumetric errors are encountered with the Volhard titration. Premature endpoints may occur if the NH_4CNS is not added by drops near the equivalence point and the solution shaken before the next addition. Nitrobenzene is used to effectively remove AgCl by forming an oily coating on the precipitate and preventing reaction with the thiocyanate.[10] Bivalent mercury, which forms a stable complexion with the thiocyanate, and substances that form insoluble silver salts interfere in the analysis and must be absent from the sample. Titration should be made at temperatures below 25° C, as is customary in other titrations with thiocyanate.[11]

The chief source of error in the iodine titration of arsenite is the failure to use sufficient bicarbonate to neutralize all the excess acid. If insufficient bicarbonate is added, serious errors may be incurred because of a fading endpoint. A reducing agent such as sulfur dioxide and oxidizing agents such as iodine, nitrogen dioxide, and ozone interfere with the iodine titration and yield high results when present in the stack gas sample.

ACID MIST SAMPLING.

The sampling apparatus is made up of a probe, a cyclone, a filter, four impingers, a dry gas meter, a vacuum pump, and a flow meter, as shown in Figure A-4.[12,13]

APPENDIX B

CHLORIDE PROCEDURES

DETERMINATION OF HYDROCHLORIC ACID EMISSIONS FROM STATIONARY S. ..ES

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from the stack and the hydrochloric acid content is measured using the mercuric nitrate titration method.

1.2 Applicability. This method is applicable for the determination of hydrochloric acid emissions from stationary sources. The upper limit of the method has not been established though samples containing 4000 parts per million hydrochloric acid have been efficiently collected and determined using two midget impingers each containing 15 milliliters of 0.1N sodium hydroxide.

Possible interferences are metal ions (usually Cu, Fe, Ni, Mg, and V) and the sulfite ion. These tend to mask the analysis endpoint. A strong acid type cationic exchange resin has been demonstrated to remove interfering metal ions satisfactorily. When gas streams containing SO_2 in excess of 300 parts per million are sampled, the SO_2 can be effectively removed by treating the sample with 3 percent hydrogen peroxide.

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 1 and the component parts are discussed below.

2.1.1 Probe. A five-foot, borosilicate glass or Teflon-lined probe is used. The inlet is packed with glass wool to remove particulate matter. The probe must have a heating system to prevent water condensation while sampling.

2.1.2 Midget Impingers. Four midget impingers are connected

in series with leak-free glass connectors. Silicone grease may be used to insure a tight seal.

2.1.3 Glass Wool. Borosilicate or quartz.

2.1.4 Temperature Gauge. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1°C (2°F).

2.1.5 Drying Tube. Tube packed with 6-to 16-mesh indicating type silica gel or equivalent to dry the gas sample and to protect the dry gas meter and pump.

2.1.6 Valve. Needle valve, to regulate sample gas flow rate.

2.1.7 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 4 percent of the selected flow rate of 2 l/min.

2.1.9 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume to three decimal places in cubic feet, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring temperature to within 3°C (5.4°F).

2.1.10 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in Hg).

2.1.11 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge, to be used for leak check of the sampling train.

2.2 Sample Recovery. The following equipment is needed for sample recovery.

2.2.1 Storage Containers. Leak-free 100 ml polyethylene or glass bottles.

2.2.2 Wash Bottle. Polyethylene or glass.

2.3 Analysis. Volumetric glassware should be class A only.

2.3.1 Erlenmeyer Flask. 125 ml.

2.3.2 Graduated Burette. 25 ml.

2.3.3 Volumetric Pipet. 1 ml.

2.3.4 Volumetric Flasks. 100 ml, one for each sample.

2.3.5 Small Funnel. For transferring sample.

2.3.6 Magnetic Stirrer.

2.3.7 Magnetic Stirring Bar.

2.3.8 Dropping Pipet or Dropper.

2.3.9 Filter Paper. Whatman No. 40.

3. Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.1 Sampling.

3.1.1 Water. Triple deionized, distilled to conform to ASTM Specification D 1193-74, Type 3.

3.1.2 Sodium Hydroxide, 0.1 N. Dissolve 4g NaOH in deionized, distilled water and dilute to 1 liter.

3.1.3 Hydrogen Peroxide, 3 Percent. Dilute 30 percent hydrogen peroxide 1:9 (V/V) with deionized, distilled water (15 ml is needed per sample). Prepare fresh daily.

3.2 Sample Recovery.

3.2.1 Sodium Hydroxide, 0.1N. As in 3.1.2.

3.2.2 Sodium Hydroxide, 0.05 N. Dissolve 2g NaOH in deionized, distilled water and dilute to 1 liter.

B 3.3 Analysis.

3.3.1 Mercuric Nitrate Solution, 0.01 N. Dissolve 1.63 g mercuric nitrate in deionized, distilled water and dilute to 1 liter. Shake well. Transfer to an amber colored reagent bottle. Standardize this solution according to the procedure in Section 5.5.

C 3.3.2 Bromophenol-Diphenylcarbazone Indicator. Dissolve 0.005 g bromophenol blue and 0.5 g diphenyl carbazone in 75 ml pure ethanol, then dilute to 100 ml therewith.

3.3.3 0.05 N HNO_3. Dilute 1.6 ml concentrated HNO_3 (69 percent) to 500 ml with distilled, deionized water.

3.3.4 0.0100 N NaCl Solution. Dissolve 0.584 g NaCl in deionized, distilled water and dilute to 1 liter.

D 3.3.5 Cation Exchange Resin. Rexyn 101 H (Fisher Scientific)[1] is one type that has been used successfully. The resin column is prepared as follows:

A small amount of the fresh resin is poured into a 250 ml beaker containing 100 ml distilled water and allowed to soak for 30 minutes. A 25 ml buret is packed at the bottom end with a small portion of glass wool to prevent plugging the tip with resin particles. The buret is then filled approximately half-full with distilled water, and the wetted resin is poured in until it reaches the 11 ml graduation mark. Care must be taken to maintain

the water level at least one inch above the resin level at all times to prevent resin channelling. The buret is filled to the 0 ml graduation mark with distilled water, and the stopcock is opened to allow the column to drain until the final water level is at the 10 ml graduation mark. This rinsing process is repeated several times and the rinses discarded. A column blank is determined by passing a 10 ml aliquot of distilled water through the column followed by a 10 ml rinse. The blank volume is then adjusted to 100 ml with distilled water and titrated with standard mercuric nitrate. One drop of titrant should be sufficient to reach the endpoint.

4. Procedure

4.1 Sampling

4.1.1 Preparation of Collection Train. Measure 15 ml of 0.1 N sodium hydroxide into each of the first two midget impingers and 15 ml of 3 percent hydrogen peroxide into the third one. Leave the final impinger dry. Assemble the train as in Figure 1. Adjust probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

4.1.2 Leak-Check Procedure. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak check procedure is as follows:

Temporarily attach a suitable (e.g., 0-40 cc/min) rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

Note: Carefully release the probe inlet plug before turning off the pump.

It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm (10 in.) Hg, plug or pinch off the outlet of the flow meter and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

Other leak-check procedures may be used, subject to the approval of the Administrator, U. S. Environmental Protection Agency.

4.1.3 Sample Collection. Record the initial dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 2.0 liters/min as indicated by the rotameter. Maintain this constant rate (± 10 percent) during the entire sample run. Take readings (dry gas meter, temperatures at dry gas meter and at impinger outlet and rate meter) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20°C (68°F) or less. At the conclusion of each run, turn off the pump, remove probe from the stack, and

record the final readings. Conduct a leak-check as in Section 4.1.2. (This leak-check is mandatory). If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage. Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate.

4.2 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the hydrogen peroxide SO_2 scrubber impinger. Pour the contents of the other impingers containing sodium hydroxide into a leak-free polyethylene or glass bottle for shipment. Rinse the impingers and the connecting tubes with deionized, distilled water, and add the washings to the same storage container. The glass wool probe plug is recovered and placed in a second storage container. The probe is rinse with 25 ml distilled water into a second storage container. The probe is rinsed 25 ml distilled water into a third storage container and marked accordingly. Seal, mark the fluid level, and identify all containers.

4.3 Sample Analysis. Note level of liquid in each container, and confirm whether any sample was lost during shipment; note this on analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

Using a small funnel, the contents of each sample container are quantitatively transferred to separate 100 ml volumetric flasks. The probe wash is filtered through Whatman Number 40 paper into a flask. The probe plug is rinsed three times with water and likewise filtered into another flask. Each flask is diluted to the mark with deionized, distilled water.

An aliquot of one out of every five samples is passed through a cationic exchange resin (prepared as in Section 3.3.5) and compared to that of untreated samples to see if interfering metal ions are present. If values differ by more than 1 percent, an aliquot of all samples should be passed through the resin prior to the analysis. To oxidize any SO_2 present, add and mix 2 ml 3 percent hydrogen peroxide solution per 100 ml sample.

Before analysis, the pH of the sample must be adjusted to 3.2 - 3.4. Pour 25 ml of the 100 ml sample into a 125 ml Erlenmeyer flask and add 5 drops of bromophenol/diphenyl carbazone while stirring the sample continuously using a magnetic stirring bar. If the sample is initially alkaline, it will turn blue or red in color after addition of the indicator. In this case, add 0.1 N nitric acid dropwise until the sample just turns yellow in color. Then add an additional 1.0 ml of 0.05 N nitric acid to bring the pH to 3.2 - 3.4. If the sample is initially acidic, the solution will turn yellow after addition of the indicator. In this case, add 0.1 N sodium hydroxide dropwise until the sample turns blue in color. Then add 0.05 N nitric acid dropwise until the sample just turns yellow. Add an additional 1.0 ml of 0.05 N nitric acid to bring the sample to the proper pH of 3.2 - 3.4. After the pH is adjusted, titrate the sample with standard 0.01 N mercuric nitrate until the first appearance of a violet color which persists for several minutes with continuous stirring. Repeat and average the titration volumes. Run a blank with each series of samples.

5. Calibration

5.1 Metering System. Before its initial use and after each field test series, leak check the metering system as described in Method 6,

Section 5.1.

5.2 Thermometers. Calibrate against mercury-in-glass thermometer.

5.3 Rotameter. The rotameter need not be calibrated but should be kept clean according to manufacturer's instructions.

5.4 Barometer. Calibrate against mercury barometer.

5.5 Mercuric Nitrate Solution. Standardize the mercuric nitrate solution by titrating against triplicate aliquots of 0.0100 N standard NaCl solution.

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

6.1 Nomenclature

C_{HCl} = Concentration of hydrogen chloride, dry basis corrected to standard conditions, mg/dscm (lb/dscf).

N = Normality of mercuric nitrate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V_{soln} = Total volume of solution in which the hydrochloric acid sample is contained, 100 ml.

V_t = Volume of mercuric nitrate titrant used for the sample, ml (average of replicate titrations).

V_{tm} = Volume of mercuric nitrate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

70.90 = Equivalent weight of hydrochloric acid.

6.2 Dry sample gas volume, corrected to standard conditions.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) = K_1 Y \frac{V_m P_{bar}}{T_m}$$

Equation 6-1

Where:

K_1 = 0.3858 °K/mm Hg for metric units.

= 17.64 °R/in. Hg for English units.

6.3 Hydrochloric acid concentration.

$$C_{HCl} = K_2 \frac{(V_t - V_{tm})\left(\frac{V_{soln}}{V_a}\right) N}{V_{m(std)}}$$

Equation 6-2

Where:

K_2 = 70.90 mg/meq. for metric units

= 1.563×10^{-4} lb/meq. for English units.

7. Bibliography

1. Cheney, J., C. Fortune, and R. Rollins. Report on the Development and Evaluation of Stationary Source Hydrochloric Acid Emissions Measurement Methodology. U. S. Environmental Protection Agency, Stationary Source Emissions Research Branch. Research Triangle Park, N. C. December, 1976.

2. Rom, J. J. Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Office of Air Programs, Environmental Protection Agency. Research Triangle Park, N. C. APTD-0576. March, 1972.

3. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, Pa. 1974. pp. 40-42.

[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

Standard Methods
For the Examination of Water and Wastewater

FOURTEENTH EDITION

Prepared and published jointly by:
AMERICAN PUBLIC HEALTH ASSOCIATION
AMERICAN WATER WORKS ASSOCIATION
WATER POLLUTION CONTROL FEDERATION

Publication Office:
American Public Health Association
1015 Eighteenth Street NW
Washington, DC 20036

408 CHLORIDE

Chloride, in the form of Cl ion, is one of the major inorganic anions in water and wastewater. In potable water, the salty taste produced by chloride concentrations is variable and dependent on the chemical composition of the water. Some waters containing 250 mg/l chloride may have a detectable salty taste if the cation is sodium. On the other hand, the typical salty taste may be absent in waters containing as much as 1,000 mg/l when the predominant cations are calcium and magnesium.

The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system. Along the sea coast, chloride may be present in high concentrations because of leakage of salt water into the sewerage system. It may also be increased by industrial processes.

A high chloride content harms metallic pipes and structures, as well as agricultural plants.

Selection of method: Four methods are presented for the determination of chlorides. Since the first two are similar in most respects, selection is largely a matter of preference. The argentometric method (A) is suitable for use in relatively clear waters when 0.15 to 10 mg Cl are present in the portion of sample titrated. The mercuric nitrate method (B) has an easier end point. The potentiometric method (C) is suitable for colored or turbid samples in which color-indicated end points might be difficult to observe. The potentiometric method can be used without a pretreatment step for samples containing ferric ions (if not present in an amount greater than the chloride concentration), chromic phosphate, and ferrous and other heavy metal ions. The ferricyanide method, given in Part 602, is an automated modification which, although used routinely by many laboratories, is listed for the first time as a tentative method.

408 A. Argentometric Method

1. General Discussion

a. Principle: In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

b. Interference: Substances in amounts normally found in potable waters will not interfere. Bromide, iodide, and cyanide register as equivalent chloride concentrations. Sulfide, thiosulfate, and sulfite ions interfere but can be removed by treatment with hydrogen peroxide. Orthophosphate in excess of 25 mg/l interferes by precipitation as silver phosphate. Iron in excess of 10 mg/l interferes by masking the end point.

2. Reagents

a. Chloride-free water: If necessary, use redistilled or deionized distilled water.

b. Potassium chromate indicator solution: Dissolve 50 g K_2CrO_4 in a little distilled water. Add silver nitrate solution until a definite red precipitate is formed. Let stand 12 hr, filter, and dilute to 1 l with distilled water.

c. Standard silver nitrate titrant, 0.0141N: dissolve 2.395 g $AgNO_3$ in distilled water and dilute to 1,000 ml. Standardize against 0.0141*N* NaCl by the procedure described in ¶3*b* below. Store in a brown bottle. Standard silver nitrate solution 0.0141*N*=500 μg Cl/1.00 ml.

d. Standard sodium chloride, 0.0141N: Dissolve 824.1 mg NaCl (dried at 140 C) in chloride-free water and dilute to 1,000 ml; 1.00 ml=500 μg Cl.

e. Special reagents for removal of interference:

1) *Aluminum hydroxide suspension:* Dissolve 125 g aluminum potassium sulfate or aluminum ammonium sulfate, $AlK(SO_4)_2 \cdot 12H_2O$ or $AlNH_4(SO_4)_2 \cdot 12H_2O$, in 1 l distilled water. Warm to 60 C and add 55 ml conc NH_4OH slowly with stirring. Let stand about 1 hr, transfer the mixture to a large bottle, and wash the precipitate by successive additions, with thorough mixing and decantations of distilled water, until free from chloride. When freshly prepared, the suspension occupies a volume of approximately 1 l.

2) *Phenolphthalein indicator solution.*

3) *Sodium hydroxide,* NaOH, 1*N*.

4) *Sulfuric acid,* H_2SO_4, 1*N*.

5) *Hydrogen peroxide,* H_2O_2, 30%.

3. Procedure

a. Sample preparation: Use a 100-ml sample or a suitable portion diluted to 100 ml.

If the sample is highly colored, add 3 ml $Al(OH)_3$ suspension, mix, let settle, filter, wash, and combine filtrate and washing.

If sulfide, sulfite, or thiosulfate is present, add 1 ml H_2O_2 and stir for 1 min.

b. Titration: Titrate samples in the pH range 7 to 10 directly. Adjust samples not in this range with H_2SO_4 or NaOH solution. Add 1.0 ml K_2CrO_4 indicator solution. Titrate with standard silver nitrate titrant to a pinkish yellow

end point. Be consistent in end-point recognition.

Standardize the silver nitrate titrant and establish the reagent blank value by the titration method outlined above. A blank of 0.2 to 0.3 ml is usual for the method.

4. Calculation

$$\text{mg/l Cl} = \frac{(A-B)\times N\times 35.450}{\text{ml sample}}$$

where A = ml titration for sample, B = ml titration for blank, and N = normality of $AgNO_3$.

$$\text{mg/l NaCl} = \text{mg/l Cl} \times 1.65$$

5. Precision and Accuracy

A synthetic unknown sample containing 241 mg/l chloride, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 1.1 mg/l nitrate N, 0.25 mg/l nitrite N, 259 mg/l sulfate, and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 41 laboratories by the argentometric method, with a relative standard deviation of 4.2% and a relative error of 1.7%.

408 B. Mercuric Nitrate Method*

1. General Discussion

a. Principle: Chloride can be titrated with mercuric nitrate because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbazone indicates the end point of this titration by formation of a purple complex with the excess mercuric ions. The error in titration is about 1% of the volume of titrant used per change of 0.1 pH unit in the pH range 2.1 to 2.8. Because exact pH adjustment is not feasible except by use of a pH meter, it is felt that keeping within a range of ±0.1 pH unit is sufficient for most water analyses. Therefore, in this method, a specific mixture of nitric acid and diphenylcarbazone is added to a water sample, adjusting the pH of most potable waters to pH 2.5±0.1. A third substance in this alcoholic mixture, xylene cyanol FF, is used as a pH indicator and as a background color to facilitate end-point detection. The introduction of 10 mg sodium bicarbonate to both the blank and the standard titration provides a pH of 2.5±0.1 when 1.0 ml indicator-acidifier reagent [¶2d1)] is added. Increasing the strength of the titrant and modifying the indicator mixture enable determination of the higher chloride concentrations common in wastewater.

b. Interference: Bromide and iodide are titrated with mercuric nitrate in the same manner as chloride. Chromate, ferric, and sulfite ions interfere when present in excess of 10 mg/l.

* United States Patent No. 2,784,064 has been issued to F.E. Clarke, relative to the mercurimetric titration of chloride. Nothing contained in this manual is to be construed as granting any right, by implication or otherwise, for manufacture, sale, or use in connection with any method, apparatus or product covered by patent, nor as insuring anyone against liability for infringement of patent.

2. Reagents

a. Standard sodium chloride 0.0141 *N*. See Method A, ¶2*d* above.

b. Nitric acid, HNO_3, 0.1*N*.

c. Sodium hydroxide, NaOH, 0.1*N*.

d. Reagents for low-chloride titrations:

1) *Indicator-acidifier reagent:* The nitric acid concentration of this reagent is an important factor in the success of the determination and can be varied as indicated in a) or b) to suit the alkalinity range of the sample being titrated. Reagent a) contains sufficient nitric acid to neutralize a total alkalinity of 150 mg/l as $CaCO_3$ to the proper pH in a 100-ml sample.

a) Dissolve, in the order named, 250 mg s-diphenylcarbazone, 4.0 ml conc HNO_3, and 30 mg xylene cyanol FF in 100 ml of 95% ethyl alcohol or isopropyl alcohol. Store in a dark bottle in a refrigerator. This reagent is not stable indefinitely. Deterioration causes a slow end point and high results.

b) Because pH control is critical in this method, adjust the pH of highly alkaline or acid samples to 2.5±0.1 with 0.1*N* HNO_3 or NaOH, not with Na_2CO_3. Use a pH meter with a non-chloride type of reference electrode for the pH adjustment. If only the usual chloride-type reference electrode is available for pH adjustment, determine the amount of acid or alkali required to achieve a pH of 2.5±0.1 and discard this sample portion. Treat a separate sample portion with the determined amount of acid or alkali and continue the analysis to its prescribed end. Under these circumstances, omit the nitric acid from the indicator reagent to maintain the proper sample pH. Alternatively, vary the nitric acid concentration of the indicator-acidifier reagent to accommodate conditions wherein water samples of very high or very low alkalinity are being analyzed.

2) *Standard mercuric nitrate titrant*, 0.0141*N*: Dissolve 2.3 g $Hg(NO_3)_2$ or 2.5 g $Hg(NO_3)_2 \cdot H_2O$ in 100 ml distilled water containing 0.25 ml conc HNO_3. Dilute to just under 1 l. Make a preliminary standardization by following the procedure described in ¶3*a*. Use replicates containing 5.00 ml standard NaCl solution and 10 mg $NaHCO_3$ diluted to 100 ml with distilled water. Adjust the mercuric nitrate titrant to exactly 0.0141*N* and make a final standardization. Store away from the light in a dark bottle. Standard mercuric nitrate titrant, exactly 0.0141*N*, is equivalent to 500 µg Cl/1.00 ml.

e. Reagents for high-chloride titrations:

1) *Mixed indicator reagent:* Dissolve 5 g diphenylcarbazone powder and 0.5 g bromphenol blue powder in 750 ml 95% ethyl or isopropyl alcohol and dilute to 1 l with ethyl or isopropyl alcohol.

2) *Strong standard mercuric nitrate titrant*, 0.141*N*: Dissolve 25 g $Hg(NO_3)_2 \cdot H_2O$ in 900 ml distilled water containing 5.0 ml conc HNO_3. Dilute to just under 1 l, and perform a preliminary standardization by following the procedure described in ¶3*b*. Use replicates containing 25.00 ml standard NaCl solution and 25 ml distilled water. Adjust the titrant to 0.141*N* and make a final standardization. The chloride equivalence of the titrant is 5.00 mg/1.00 ml.

3. Procedure

a. Titration of low chloride concentrations: Use a 100-ml sample or smaller portion so that the chloride content is less than 10 mg.

Add 1.0 ml of indicator-acidifier reagent to the sample. (The color of the solution should be green-blue at this point. A light green indicates a pH of less than 2.0; a pure blue indicates a pH of more than 3.8. For most potable waters, the pH after this addition will be 2.5±0.1. For highly alkaline or acid waters, adjust pH to about 8 before adding the indicator-acidifier reagent.)

Titrate the treated sample with 0.0141*N* mercuric nitrate titrant to a definite purple end point. The solution will turn from green-blue to blue a few drops from the end point.

Determine the blank by titrating 100 ml distilled water containing 10 mg $NaHCO_3$.

b. Titration of high chloride concentrations: Place 50.0 ml sample in a 150-ml beaker (5.00 ml sample may be used when more than 5 ml titrant are needed). Add approximately 0.5 ml mixed indicator reagent and mix well. The color should be purple. Add 0.1*N* HNO_3 dropwise until the color just turns yellow. Titrate with 0.141*N* mercuric nitrate titrant to the first permanent dark purple. Titrate a distilled water blank using the same procedure.

4. Calculation

$$\text{mg/l Cl} = \frac{(A-B)\times N\times 35{,}450}{\text{ml sample}}$$

where A = ml titration for sample, B = ml titration for blank, and N = normality of $Hg(NO_3)_2$.

$$\text{mg/l NaCl} = \text{mg/l Cl} \times 1.65$$

5. Precision and Accuracy

A synthetic unknown sample containing 241 mg/l chloride, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 1.1 mg/l nitrate N, 0.25 mg/l nitrite N, 259 mg/l sulfate, and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

APPENDIX C

METHOD 5A
PARTICULATE AND CONDENSABLE HYDROCARBONS PROCEDURE

METHOD 5A. DETERMINATION OF PARTICULATE AND CONDENSIBLE ORGANIC MATTER FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of particulate and condensible organic matter within the context of the following definition: "Particulate matter" means any finely divided solid or liquid material, other than uncombined water, that condenses at or above the filtration temperature, and is collected by the front half of the sampling train. "Condensible organic matter" means any material which remains after extraction, filtration, and ambient evaporation of the ether-chloroform extract of the impinger portion of the train.

1.2 Principle. Particulate and condensible organic matter is withdrawn isokinetically from the source. Particulate matter is collected on a glass fiber filter maintained at temperatures of 120 ± 14°C, or such other temperature as specified by an applicable subpart of the standards or by the Administrator for a particular application. The particulate mass is determined gravimetrically after removal of uncombined water. Condensed organics are collected in the water-filled Greenburg-Smith impingers at temperatures less than 20 ± 5°C. The condensed organics are analyzed gravimetrically after extraction from the water by ether and chloroform.*

A

B

* Warning: Chloroform is a suspected carcinogen. The vapors of ethyl ether are an explosion hazard. All work should be done under an explosion proof hood with the analyst protected from exposure to these chemicals. Ether should not be retained beyond the container date; opened containers should not be stored for more than six months.

2. Apparatus

2.1 Sampling Train. Same as Method 5, Section 2.1, except the Greenburg-Smith system shall be used to determine stack gas moisture content and condensible organic matter. In addition, before use, clean the impingers and filter assembly with chromic acid cleaning solution followed by deionized distilled water and acetone rinses.

2.2 Sample Recovery. Same as Method 5, Section 2.2. In addition, clean all glassware used to handle the sample with chromic acid cleaning solution as described in Section 2.1.

2.3 Analysis. Same as Method 5, Section 2.3, with the following additional items:

2.3.1 Separatory Funnels. Two, 100-ml capacity.

2.3.2 Buchner Funnel. 47-mm diameter.

2.3.3 Erlenmeyer Flask. 500-ml.

3. Reagents

3.1 Sampling and Sample Recovery. Same as Method 5, Sections 3.1 and 3.2, respectively, with the following additions:

3.1.1 Water. Deionized distilled to conform to ASTM specification D1193-74, Type 3. Analyze blanks prior to field use to eliminate a high blank on test samples.

3.1.2 Chromic Acid Cleaning Solution. Prepare by slowly adding 1 liter concentrated sulfuric acid, with stirring, to 35 ml saturated sodium dichromate solution. HANDLE WITH CAUTION.

3.2 Analysis. Same as Method 5, Section 3.3, except the following additional reagents are required for the analysis.

3.2.1 Ethyl Ether. Reagent grade, $\leq$ 0.001 percent residue in suitable containers to retain low residue blank but still meet safety requirements.

3.2.2 Chloroform. Reagent grade, $\leq$ 0.001 percent residue, in glass bottles.

3.2.3 Water. Deionized distilled as described in Section 3.1.

3.2.4 Filters. 47-mm diameter glass fiber filters as described in Method 5, Section 3.1.1.

3.2.5 Hydrochloric Acid, Concentrated. HANDLE WITH CAUTION.

3.2.6 Sodium Hydroxide, 10 N. Dissolve 40 g NaOH in deionized distilled water and dilute to 100 ml. HANDLE WITH CAUTION.

4. Procedure

4.1 Sampling. Same as Method 5, Section 4.1, except use deionized distilled water in the impingers.

4.2 Sample Recovery. Same as Method 5, Section 4.2, with the addition of the following:

4.2.1 Container No. 4 (Impinger Water). Treat the first three impingers as follows: Leaving each impinger intact to transfer the liquid, cap off the inlet, and pour the liquid through the outlet into a graduated cylinder or directly into a tared sample container. Record the volume to within $\pm$ 1.0 ml or determine the liquid weight to within $\pm$ 0.5 g.

After transferring the water and condensible organic matter to the sample container, tighten the lid on the sample container so that water will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine later whether leakage occurred during transport. Label the container to clearly identify its contents.

4.2.2 Container No. 5 (Acetone Wash). After insuring that all joints of the impinger section glassware are wiped clean of silicone grease, rinse the inside surfaces of the first three impingers and the glass connecting joints with acetone. Rinse all surfaces three times or more if necessary to remove visible particulate. A Nylon bristle brush may be used to facilitate removal of any adhering material.

After all acetone washings and particulate matter are collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine later whether leakage occurred during transport. Label container to clearly identify its contents.

4.2.3 Water Blank. Save a portion of the deionized distilled water used in the impingers. Take 200 ml of this water and place it in a glass sample container labeled "water blank."

4.3 Analysis. Same as Method 5, Section 4.3. In addition, handle Containers No. 4 and 5 as follows (an example data sheet is shown in Figure 5A-1):

4.3.1 Container No. 4. Note level of liquid in container and confirm on analysis sheet whether leakage occurred during transport. Measure the liquid in this container either volumetrically to $\pm$ 1 ml or gravimetrically to $\pm$ 0.5 g. Adjust the sample to a pH of 7 with hydrochloric acid or sodium hydroxide using short range 6 to 8 pH paper. Transfer the contents to a separatory funnel. Extract the water with three 25-ml portions of ether, followed by three 25-ml portions of chloroform. (Note: Due to the flammability of ether and the health related effects of chloroform, the use of these reagents should be carefully supervised.) Combine the organic phases in another separatory funnel and back extract

1 Plant _____ 2 Date _____

Run No. _____ 4 Acetone blank volume, ml _____

5 Acetone wash volume, ml _____ 6 Acetone blank concentration, mg/mg _____

Acetone wash blank, mg _____ 8 E-C water blank volume, ml _____

Water volume in impingers, ml _____

10 E-C wash blank, mg _____ 11 Filter no. _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
Less acetone blank			
Weight of particulate matter			m_n =

CONTAINER NUMBER	WEIGHT OF CONDENSABLE ORGANIC MATTER COLLECTED, mg		
	FINAL WEIGHT*	TARE WEIGHT	WEIGHT GAIN
4			m_c =
5*			m_b =
TOTAL			
Less E-C water blank			
Weight of condensable organic matter			m_o =

*Data corrected for acetone blank

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml).

$$\frac{\text{INCREASE, g}}{1\ \text{g/ml}} = \text{VOLUME WATER, ml}$$

Figure 5A-1. Analytical data.

with 100 ml of deionized distilled water. The aqueous phase is not retained for analysis.

Filter the organic phase through a 47-mm glass fiber filter to remove any particulates entrained in the solvent. Then, evaporate the filtrate at ambient temperature and pressure until the solvent appears evaporated. Desiccate the remaining residue for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

4.3.2 Container No. 5. Note level of liquid in container and confirm on analysis sheet whether leakage occurred during transport. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to a tared 250-ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg. If more than 10 mg of residue is present, dissolve in 25 ml of ether followed by 25 ml chloroform. Combine the extracts and filter through a 47-mm glass fiber filter into a tared 250-ml beaker. Evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Combine with the weight obtained for Container No. 4 in Section 4.3.1.

4.3.3 Water-Ether-Chloroform Blank. Transfer 100 ml of water taken in the field as a water blank into a separatory funnel. Extract the water with three 25-ml portions of ether followed by three 25-ml portions of chloroform. Combine the organic extract in a tared container and evaporate the contents at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

5. Calibration

The calibration procedures are the same as Method 5, Section 5.

6. Calculations

All calculations and nomenclature are the same as in Method 5, Section 6, with the following additions.

6.1 Nomenclature. Add the following:

C_e = Ether-chloroform-water blank residue concentration, mg/ml.

m_b = Residue mass from acetone rinse of impingers after ether-chloroform extraction and evaporation, mg.

m_c = Residue mass from EC extraction of impinger water after evaporations, mg.

m_e = Extract residue mass of water blank, mg.

m_o = Total amount of condensed organic matter collected, mg.

V_e = Volume of water blank used in the EC extraction, ml.

V_{ww} = Volume of liquid collected in the impingers (see Figure 5A-1), ml.

W_e = Total extract residue mass of water blank, mg.

6.2 Ether-Chloroform-Water Blank Concentration.

$$C_e = \frac{m_e}{V_e} \qquad \text{Eq. 5A-1}$$

$$W_e = C_e V_{ww} \qquad \text{Eq. 5A-2}$$

$$m_o = m_c + m_b - W_e \qquad \text{Eq. 5A-3}$$

6.5 Total Particulate and Condensed Organic Matter Concentration.

$$C_t = (0.001\ g/mg)(m_n + m_o) / V_{m(std)} \qquad \text{Eq. 5A-4}$$

7. Bibliography

7.1 Same as Method 5, Citations 1 to 9.

7.2 McGaughey, J.F., and D.E. Wagoner. Special Analyses of Samples from Sinter Plants in the Iron and Steel Industry. Research Triangle Institute. Research Triangle Park, N.C. July 1978.

7.3 Evaluation of Sampling Techniques for Sintering in the Iron and Steel Industry. A Draft Report by PEDCo Environmental, Inc., 11499 Chester Road, Cincinnati, Ohio 45246.

APPENDIX D

CHLORINE TEST FIELD DATA SHEETS

DATA SHEET

CHLORINE COMPOUND TESTS

PLANT NASCO Wilm., Dela.

DATE 12-18-80

SAMPLE NUMBER 2BA (on bottles as I-B)

	1st	2nd	3rd	avg calc
Sample volume after rinse	152 ml	145	151	100

CHLORINE 1st imp. arsenite blank 2ml/50ml for zero reference

time begin 1430

Impinger No.	Dilution Required	Absorbance	mg/l Cl_2	ml H_2O_2* Added
10ml samp. 1	0.1ml/50ml	1.35		
" 1	0.1ml/50ml	1.21		
" 2	0.1ml/50ml	0.192		
" 2	0.1ml/50ml	0.199		
" 3	0.5ml/50ml	0.039		
" 3	0.5ml/50ml	0.022		
" Cyclone catch	2ml/50ml	0.112		
" Cyclone catch	2ml/50ml	0.115		

end @ approx. 1600

* ml 30% H_2O_2 required = (sample volume, ml) (Cl_2 concentration, mg/l) x 0.003

Cyclone catch arsenite blank 2ml/50

CHLORIDE

Impinger No.	Cl^- mg/l By $HgCl_2$	HCl mg/l By $HgCl_2$	Cl^- mg/l By AgCl	HCl mg/l By AgCl

DATA SHEET

CHLORINE COMPOUND TESTS

PLANT NASCO Wilm, Dela.

DATE 12/18/80

SAMPLE NUMBER 2B (on bottles as IB)

1st- Sample volume after rinse - 149 ml 2nd-149ml 3rd-147.5

CHLORINE 2 ml/50ml for Arsenite blank from 1st Impinger.

time begin 1230

	Impinger No.	Dilution Required	Absorbance	mg/l Cl_2	ml H_2O_2* Added
10 ml samp.	1	2ml/50ml	0.3 (brown)*		
"	1	0.1ml/50ml	1.5 (blue) ~ 2400		
"	1	"	1.5 (blue)		
"	2	0.1ml/50ml	0.755 (blue)		
"	2	"	0.88 (blue)		
"	3	0.1ml/50ml	0.049 (blue)		
"	3	"	0.040 (blue)		
"	Cyclone catch	0.1ml/50ml	0.009		
"	Cyclone catch	1ml/50ml	0.02		

* ml 30% H_2O_2 required = (sample volume, ml) (Cl_2 concentration, mg/l) x 0.003

Cyclone catch contained bits of filter - 148.5ml

Necessary to make separate arsenite blank for cyclone catch

CHLORIDE

Impinger No.	Cl^- mg/l By $HgCl_2$	HCl mg/l By $HgCl_2$	Cl^- mg/l By AgCl	HCl mg/l By AgCl

* after mix green to brown; absorbance reading dropped off quickly

DATA SHEET

CHLORINE COMPOUND TESTS

PLANT NASCO Wilmington, Delaware

DATE 12-18-80

SAMPLE NUMBER 3A

Volume after rinse (ml)	1st	2nd	3rd	Cyclone
	149	140.5	148.5	101

CHLORINE

Time begin 1658

Impinger No.	Dilution Required	Absorbance	mg/l Cl_2	ml H_2O_2* Added
1	0.1ml/50ml	0.070		
1	0.1ml/50ml	0.070		
2	0.5ml/50ml	0.020	2.14	
2	2.0ml/50ml	0.099		
3	4.0ml/50ml	0.010		
3	none	0.012		
Cyclone catch	1ml/50ml	0.050		
Cyclone catch	1ml/50ml	0.041		

* ml 30% H_2O_2 required = (sample volume, ml) (Cl_2 concentration, mg/l) x 0.003

Cyclone catch arsenite blank 10 ml samp no dilution

CHLORIDE

Impinger No.	Cl^- mg/l By $HgCl_2$	HCl mg/l By $HgCl_2$	Cl^- mg/l By AgCl	HCl mg/l By AgCl

DATA SHEET

CHLORINE COMPOUND TESTS

PLANT NASCO Wilmington, Delaware

DATE 12-18-80

SAMPLE NUMBER 3B

Volume (ml) after rinse	1st	2nd	3rd	Cyclone
	152.5	140.0	144.0	68

CHLORINE

1st Impinger arsenite blank 2ml/50ml

time begin 1840

Impinger No.	Dilution Required	Absorbance	mg/l Cl_2	ml H_2O_2* Added
1	2ml/50ml	1.380	14.42	
1	0.5ml/50ml	0.329	14.89	
2 → 2	4ml/50ml	0.060		
2	4ml/50ml	0.160		
3	none	0.010		
3	none	0.015		
2	4ml/50ml (Fischer H_2O dilute)	0.155		
Cyclone	4ml/50ml	0.60		
Cyclone	4ml/50ml	0.55		

end 2000

* ml 30% H_2O_2 required = (sample volume, ml) (Cl_2 concentration, mg/l) x 0.003

Cyclone arsenite blank 4ml/50ml

CHLORIDE

Impinger No.	Cl^- mg/l By $HgCl_2$	HCl mg/l By $HgCl_2$	Cl^- mg/l By AgCl	HCl mg/l By AgCl

DATA SHEET

CHLORINE COMPOUND TESTS

PLANT NASCO Wilmington, Delaware

DATE December 19, 1980

SAMPLE NUMBER 4A

rinse & sample volume 1st 139 2nd 110 3rd 130 Cyc 49

CHLORINE 1st impin. arsenite blank 2ml/10ml

Impinger No.	Dilution Required	Absorbance	mg/l Cl_2	ml H_2O_2* Added
1	0.05/50ml	0.241		
1	0.05/50ml	0.232		
2	1ml/50ml	0.332		
2	1ml/50ml	0.355		
3	none	0.01 (thermal brown)	—	
3	5ml/10ml	<0.01 (" ")		
3	1ml/50ml	0.015		
Cyclone	5ml/20ml	too high		
Cyclone	2ml/50ml	0.054		
Cyclone	2ml/50ml	0.091		

* ml 30% H_2O_2 required = (sample volume, ml) (Cl_2 concentration, mg/l) x 0.003

Cyclone arsenite blank 2ml/50ml

CHLORIDE

Impinger No.	Cl^- mg/l By $HgCl_2$	HCl mg/l By $HgCl_2$	Cl^- mg/l By AgCl	HCl mg/l By AgCl

DATA SHEET

CHLORINE COMPOUND TESTS

PLANT NASCO Wilmington, Delaware

DATE December 19, 1980

SAMPLE NUMBER 4B

	1st	2nd	3rd	Cyclone
rinse & sample vol.	148	145	130	35

CHLORINE

arsenite blank from 1st impinger 2ml/10ml

Impinger No.	Dilution Required	Absorbance	mg/l Cl_2	ml H_2O_2* Added
1	0.05ml/50ml	0.230		
1	0.05ml/50ml	0.219		
2	0.1 ml/50ml	0.015	6.3 too low	
2	1ml/50ml	0.83	7.0	
3	1ml/20ml	0.005	too low	
3	none	0.015	too low	
Cyclone	4ml/50ml	0.01		
Cyclone	5ml/10ml	0.232		

* ml 30% H_2O_2 required = (sample volume, ml) (Cl_2 concentration, mg/l) x 0.003

Cyclone arsenite blank 1ml/10ml (turbidity)

CHLORIDE

Impinger No.	Cl^- mg/l By $HgCl_2$	HCl mg/l By $HgCl_2$	Cl^- mg/l By AgCl	HCl mg/l By AgCl

Dec. 15, 1980

Standard Solutions of Bleach:

0.96 ml to 1 liter ≈ 50 mg/l

25 ml Bleach soln → 25 ml DH_2O, 2 ml AcAc Acid, 1 g KI, Stand (0.02545N)

1.25 ml 0.025 N NaThiosulfate Titrant

Blank — 0.04 ml 0.02545 N " "

$$mg/l\ Cl = \frac{(1.25 - 0.04)\,0.02545\,N\,(35.45)}{25\ ml} = 43.67$$

Spectrophotometer:

(2) Zero transmittance

(3) Zero " 1 cm absorbance

with DH_2O blank

(3) treated blank .002 Absorbance

(4) (A) 1:100 → 0.125 ABS.

$1\ ml/100\ ml \times .04367\ mg/ml = 0.4367\ mg/l$

(B) 3:100 → 0.590 ABS

$3\ ml/100\ ml \times .04367\ mg/ml = 1.3101\ mg/l$

(C) 1:500 → 0.035 "

$1\ ml/500\ ml \times .04367\ mg/ml = 0.08734\ mg/l$

(5) ARSENITE BLANK .001

Continued on Page

Read and Understood By

Signed Date Signed Date

DEC 16, 1980

Standard Solns. of Bleach (HOCl):

0.096 ml Bleach up to 1 liter

25 ml DH$_2$O
2 ml Acetic
1 g KI
Starch
25 ml Cl$^-$ Soln.

} Consumed 1.3 ml .025N Na$_2$S$_2$O$_3$

Blank → Consumed 0.05 N Na$_2$S$_2$O$_3$

$$\text{mg Cl/ml} = \frac{(1.3 - 0.05)0.025N \times 35.45}{25 ml}$$

$$= .04431 \quad \text{or} \quad 44.31 \text{ mg/l}$$

Continued on Page

Read and Understood By

Signed Date Signed Date

Dec. 16

Chlorine Standards :

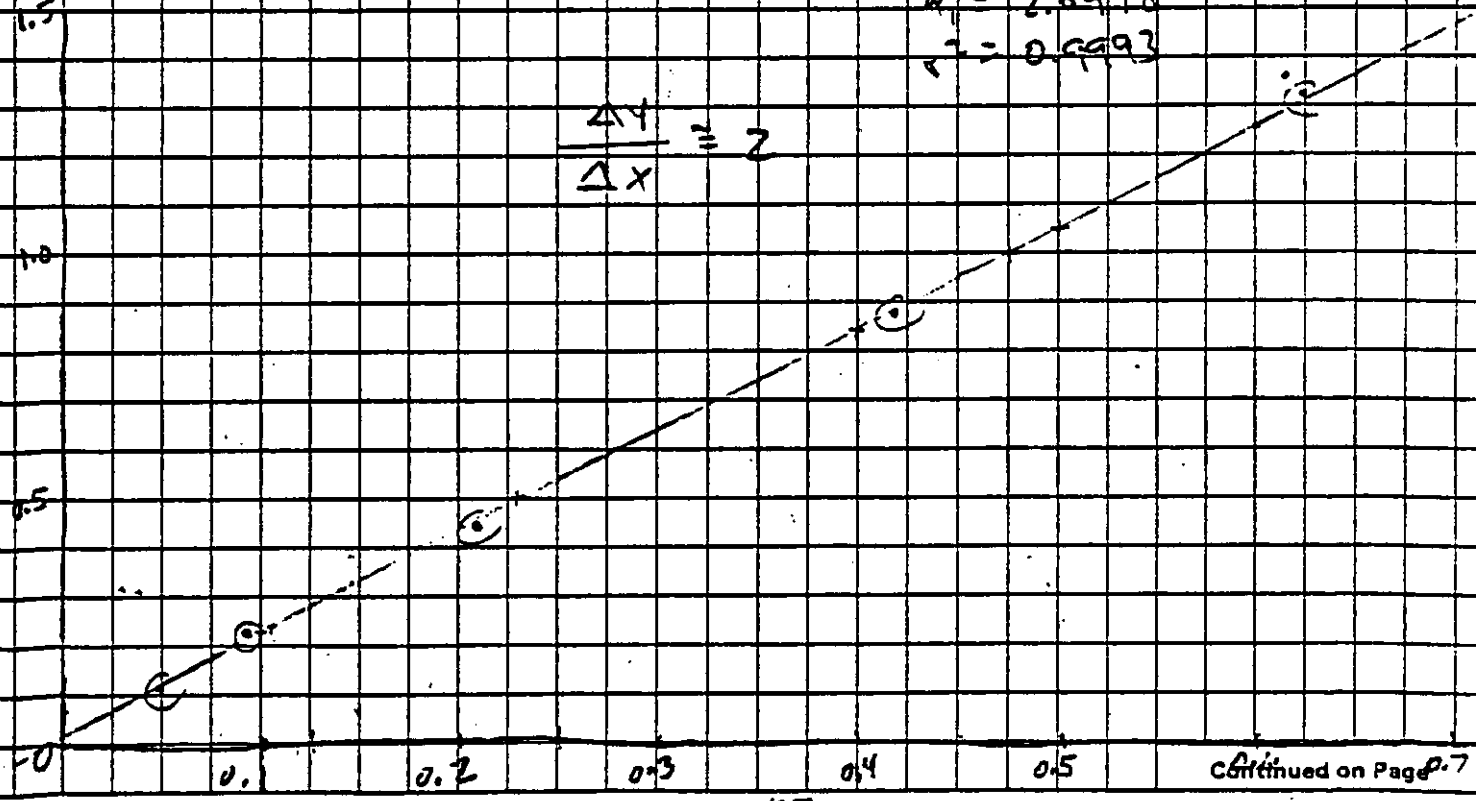
treated DH_2O (Chlorine demand free) used as 0 absorbance blank

dilutions :

		Absorbance	Conc. mg/l
1 ml / 100 ml	1 : 100	0.210	0.4431
3 ml / 100 ml	3 : 100	0.622	1.3293
0.25 ml / 100 ml	1 : 400	0.047	0.1108
1 ml / 50 ml	1 : 50	0.420	0.8862
1 ml / 200 ml	1 : 200	0.099	0.2216

$a_0 = .0154$
$a_1 = 2.0978$
$r = 0.9993$

$\frac{\Delta y}{\Delta x} = 2$



$y = a_0 + a_1 x$

ABSORBANCE

Continued on Page 7

Read and Understood By

Signed Date Signed Date

Dec 16, 1980

EPA Audit Samples

sample #	dilution	sample volume	arsenite blank	absorbance
2256	2 ml/50 ml	~~blank~~ 50	prep used as 0 blank	too great
2256	0.5 ml/200 ml	200	"	0.19
2285	0.5/200 ml	BLANK	prep. used as blank	0.098
~~3071~~				
3071	1 ml/100 ml	50 ml aliquot	blank used for zero	0.89
3087	1 ml/100 ml	50 ml aliquot	blank used for zero	0.80
"	"	from the above	"	0.81

	dilution vol.	sample vol.	APPROXIMATION Conc. (mg/l)	1/6 ft calculated
2256	200	10	~94	98.5
2285	200	"	~89	88.4
3071	100	"	~100	88.2
3087	100	"	~160	170.4

Continued on Page

Read and Understood By

Signed _____ Date _____ Signed _____ Date _____

Dec. 18 1980

Standardization of Na Thiosulfate

titration =

10 ml Dichromate solution → 9.92
(0.1N)

Na thiosulfate Normality = $\frac{1}{9.92}$ = 0.1008N

Standard Chlorine soln:

0.96 ml up to 1 liter
Chlorine

0.025N NaThio prepared

1.57 ml 0.025N NaThio consumed
when titrating with D_2O water acid, KI, and Cl soln

Blank − 0.0 ml (no color development)

$$mg/ml\ Cl = \frac{(1.57)\ .025N\ (35.45)}{25\ ml}$$

$$= 55.6\ mg/l$$

56.1

Continued on Page

Read and Understood By

Signed Date Signed Date

PROJECT

Notebook No. _____ COPY

Continued From Page _____

Dec. 18, 1980

Standard Cl soln. dilutions on Spec. :

Blank as zero OD.

				Conc.	
10 ml samp.	1:100	→	0.155	~~0.556~~	0.561
" "	3:100	→	0.59	~~1.669~~	1.68
" "	0.5:100	→	0.086	~~0.2983~~	.28
" "	1:50	→	0.392	~~1.1132~~	1.12
"	~~0 1:50~~	→			

$a_0 = .0988$

$a_1 = 2.6669$

$r^2 = .9965$

Continued on Page 0.6

Read and Understood By

Signed _____ Date _____ Signed _____ Date _____

Dec 18, 1980

SAMPLES on Spectrophotometer -

Arsenite blank from 1st Impinger as zero reference

SAMPLE No. 2A & 2B

Impinger No	Dilution	Absorbance	mg/l Cl_2
	see data sheets for numbers		

NOTES:

* Initial dilution from 1st Impinger 2B sample train @ 2:50 ml over high → color shift to brown necessary to dilute to 0.1:50 (1:500)

* Cyclone catch from 2B contains bits of filter. Also necessary to run arsenite blank for cyclone catch - noticable turbidity.

* Samples 2A & 2B were run on the spectrophotometer from 1230 - 1600 approx.

* Duplicate aliquots taken from each dilution for each sample bottle

time	Cl_2 (according to plant operator)	
13:30 →	0.45	appropriate for Sample 3
16:15 →	0.28	

Continued on Page

Read and Understood By

Signed Date Signed Date

Dec 18

SAMPLES 3A & 3B

Start time: completed by 2400 hrs

Dec. 18, 1980

EPA Audit Samples

	dilution	Absorbance	2000 hr mg/l
Sample 4050	0.5 ml / 50 ml	1.00	276.6
" "	0.5 ml / 50 ml	1.12	308.6

Continued on Page

Read and Understood By

Signed Date Signed Date

Dec 19, 1980

Thiosulfate Standardization:

20 ml DiH_2O, 1 ml H_2SO_4, 10 ml Potassium Dichro
1 g KI → 2 min minute in dark

9.95 ml 0.1 N Nathiosulfate Consumed

Normality of Nathiosulfate = $\frac{1}{9.95}$

= .01005 N

Nathiosulfate dilution = 0.02512

Chloride Data Standardization (from Dec 18, 1980)

1.60 ml .02512 N Nathiosulfate
0.05 ml / blank "

$\therefore$ mg/ml Cl = $\frac{(1.6 - 0.05)\ N\ (35.45)}{25\ ml}$

= 55.21 mg/l

Continued on Page

Read and Understood By

Signed Date Signed Date

DEC 19, 1980

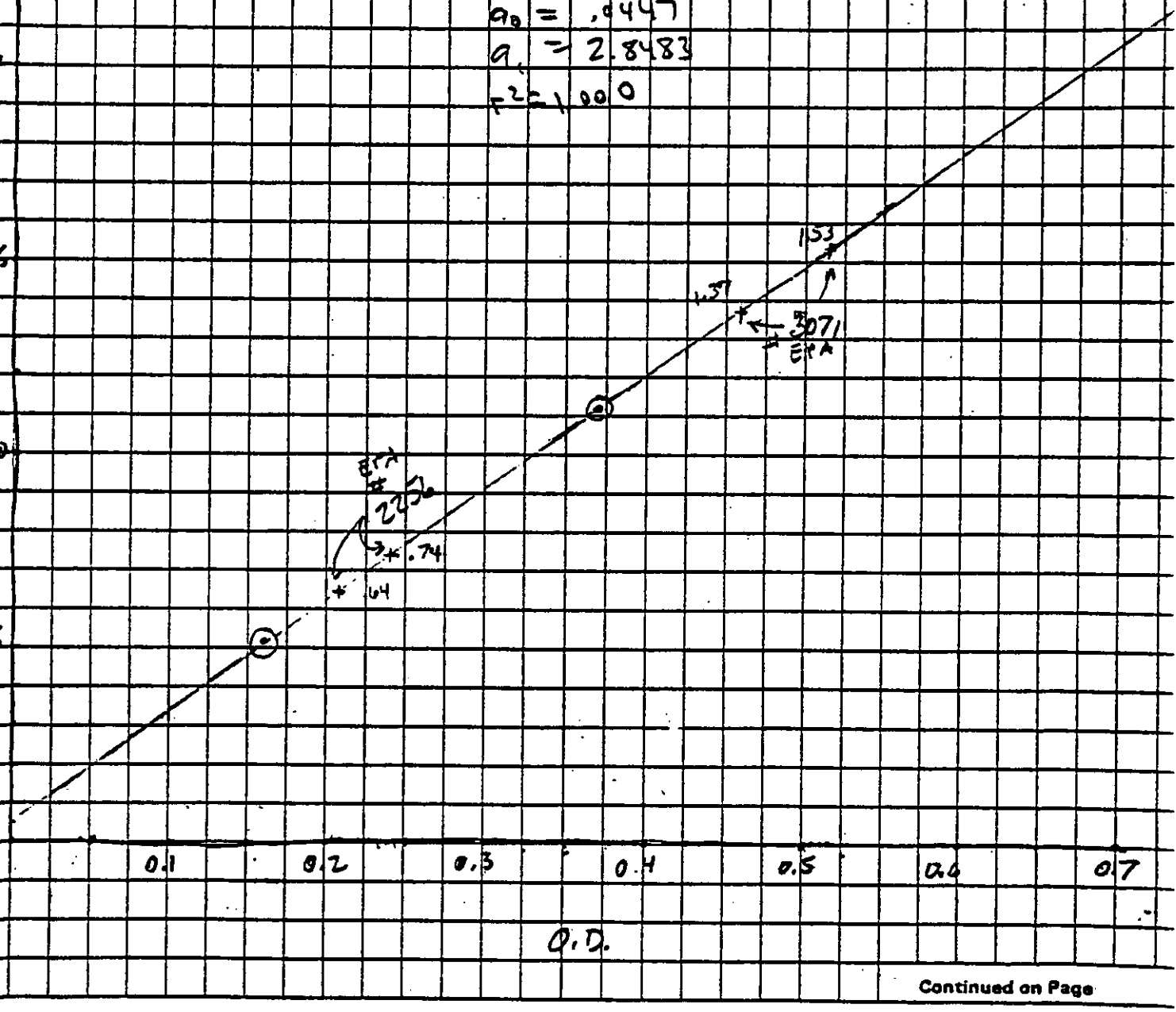
Standard Dilutions of Cl_2 on Spectrophotometer

		Abs	mg/l
~~1:50~~	→	~~0.00~~	
1:50	→	.371	1.1042
(From 1:50) 10:20	→	0.163	0.5071
2:50	→	0.760	2.2084

$a_0 = .0447$

$a_1 = 2.8483$

$r^2 = 1.000$



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Read and Understood By

Signed Date Signed Date

Dec 19, 1980

EPA Audit

arsenate blanks prepared

	dilution	OD	mg/l	
2256	@.25 ml/50 ml	0.240	145.6	
2256	@.25 ml/50 ml	0.209	128.0	1368
3071	0.1 ml /20 ml	0.515	302.3	
3071	0.1 ml /20 ml	0.462	272.1	287.2

Jan 6

10 ml 0.1 N K Dichromate — ml of .1 N Na Thio Sulfate
98 ml
98 ml

2 ml 0.1 N K Dichromate ml of 0.025 N Thio sulfa
8.0 ml
8.0 ml

25 ml (@ 50 mg/l Chlorine) ml of 0.025 N Thio sulf
1.49 ml
1.50 ml

Blank ml of 0.025 N Thiosulfate
0.13 ml
0.11 ml

Fitches H_2O
25 ml DH_2O — no color with starch add
25 ml — 50 mg/l above. 1.39 ml

Continued on Page

Continued From Page

Jan 6, 1980

$$mg/l\ Cl^- = \frac{(A-B)\,N\,(35.45)}{ml.\ sample} \cdot 1000\ \frac{ml}{l}$$

$$= \frac{(1.495-.12)\,0.025N\,(35.45)}{25} \cdot 1000\ mg/l$$

$$= 48.74\ mg/l\ Cl^-$$

Jan 7, 1980

2 ml .1N K Dichromate

Blank 0

ml 0.025 N	This
8.03	
8.00	

29 ml ≈ 50 mg/l chloride

ml 0.025 N	This
1.31	
1.36	Ave = 1.34
1.34	
1.34	

47.41 mg/l Cl

using above chloride soln

	% T			
1:100	81			
2:100	37.2	.5		
3:100	33	.46	.16	6
4:100	51.0	.3	.15	.4
1:100	81	.1		.2
1:100	78			

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Read and Understood By

Signed Date Signed Date

$A = \log\left(\frac{100}{T}\right)$ Bl

	%T	A	C mg/l	
1:100	82%	0.086	0.474	0
2:100	51.5	0.288	0.948	
3:100	35	0.456	1.422	0
1:200	95%	0.020	0.237	
1:200	96%			0
5:100	15	0.824	2.371	0

All 5 points
$a_0 = .211$
$a_1 = 2.625$
$r^2 = 0.999$

(2)

Sample #	Blank	mg/l	vs Blank			Dil
2285	0.02	1.167	43%	0.364		1:100
2285	0.05		43.5%			1:100
2256	0.07	1.246	40.3	0.394		1:100
2256	0.05		40.5			1:100
3071	0.02	1.122 1.059	47.5	0.323	0.347	1:200
3071	0.02	1.188	43.5	0.372		1:200
3087	0.07	1.319 1.353	36.7	0.435	0.422	1:200
3087	0.07	1.285	39.0	0.409		1:200
4050	0.02	1.466	33.0	0.478		1:250
4052	"		33.5			1:250

3:100	~~46.5~~	26.5		A	C
3:100		30.0	28.7	0.543	1.422
3:100		29.5			
2:100		46.5	45.7	0.340	0.948
2:100		45.0			↑ From calibration

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Read and Understood By

Signed Date Signed Date

PROJECT Spectrophotometer Check

Continued From Page

Wave length ck

	Abs (5th. Cobalt Chloride Soln)
500 nm	.465
505 nm	.480
510 nm	.485
515 nm	.485
520 nm	.460

Linearity (Dil. Ck)

	Abs (1300 1/8/81)	Abs (1700 1/8/81)	1410 1/9/81
Blk	∞	∞	
1/2 Sth	0.235	0.235	.245
1 Sth	0.485	0.485	.490
1/4 Sth	0.117	0.116	.121

[illegible]

1500	1/10/80
1/4 Sth	57
1/2 "	34
1 "	75.5

Continued on Page

Read and Understood By

Signed Date Signed Date

Tan 9

2 ml Dichromate — ml ~ 0.02 N Na Thiosulfate
10.0 ml
10.0 ml

N Na Thiosulfate = 0.020

.25 ml ~ 50 mg/l bleach — ml 0.020 N Na Thiosulfate
17.5
17.55

working bleaching standard 49.7

	Bl vs H_2O	% Transmittance Sample vs Blank	A	C
1:100	0.00 99.5%	69.3%	.153	.477
1:100	— "	71.3		
2:100	99.5%	39.7	.413	.994
2:100	"	37.5		
3:100	99.0	26.0	.606	1.491
3:100	"	23.5		
4:200	99.5	62.5		
4:200	99.5	79.5	0.100	0.249
5:200	99.5	79.5		
5:200	99.5	62.3		

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Read and Understood By

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PROJECT

Continued From Page

Jan 11

25 ml of ~ 50 mg/l Chlorine

ml of 0.020N $Na_2S_2O_3$

1	1.73
	1.72

1:200	800 %	0.0969	0.249
1:100	63 %	0.201	0.497
1:100	37.7	0.424	0.794
1:100	27	0.593	1.491
1:100	24		

$a_0 = -.003$

$a_1 = 2.467$

$r^2 = .996$

2285	30.5 %	0.516	1:100	127.0
3087	30	0.444	1:200	218.4
4050	33.5	0.475	1:250	292.1

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Read and Understood By

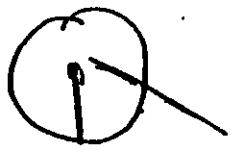
Signed Date Signed Date

FIELD DATA

67.08

PLANT NASCO
DATE 12/18/80
SAMPLING LOCATION Scrubber
SAMPLE TYPE chlorine compounds
RUN NUMBER 1 (A) ALG
OPERATOR
AMBIENT TEMPERATURE 26
BAROMETRIC PRESSURE 30.02
STATIC PRESSURE, (P_s) -35" H_2O
FILTER NUMBER (s) 784

PROBE LENGTH AND TYPE 2'
NOZZLE I.D. 0.25
ASSUMED MOISTURE, % 5
SAMPLE BOX NUMBER
METER BOX NUMBER
METER AH@ 1.87
C FACTOR 0.90
PROBE HEATER SETTING
HEATER BOX SETTING
REFERENCE Δp 70 0.50
80 0.54
60 0.48



SCHEMATIC OF TRAVERSE POINT LAYOUT

INITIAL leak check 0.00 cfm @ 16" Hg
FINAL leak check (first broke) bad leak check

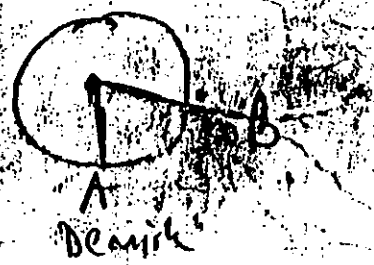
READ AND RECORD ALL DATA EVERY 5 MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft³	O_2 / %e	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O DESIRED	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O ACTUAL	STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE INLET ($T_{m\,in}$), °F	DRY GAS METER TEMPERATURE OUTLET ($T_{m\,out}$), °F	PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
A	0	1047	408.750		.80	2.86	2.86	67	52		8	209	42
	3	1050	411.400		.80	2.86	2.86	65	55		11	207	42
	6	1053	414.400		.80	2.86	2.86	66	57		15	206	42
	9	1056	416.700		.80	2.86	2.86	67	58		18	209	42
blow C.U.	12	1059	419.400		.80	2.86	2.86	66	59		19	213	48
	15	1102	422.100		.80	2.86	2.86	65	60		11	239	85
	18	1105	425.000		.80	2.86	2.86	69	60		10	247	110
	21	1108	427.600		.80	2.86	2.86	68	61		10	251	105
	24	1111	430.400		.80	2.86	2.86	68	62		10	253	95
	27	1114	433.100		.80	2.86	2.86	69	62		10	253	90
	30	1117	435.700		.80	2.86	2.86	69	63		10	253	80
	33	1120	438.700		.80	2.86	2.86	67	63		10	252	80
	35.5	1122 30	440.862										
			38.112		.80	2.86		68.8	0	92.5		232	107

FIELD DATA

6128

PLANT NASCO
DATE 12-18-80
SAMPLING LOCATION Scrubber
SAMPLE TYPE Method 6
RUN NUMBER 1-B
OPERATOR Michael Hackett
AMBIENT TEMPERATURE 28°F
BAROMETRIC PRESSURE 30.03
STATIC PRESSURE, (P_s) -35" (30 - 7.5 Hg
FILTER NUMBER (s) 78



PROBE LENGTH AND TYPE 3' glass
NOZZLE I.D. .250
ASSUMED MOISTURE, % 3
SAMPLE BOX NUMBER
METER BOX NUMBER
METER $\Delta H_@$
C FACTOR
PROBE HEATER SETTING 100%
HEATER BOX SETTING 100%
REFERENCE Δp 0.50

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 5 MINUTES

initial leak check 0.00 cfm @ 15" Hg
Final leak check (after last test) had check

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft³	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O DESIRED	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O ACTUAL	STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE INLET ($T_{m\,in}$), °F	DRY GAS METER TEMPERATURE OUTLET ($T_{m\,out}$), °F	PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
	0											
B	0	1044	514.650	.80	2.86	2.86	67	52		7	209	42
	3	1047	517.600	.80	2.86	2.86	67	54		10	160	42
	6	1050	520.000	.80	2.86	2.86	66	57		11	155	42
	9	1053	522.700	.80	2.86	2.86	66	58		18	155	42
	12	1056	525.100	.80	2.86	2.86	67	58		21	155	42
	15	1059	527.500	.80	2.86	2.20	66	59		22	155	48
	18	1102	529.900	.80	2.86	2.10	65	60		22	155	85
	21	1105	532.200	.80	2.86	1.80	68	62		23	155	110
blow back	24	1108	534.300	.80	2.86	1.60	68	63		23	155	105
	27	1111	537.500	.80	2.86	2.86	68	62		5	190	95
	30	1114	540.100	.80	2.86	2.86	69	62		6	192	90
	33	1117	542.900	.80	2.86	2.86	69	63		6	188	80
	36	1120	545.600	.80	2.86	2.86	67	64		6	189	80
	37.75	1121	547.800									
	~~38.75~~											

FIELD DATA

14.35

PLANT NASCO
DATE 12-18-80
SAMPLING LOCATION Scrubber
SAMPLE TYPE Method 5/Chlorine
RUN NUMBER 3A
OPERATOR Michael HACKETT
AMBIENT TEMPERATURE 40°F
BAROMETRIC PRESSURE 30.03
STATIC PRESSURE, (P_g) -4.5" Hg
FILTER NUMBER (s)

PROBE LENGTH AND TYPE 2' glass
NOZZLE I.D. .125
ASSUMED MOISTURE, % 3
SAMPLE BOX NUMBER
METER BOX NUMBER E5-6
METER $\Delta H_@$ 1.87
C FACTOR .90
PROBE HEATER SETTING 100%
HEATER BOX SETTING 100%
REFERENCE Δp 8.0

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 3 MINUTES

INITIAL leak check 0.00 cfm @ 15" Hg
FINAL leak check

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
					DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			
	0	1453.5	443.100	1.0	.245	.245	72	51		4	263	52
	3	1456	443.900	1.0	.245	.245	74	52		4	248	51
	6	1459	~~444.800~~ 444.700	1.0	.245	.245	74	52		4	245	49
	9	1502	445.500	1.0	.245	.245	74	52		4	238	48
	12	1505	446.300	1.0	.245	.245	74	53		4	226	47
	15	1508	447.100	1.0	.245	.245	74	54		4	219	45
	18	1511	448.000	1.0	.245	.245	74	54		4	214	44
	21	1514	448.700	1.0	.245	.245	74	55		4	211	43
	24	1517	449.500	1.0	.245	.245	75	56		4	207	42
	27	1520	450.400	1.0	.245	.245	75	57		4	202	43
	30	1523	451.200	1.0	.245	.245	74	58		4	204	42
	33	1526	452.000	1.0	.245	.245	74	58		4	204	42
	36	1529	452.800	1.0	.245	.245	75	59		4	204	44
	39	1532	453.600	1.0	.245	.245	75	59		4	203	44
	42	1535	454.400	1.0	.245	.245	75	59		4	203	45
	45	1538	455.300	1.0	.245	.245	75	60		4	203	44
	48	1541	456.100	1.0	.245	.245	75	60		4	203	44
	51	1544	~~457.2~~ 457.2	1.0	.245	.245	75	60		4	198	43
	54	1547	457.8	1.0	.245	.245	75	60		4	197	45
	57	1550	458.7	1.0	.245	.245	74	60		4	196	45

FIELD DATA

Sheet 2

15.23

PLANT Nasco
DATE 12-18-80
SAMPLING LOCATION Scrubber
SAMPLE TYPE Method 5
RUN NUMBER 1 A
OPERATOR Lee Gamble
AMBIENT TEMPERATURE 28°F
BAROMETRIC PRESSURE 30.03
STATIC PRESSURE, (P_g)
FILTER NUMBER (s)

INITIAL LEAK check

FINAL LEAK check

PROBE LENGTH AND TYPE 2' glass
NOZZLE I.D. .250
ASSUMED MOISTURE, %
SAMPLE BOX NUMBER
METER BOX NUMBER
METER AH@
C FACTOR
PROBE HEATER SETTING 100%
HEATER BOX SETTING 100%
REFERENCE Δp

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY _____ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (16 hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			
	60 1553	459.1	1.0	.245	.245	75	61		4	202	44
	63 1556	460.2	1.0	.245	.245	75	61		4	202	44
	66 1559	461.0	1.0	.245	.245	75	61		4	205	44
	69 1602	461.9	1.0	.245	.245	75	62		4	210	44
	72 1605	462.7	1.0	.245	.245	75	62		4	210	44
	75 1608	463.5	1.0	.245	.245	75	62		5	214	43
	78 1611	464.3	1.0	.245	.245	75	62		5	221	43
	81 1614	465.1	1.0	.245	.245	75	62		5	221	43
	84 1617	466.0	1.0	.245	.245	75	62		5	226	43
	87 1620	466.8	1.0	.245	.245	75	62		5	227	43
	90 1623	467.6	1.0	.245	.245	75	62		5	226	43
	93 1626	468.4	1.0	.245	.245	75	62		5	225	43
	96 1629	469.2	1.0	.245	.245	75	62		5	226	43
	98 1631	469.824		END TEST							

FIELD DATA

14.79

PLANT NASCO
DATE 12-18-80
SAMPLING LOCATION Scrubber
SAMPLE TYPE Method 5/Chlorine
RUN NUMBER 3B
OPERATOR Michael Hackett
AMBIENT TEMPERATURE 40°F
BAROMETRIC PRESSURE 30.03
STATIC PRESSURE, (P_s) -4.5" Hg
FILTER NUMBER (s) 0

PROBE LENGTH AND TYPE 3' glass
NOZZLE I.D. .125
ASSUMED MOISTURE, % 3
SAMPLE BOX NUMBER
METER BOX NUMBER ES-5
METER $\Delta H_@$ 1.87
C FACTOR .90
PROBE HEATER SETTING 100%
HEATER BOX SETTING 100%
REFERENCE Δp 8.0

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 3 MINUTES

In-mal leak check 0.00 cfm @ 15" Hg
Final leak check

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft³	O_2 %	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O DESIRED	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O ACTUAL	STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE INLET ($T_{m\,in}$), °F	DRY GAS METER TEMPERATURE OUTLET ($T_{m\,out}$), °F	PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
	0	1451	548.400		1.0	.245	.245	72	52		6	228	60
	3	1454	549.800		1.0	.245	.245	74	52		6	229	60
	6	1457	550.600		1.0	.245	.245	74	52		6	230	60
	9	1500	551.100		1.0	.245	.245	74	53		6	230	60
	12	1503	551.900		1.0	.245	.245	74	53		6	229	60
	15	1506	552.800		1.0	.245	.245	74	53		6	227	60
	18	1509	553.700		1.0	.245	.245	74	54		6	226	55
	21	1512	554.500		1.0	.245	.245	74	54		6	224	55
	24	1515	555.400		1.0	.245	.245	75	55		6	222	55
	27	1518	556.300		1.0	.245	.245	75	55		6	220	54
	30	1521	557.200		1.0	.245	.245	75	56		6	218	54
	33	1524	558.000		1.0	.245	.245	75	56		6	214	54
	36	1527	558.900		1.0	.245	.245	75	56		6	214	54
	39	1530	559.700		1.0	.245	.245	75	57		6	214	54
	42	1533	560.600		1.0	.245	.245	75	58		6	214	54
	45	1536	561.500		1.0	.245	.245	75	58		6	211	55
	48	1539	562.300		1.0	.245	.245	75	59		6	211	55
	51	1542	563.2		1.0	.245	.245	75	59		6	211	55
	54	1545	564.2		1.0	.245	.245	75	6		6	208	55
	57	1548	564.8		1.0	.245	.245	75	6			209	58
	60	1551	565.8		1.0	.245	.245	75	6		6	215	58

FIELD DATA

PLANT _____
DATE _____
SAMPLING LOCATION _____
SAMPLE TYPE _____
RUN NUMBER 5
OPERATOR _____
AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
STATIC PRESSURE, (P_g) _____
FILTER NUMBER (s) _____

Sheet 2

Chlorinator bis furnace mid run

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER $\Delta H_@$ _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE Δp _____

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 7 MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft^3	O_2 % CO_2 %	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
						DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			
	63	1554	566.6		1.0	.245	.245	75	61		6	209	57
	66	1557	567.4		1.0	.245	.245	75	61		6	209	57
	69	1600	568.4		1.0	.245	.245	76	61		6	209	57
	72	1603	569.3		1.0	.245	.245	76	62		6	208	60
	75	1606	570.1		1.0	.245	.245	75	62		7	208	60
	78	1609	570.9		1.0	.245	.245	74	62		7	205	60
	81	1612	571.9		1.0	.245	.245	74	62		7	204	60
	84	1615	572.7		1.0	.245	.245	74	62		7	204	60
	87	1618	573.6		1.0	.245	.245	75	62		7	204	60
	90	1621	574.5		1.0	.245	.245	75	62		7	204	65
	93	1624	575.3		1.0	.245	.245	75	62		8	204	65
	96	1627	576.2		1.0	.245	.245	75	62		8		65
	99	1630	577.125			END TEST							

Plant used chlorophenol for spent pickling scrubbing

1.42

First SL start 1316
second " 1330
third " 1340

FIELD DATA

PLANT NASCO
DATE 12-19-80
SAMPLING LOCATION Scrubber
SAMPLE TYPE Method 8/Chlorine
RUN NUMBER MS-4A
OPERATOR Michael Hackett (1) ALG
AMBIENT TEMPERATURE 40°F
BAROMETRIC PRESSURE 30.05
STATIC PRESSURE, (P_s) -4.5" Hg (-35")
FILTER NUMBER (s)

Some adjustment to scrubber water spray during run. pitot liner not blocked this run

PROBE LENGTH AND TYPE 2' glass
NOZZLE I.D. .125
ASSUMED MOISTURE, % 3
SAMPLE BOX NUMBER
METER BOX NUMBER
METER $\Delta H_@$ 1.87
C FACTOR .90
PROBE HEATER SETTING 100%
HEATER BOX SETTING 100%
REFERENCE Δp 8.0

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 5 MINUTES

Initial leak check 0.00 cfm @ 15" Hg
Final leak check

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft³	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
					DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			
	0	1315	542.20									
A	5	1320	543.7	1.0	.250	.250	52	44		4.0	235	41
	10	1325	545.2	"	"	"	58	45		4.0	233	44
	15	1330	546.4	"	"	"	62	47		4	223	38
	20	1335	547.8	"	"	"	64	48		4.5	216	40
	25	1340	549.2	"	"	"	66	49		4.5	215	40
	30	1345	550.6	1.1	.275	.275	68	50		5.0	222	40
	35	1350	552.274	1.2	.30	.30	70	51		5.5	223	40
	40	1355		END	OF	IT	(40 cfm)	No flow				
	0	1408	552.274									
	5	1413	553.8	1.0	.25	.25	70	49		5.0	262	46
	10	1418	555.3	1.15	.285	.285	73	49		5.5	259	40
	15	1423	556.8	1.10	.275	.275	74	50		5.5	245	40
	20	1428	558.2	1.10	.275	.275	73	51		5.5	231	40
	25	1433	559.7	1.15	.285	.285	75	51		6	226	40
	30	1438	561.1	1.10	.275	.275	78	51		6	216	40
	35	1443	562.4	1.05	.265	.265	80	52		6.5	216	40
	40	1448	564.0	1.10	.270	.270	80	52		6.5	220	40
	45	1453	565.3	1.10	.270	.270	80	53		7.0	231	40
	50	1458	566.1	1.1	.270	.270	78	53		7.5	231	40
	55	1503	568.2	1.1	.270	.27	78	53		7.5	226	40
	60	1508	569.632	1.1	.270	.270	78	53		8.0	222	40

COMMENTS:

7142

FIELD DATA

small Furnace Chlorinated 1st ; Cl2 smell from sump much stronger during second run

PLANT NASCO
DATE 12-19-80
SAMPLING LOCATION Scrubber
SAMPLE TYPE Method 5/Chlorine
RUN NUMBER 4B
OPERATOR ~~Michael Hackett~~ @ALG
AMBIENT TEMPERATURE 40°F
BAROMETRIC PRESSURE 30.05
STATIC PRESSURE, (P_s) -4.5" Hg (= 35")
FILTER NUMBER (s) 0

NO water in cyclone at all after 1st batch

PROBE LENGTH AND TYPE 31 glass
NOZZLE I.D. .175
ASSUMED MOISTURE, % 3
SAMPLE BOX NUMBER
METER BOX NUMBER
METER $\Delta H_@$ 1.87
C FACTOR .90
PROBE HEATER SETTING 100%
HEATER BOX SETTING 100%
REFERENCE Δp 8.0

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 5 MINUTES

INITIAL leak check 0.00 cfm @ 16" Hg
FINAL leak check

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft³	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
					DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			
	0	1315	650.310									
2	5	1320	651.8	1.1	.290	.290	52	46		5.5	250	44
	10	1325	653.3	11	11	11	58	46		5.5	247	44
	15	1330	654.6	11	11	11	62	49		6	240	44
	20	1335	656.1	11	11	11	64	50		6	237	44
	25	1340	657.4	11	11	11	66	52		6.5	235	44
	30	1345	658.7	0.95	0.24	0.24	68	53		6.5	238	44
	35	1350	660.441	1.05	0.265	0.265	70	53		7.0	233	44
	40	1355		END	OF	First	Chlorination					
	0	1409	660.441									
	5	1413	662.0	1.0	.25	.25	70	50		7.0	235	42
	10	1418	663.4	1.05	.265	.265	73	50		7.5	240	42
	15	1423	664.9	1.05	.265	.265	74	51		7.5	235	43
	20	1428	666.3	1.0	.250	.250	73	52		7.5	234	42
	25	1433	667.7	0.98	.245	.245	75	53		7.5	232	42
	30	1438	669.1	0.98	.245	.245	78	53		8.0	230	43
	35	1443	670.4	0.96	.240	.240	80	54		8.5	226	44
	40	1448	671.4	0.95	.245	.245	80	54		8.5	225	44
	45	1453	673.1	0.98	.245	.245	80	55		9.0	225	44
	50	1458	674.6	0.98	.245	.245	78	55		9.5	225	—
	55	1503	676.0	0.98	.245	.245	78	55		10.0	225	—
	60	1506	676.874	0.98	.245	.245	78	55		10.5	225	—

COMMENTS:

ANALYTICAL DATA

PLANT NASCO

DATE 12/18/80

SAMPLING LOCATION Chloride Scrubber

SAMPLE TYPE Chlorine Compounds

RUN NUMBER 2A

SAMPLE BOX NUMBER _____

CLEAN-UP MAN _____

COMMENTS:

Filter fell apart - some pieces unrecovered

Filter caked up support sucked out

FRONT HALF

LABORATORY RESULTS

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

FILTER NUMBER 784 _____ — CONTAINER _____ _____ mg

_____ _____

_____ _____

switched (?)

FRONT HALF SUBTOTAL _____ mg

BACK HALF

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

ETHER-CHLOROFORM EXTRACTION _____ mg

ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

Final

1st IMPINGER - 609.7 — 573.6

2nd IMPINGER - 598.0 — 558.8

3rd IMPINGER - 610.0 — 590.1

BACK HALF SUBTOTAL _____ mg

TOTAL WEIGHT _____ mg

MOISTURE

IMPINGERS

FINAL VOLUME _____ ml

INITIAL VOLUME _____ ml

NET VOLUME _____ ml

SILICA GEL			
FINAL WEIGHT	248.3 g	240.2 g	_____ g
INITIAL WEIGHT	244.4 g	220.3 g	_____ g
NET WEIGHT	_____ g	_____ g	_____ g

TOTAL MOISTURE _____

EPA (Dur) 231

4/72

ANALYTICAL DATA

PLANT NASCO

DATE 12/18/85

SAMPLING LOCATION Chloride Scrubber

SAMPLE TYPE Chlorine Compounds

RUN NUMBER 2B

SAMPLE BOX NUMBER _____

CLEAN-UP MAN _____

COMMENTS:

Filter caked up with white particle form at edge

FRONT HALF

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER

FILTER NUMBER		
~~700~~ 783		

LABORATORY RESULTS

CONTAINER _____ _____ mg

CONTAINER _____ _____ mg

some of filter lost in cyclone

FRONT HALF SUBTOTAL _____ mg

BACK HALF

Switched (?)

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER

Final

ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER

1st IMPINGER – ~~[illegible] g~~ 599.4 g

2nd IMPINGER – ~~[illegible] g~~ 550.5 ~~[illegible]~~

3rd IMPINGER – 597.9 g.

CONTAINER _____ _____ mg

ETHER-CHLOROFORM EXTRACTION _____ mg

CONTAINER _____ _____ mg

BACK HALF SUBTOTAL _____ mg

TOTAL WEIGHT _____ mg

MOISTURE

		578.5	581.0	592.7
		1	2	3
IMPINGERS				
FINAL VOLUME	_____ ml	599.4	550.5	597.9
INITIAL VOLUME	_____ ml	~~[illegible]~~	~~592.2~~	
NET VOLUME	_____ ml		~~[illegible]~~	
SILICA GEL				
FINAL WEIGHT	216.2 g	264.9 g	_____ g	
INITIAL WEIGHT	222.8 g	230.2 g	_____ g	
NET WEIGHT	_____ g	_____ g	_____ g	

TOTAL MOISTURE _____

EPA (Dur) 231
4/72

ANALYTICAL DATA

PLANT NASCO

DATE 12/18/80

SAMPLING LOCATION scrubber

SAMPLE TYPE chloride

RUN NUMBER 3A

SAMPLE BOX NUMBER

CLEAN-UP MAN ALG

COMMENTS:

noticeable cake on filter
all of filter not recovered

FRONT HALF

LABORATORY RESULTS

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

FILTER NUMBER 770 _____ — CONTAINER _____ _____ mg

_____ _____

_____ _____

cyclone catch 50 ml
turbid white

FRONT HALF SUBTOTAL _____ mg

BACK HALF

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

ETHER-CHLOROFORM EXTRACTION _____ mg

ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

BACK HALF SUBTOTAL _____ mg

TOTAL WEIGHT _____ mg

MOISTURE

IMPINGERS		599.9	558.6	583.3
FINAL VOLUME	_____ ml	585.3	552.8	580.9
INITIAL VOLUME	_____ ml			
NET VOLUME	_____ ml			
SILICA GEL		249.1	190.8	
FINAL WEIGHT	~~2358~~ g	~~1880~~ g	_____ g	
INITIAL WEIGHT	231.5 g	202.7 g	_____ g	
NET WEIGHT	_____ g	_____ g	_____ g	

TOTAL MOISTURE _____

EPA (Dur) 231
4/72

ANALYTICAL DATA

PLANT NASCO

DATE 12/18/80

SAMPLING LOCATION scrub

SAMPLE TYPE chlorine

RUN NUMBER 3B

SAMPLE BOX NUMBER

CLEAN-UP MAN

COMMENTS:

stack had dense white plume - scrubbing liquor seemingly had high pH

noticable white cake on filter - all of filter not recovered

FRONT HALF

LABORATORY RESULTS

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

FILTER NUMBER 77 — CONTAINER _____ _____ mg

50 ml in cyclone catch turbid white - looks identical to SA

FRONT HALF SUBTOTAL _____ mg

BACK HALF

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

ETHER-CHLOROFORM EXTRACTION _____ mg

ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

BACK HALF SUBTOTAL _____ mg

TOTAL WEIGHT _____ mg

MOISTURE

CF 5.3 fix / 603.5 612.4

590.1 599.2 601.4

IMPINGERS

FINAL VOLUME	_____ ml		
INITIAL VOLUME	_____ ml		
NET VOLUME	_____ ml		

SILICA GEL

FINAL WEIGHT	~~200.0~~ 211.5 g	~~243.5~~ 254.4 g	_____ g
INITIAL WEIGHT	216.5 g	239.3 g	_____ g
NET WEIGHT	_____ g	_____ g	_____ g

TOTAL MOISTURE _____

EPA (Dur) 231
4/72

ANALYTICAL DATA

PLANT NASCO

DATE 12/19/80

SAMPLING LOCATION scrubber

SAMPLE TYPE Cl2

RUN NUMBER 4A

SAMPLE BOX NUMBER _____

CLEAN-UP MAN ALG

COMMENTS:

dense white filter cake
some specs of filter not recoverable

FRONT HALF

LABORATORY RESULTS

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

FILTER NUMBER 777 _____ — CONTAINER _____ _____ mg

_____ _____

_____ _____

x 30 ml murky soln. in cyclone

FRONT HALF SUBTOTAL _____ mg

BACK HALF

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

ETHER-CHLOROFORM EXTRACTION _____ mg

ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

1st impinger has suspended white particle

BACK HALF SUBTOTAL _____ mg

TOTAL WEIGHT _____ mg

MOISTURE

IMPINGERS				
FINAL VOLUME	_____ ml	613.4	568.5	598.8
INITIAL VOLUME	_____ ml	581.6	566.4	598.2
NET VOLUME	_____ ml			

SILICA GEL				
FINAL WEIGHT	197.7 g	240.0 g	_____ g	
INITIAL WEIGHT	192.8 g	238.4 g	_____ g	
NET WEIGHT	_____ g	_____ g	_____ g	

TOTAL MOISTURE _____ g

EPA (Dur) 231
4/72

ANALYTICAL DATA

PLANT NASCO

DATE 12/14/80

SAMPLING LOCATION Scrubber

SAMPLE TYPE Cl2

RUN NUMBER 4B

SAMPLE BOX NUMBER

CLEAN-UP MAN ALG

COMMENTS: dense white Filter cake some small specs not recoverable

FRONT HALF

LABORATORY RESULTS

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

FILTER NUMBER 778 _____ — CONTAINER _____ _____ mg

_____ _____

_____ _____

≈ 20 ml mark soln. in cyclone

FRONT HALF SUBTOTAL _____ mg

BACK HALF

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ ml

ETHER-CHLOROFORM EXTRACTION _____ ml

ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ ml

1st impinger murky white

BACK HALF SUBTOTAL _____ ml

TOTAL WEIGHT _____ ml

MOISTURE

IMPINGERS	620.0	611.5	610
FINAL VOLUME ml	601.8	590.6	609.9
INITIAL VOLUME ml	~~581.8~~	~~566.4~~	598.2
NET VOLUME ml			
SILICA GEL	2426	234.9	
FINAL WEIGHT g	213.8	245.8	
INITIAL WEIGHT g			
NET WEIGHT g			

TOTAL MOISTURE _____

EPA (Dur) 231
4/72

APPENDIX E

CHLORIDES TITRATION LAB SHEETS

Cl^- Results

Sample No.	Sample Vol.	N $Hg(NO_3)_2$	Titer 1	Titer 2
1A FI	5 ml	0.00988	29.20	29.50
SI	↓	0.00975	4.75	4.70
TI	↓	↓	0.10	0.15
TI	50	↓	2.50	—
1B FI	5 ml	0.00975	43.35	43.35
SI	↓	↓	11.60	11.70
TI	↓	↓	0.85	0.90
TI	25	↓	4.1	—
3A FI	5 ml	0.00975	4.50	4.50
SI	↓	↓	0.40	0.35
SI	25	↓	2.1	—
TI	5	↓	0.40	0.40
TI	25	↓	1.80	—
3B FI	5 ml	0.00975	2.90	2.85
SI	↓	↓	0.30	0.20
SI	25	↓	0.80	—
TI	5	↓	0.05	0.10
TI	10	↓	0.05	0.10
TI	25	↓	0.25	—
4A FI	5 ml	0.00975	24.40	24.60
SI	10	↓	2.50	2.50
TI	10	↓	0.20	0.20
TI	25	↓	0.45	—
4B FI	5 ml	0.00988	21.00	20.80
SI	10	0.00975	1.60	1.65
TI	10	↓	0.15	0.10
TI	50	↓	0.70	—

PROJECT _____ JOB NO. _____ DATE _____ BY _____

DETAIL _____ BY _____ OF _____

Cl^- Results (Continued)

1A Cyclone	5 ml	0.00975	5.30	5.30
PW	25	↓	0.80	0.80
1B Cyclone	5 ml	0.00975	1.95	2.00
Cyclone	10		3.90	3.85
PW	25		0.90	1.00
3A Cyclone	5 ml	0.00975	1.50	1.50
Cyclone	10		3.00	3.05
PW	25		0.20	0.20
3B Cyclone	5 ml	0.00975	3.70	3.75
PW	25		0.25	0.25
4A Cyclone	10 ml	0.00975	9.15	9.15
PW	25		0.55	0.50
4B Cyclone	10 ml	0.00975	15.00	15.00
PW	25		0.45	0.55
Filter 777	5 ml	0.00972	7.30	7.30
771			1.70	1.65
733			2.30	2.40
784			9.10	9.00
778			8.10	8.20
770			1.70	1.75
772			0.10	0.10
772	25		0.15	0.15
773	5		0.10	0.10
773	25		0.15	0.15
770	10 (Renyn)		3.40	3.50
Blank			0.05	0.05

PROJECT _____ JOB NO. _____ DATE _____ SHT. _____

DETAIL _____ BY _____ OF _____

APPENDIX F

HYDROCARBONS FIELD DATA SHEETS AND STRIP CHARTS

FIELD DATA

PLANT NASCO
DATE 12-17-80
SAMPLING LOCATION Baghouse
SAMPLE TYPE Method 5
RUN NUMBER M5-1
OPERATOR Michael Hackett
AMBIENT TEMPERATURE 30°F
BAROMETRIC PRESSURE 30.01
STATIC PRESSURE, (P_s) +.22
FILTER NUMBER (s)

PROBE LENGTH AND TYPE 3' glass
NOZZLE I.D. .375
ASSUMED MOISTURE, % 2
SAMPLE BOX NUMBER 25-3
METER BOX NUMBER 25-6
METER $\Delta H_@$ 1.87
C FACTOR 1.03
PROBE HEATER SETTING 100%
HEATER BOX SETTING 100%
REFERENCE Δp .086

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 3 MINUTES

Initial leak check 0.006 cfm @ 15" Hg
Final leak check

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft³	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
					DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			
A-12	0	1005	93.704	.08	1.72	1.12	72	36		0	272	28
A-11	3	1008	95.450	.13	2.71	2.11	73	37		1	262	28
A-10	6	1011	97.600	.15	3.10	2.50	74	40		1	268	28
A-9	9	1014	100.000	.16	3.30	2.70	75	42		1	235	28
A-8	12	1017	102.400	.16	3.30	2.70	75	44		1	235	28
A-7	15	1020	104.900	.18	3.75	3.15	75	46		2	236	28
A-6	18	1023	107.200	.22	4.45	3.85	74	49		3	238	28
A-5	21	1026	111.000	.22	4.45	3.85	73	50		3	233	33
A-4	24	1029	114.100	.22	4.45	3.85	73	52		3	235	39
A-3	27	1032	117.000	.22	4.45	3.85	73	54		3	235	43
A-2	30	1035	120.200	.23	4.70	4.10	77	57		3	235	45
A-2	33	1038	123.900	.23	4.70	4.10	75	58		4	236	49
A-2	36	1041	126.740		STOP TEST - change ports							
B-12	36	1100	126.740	.22	4.45	3.85	72	45		3	215	40
B-11	39	1103	129.600	.25	5.10	4.50	71	46		4	248	42
B-10	42	1106	133.000	.29	5.90	5.30	71	49		5	250	45
B-9	45	1109	136.800	.29	5.90	5.30	72	51		5	263	52
B-8	48	1112	140.100	.36	7.30	6.70	74	55		6	272	58
B-7	51	1115	144.400	.38	7.70	7.10	75	58		6	268	60
B-6	54	1118	148.200	.40	8.30	7.70	75	60		7	268	62

PAGE 2 - RUN M5-1 Baghouse

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			
B-5	57 1121	153.100	.40	8.30	7.70	74	62		7	252	64
B-4	60 1124	157.300	.44	9.00	8.40	73	64		7	248	62
B-3	63 1127	162.100	.44	9.00	8.40	69	66		7	242	62
B-2	66 1130	166.800	.48	9.70	9.10	69	69		8	240	60
B-1	69 1133	171.400	.48	9.70	9.10	71	70		8	240	58
	72 1136	176.142		STOP	TEST	END					
		82.4x	.376		8.0K	73.1	52.5				

Need to switch nozzle after port change — keep sampling because HC are high

Δ H subtraction factor = 0.5

Fyrite O_2 - 21%

(O_2 - 0%)

FIELD DATA

PLANT NASCO
DATE 12-17-80
SAMPLING LOCATION Baghouse
SAMPLE TYPE Method 5
RUN NUMBER M5-2
OPERATOR LeeGendek
AMBIENT TEMPERATURE 40°F
BAROMETRIC PRESSURE 30.01
STATIC PRESSURE, (P_s) +.22
FILTER NUMBER (s)

initial leak check = 0.015 cfm @ 10" Hg
Final leak check = .008 cfm @ 11" Hg

PROBE LENGTH AND TYPE 3' glass
NOZZLE I.D. .250
ASSUMED MOISTURE, % 2
SAMPLE BOX NUMBER ES-3
METER BOX NUMBER ES-6
METER $\Delta H_@$ 1.87
C FACTOR
PROBE HEATER SETTING 100%
HEATER BOX SETTING 100%
REFERENCE Δp

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 3 MINUTES

initial leak check
Final leak check

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O DESIRED	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O ACTUAL	STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE INLET ($T_{m\,in}$), °F	DRY GAS METER TEMPERATURE OUTLET ($T_{m\,out}$), °F	PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
	0 / 1504	177.495									
B 12	3 / 1504	180.5	0.97	3.0	2.50	74	43		4	230	26
11	6 / 1507	183.0	1.05	4.0	3.50	71	49		6	232	28
10	9 / 1510	185.7	1.05	4.0	3.50	70	44		6	236	28
			Fine in pitot line								
9	12 / 1513	186.778	0.18	0.74	0.24	69	49		1	238	29
			shut down i pitot probing								
	12 / 1531		sw. tch	umbilicals	leak	check			OK		
B 8	18 / 1534	188.2	0.30	1.24	0.74	76	43			220	28
7	18 / 1537	189.4	0.28	1.18	0.68	77	43		1	225	28
6	21 / 1540	190.8	0.26	1.08	0.58	79	44		1	228	26
B 5	24 / 1543	192.0	0.26	1.08	0.58	84	45		1	230	28
4	27 / 1546	193.1	0.22	0.91	0.41	80	46		1	232	28
3	30 / 1549	194.2	0.22	0.91	0.41	77	47		1	234	27
2	33 / 1552	195.2	0.21	0.86	0.36	74	47		1	235	27
1	36 / 1555	196.202	0.22	0.91	0.41	72	49		1	235	27
			sw. tch		b	0.375	nozzle ref bp			0.088	
	36 / 1613										
A 12	39 / 1616	200.1	.31	6.3	5.8	72	46		10	230	26
11	42 / 1619	204.3	0.30	6.1	5.6	71	50		10	230	26
10	45 / 1622	208.5	0.31	6.3	5.8	77	54		10	228	28
9	48 / 1625	211.5	0.31	6.3	5.8	77	57		10	226	28
8	51 / 1628	214.7	0.30	6.1	5.6	76	60		10	224	30
7	54 / 1631	218.0	0.29	6.0	5.5	75	61		10	226	33

COMMENTS:

HC peak occurred in here

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
					DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			
A-6	57	1634	222.8	0.28	5.1	5.2	79	64		10	230	35
5	60	1637	226.5	0.25	5.1	4.6	81	66		9	230	35
4	63	1640	229.2	0.20	4.1	3.6	75	66		7	228	35
3	66	1643	232.0	0.25	5.1	4.6	78	66		9	224	35
2	69	1646	235.8	0.18	3.8	3.3	82	68		6	220	35
1	72	1649	238.612	0.18	3.8	3.3	78	68		6	215	35
					END		OF TEST					
			38.512	.16		0	362	60				
				.555		3.03	76.0	52.9				

EPA (Dur) 236

ANALYTICAL DATA

PLANT NASCO

DATE 12/17/80

SAMPLING LOCATION Baghouse

SAMPLE TYPE M5 ① condensate

RUN NUMBER 2

SAMPLE BOX NUMBER

CLEAN-UP MAN ALG

COMMENTS:

FRONT HALF

LABORATORY RESULTS

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

FILTER NUMBER ~~leaky filter~~ _____ — CONTAINER _____ _____ mg

773 _____

_____ _____

Filter difficult to recover again —

FRONT HALF SUBTOTAL _____ mg

BACK HALF

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

ETHER-CHLOROFORM EXTRACTION _____ mg

ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

BACK HALF SUBTOTAL _____ mg

TOTAL WEIGHT _____ mg

MOISTURE

		①	②	③	
IMPINGERS					
FINAL VOLUME	_____ ml	590.6	588.1	504.2	9.7
INITIAL VOLUME	_____ ml	600.3	584.6	503.1	4.6
NET VOLUME	_____ ml	−9.7	3.5	1.1	−5.1
SILICA GEL					
FINAL WEIGHT	214.0 g	241.9 g	_____ g		
INITIAL WEIGHT	219.5 g	226.0 g	_____ g		
NET WEIGHT	−5.5 g	15.9 g	_____ g		

TOTAL MOISTURE 5.3

EPA (Dur) 231
4/72

silica gel 10.4

ANALYTICAL DATA

PLANT NASCO

DATE 12/17/80

SAMPLING LOCATION Baghouse

SAMPLE TYPE M5 - plus organics

RUN NUMBER 1

SAMPLE BOX NUMBER _____

CLEAN-UP MAN ALG

COMMENTS:

FRONT HALF

LABORATORY RESULTS

ACETONE WASH OF NOZZLE, PROBE, CYCLONE (BYPASS), FLASK, FRONT HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

FILTER NUMBER 772 — CONTAINER _____ _____ mg

Filter pieces were charged electrostatically

Filter stuck to frit — Recovered as much as possible - Filter looked very clean - some small specs lost

FRONT HALF SUBTOTAL _____ mg

BACK HALF

IMPINGER CONTENTS AND WATER WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

ETHER-CHLOROFORM EXTRACTION _____ mg

ACETONE WASH OF IMPINGERS, CONNECTORS, AND BACK HALF OF FILTER HOLDER — CONTAINER _____ _____ mg

BACK HALF SUBTOTAL _____ mg

TOTAL WEIGHT _____ mg

MOISTURE

		1	2	3	
IMPINGERS					42.9
FINAL VOLUME	ml	555.0	601.2	507.8	25.1
INITIAL VOLUME	ml	580.1	565.2	500.9	
NET VOLUME	ml	-25.1	36.0	6.9	17.8
SILICA GEL					
FINAL WEIGHT	g	230.5	265.6		
INITIAL WEIGHT	g	232.0	240.9		
NET WEIGHT	g	-1.5	24.7		

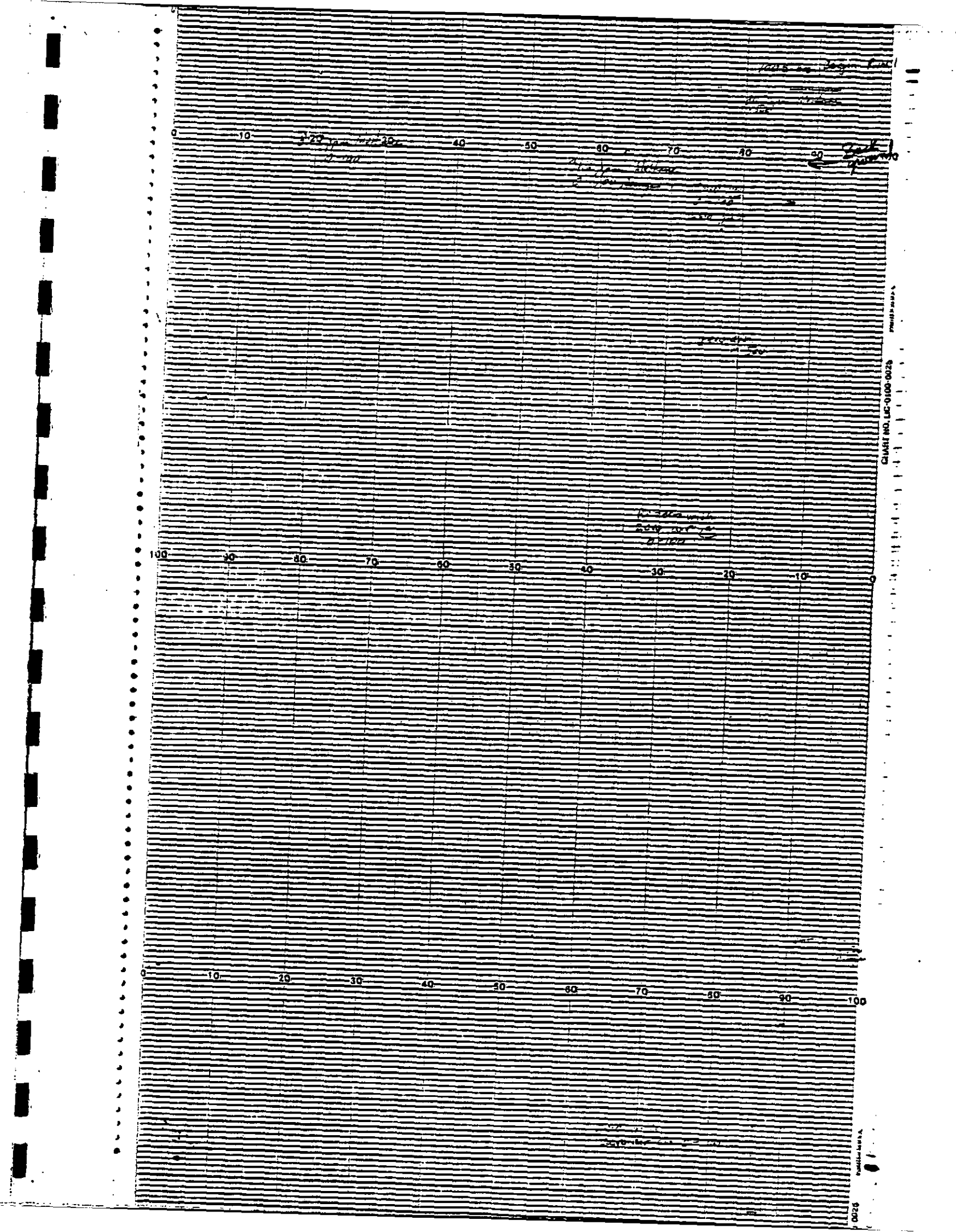
TOTAL MOISTURE 42.5

24.7

17.8
24.7
42.5

EPA (Dur) 231
4/72

0
10
20
30
40
50
60
70
80
90
100
CHART NO. MC-0100-0025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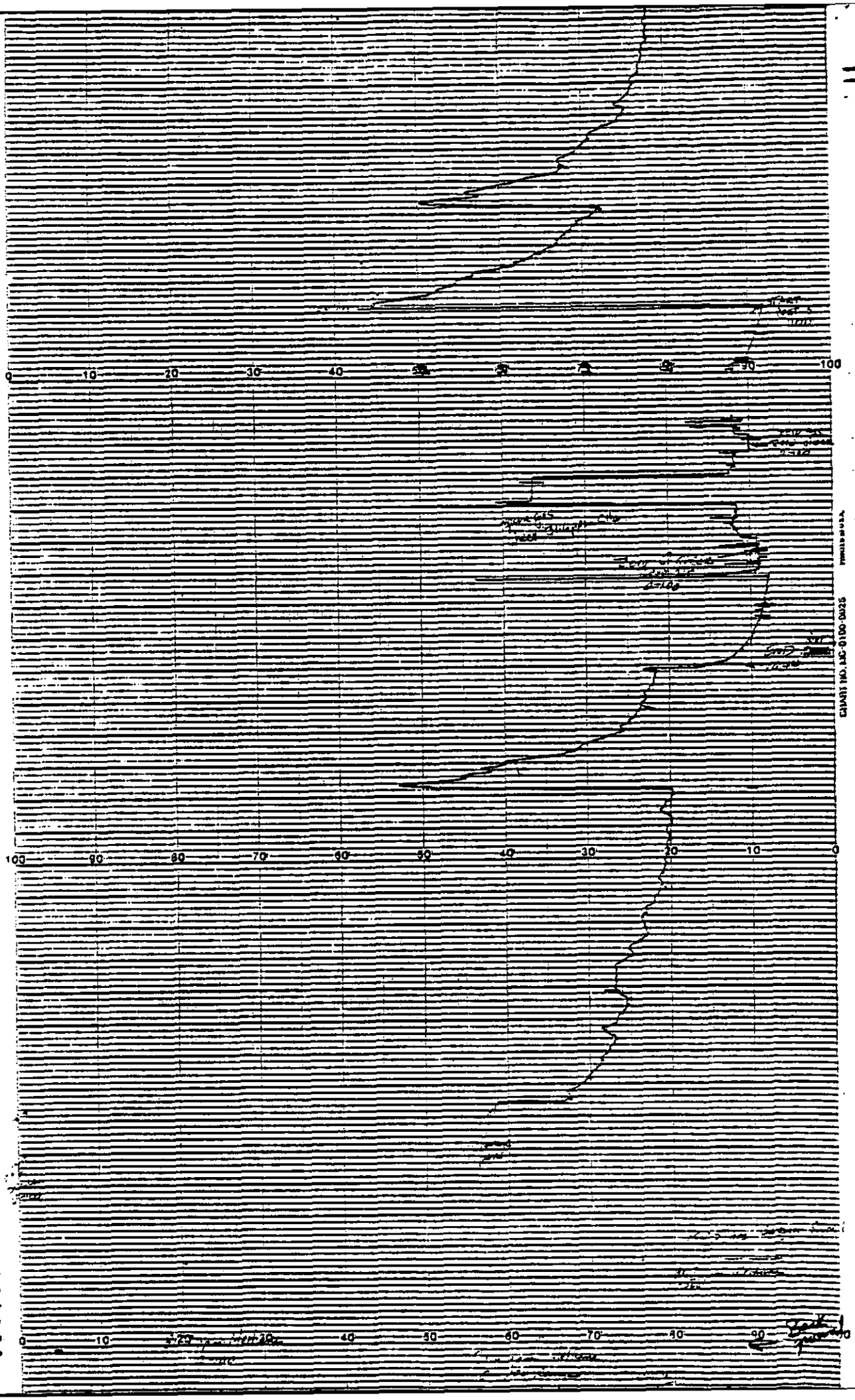
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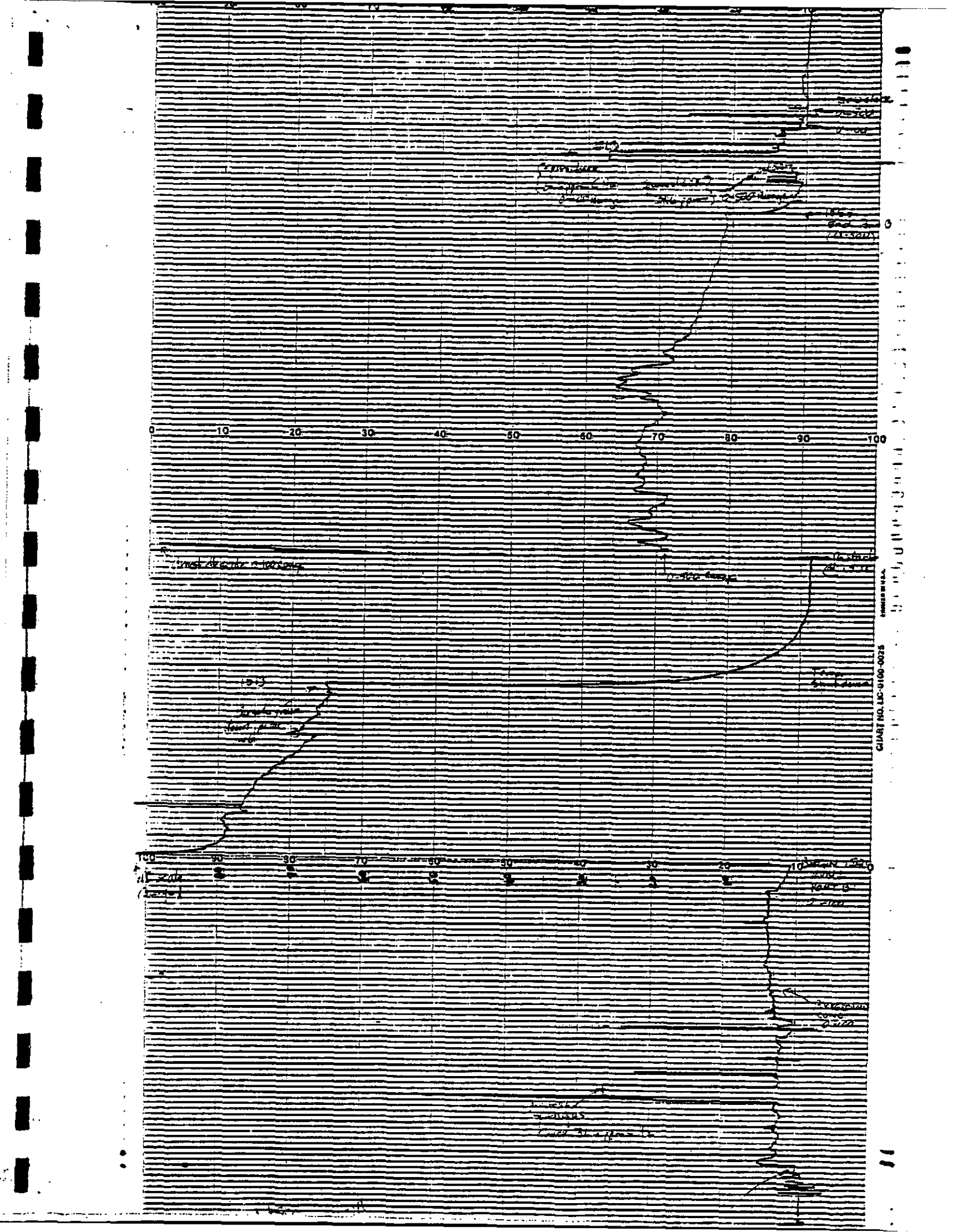
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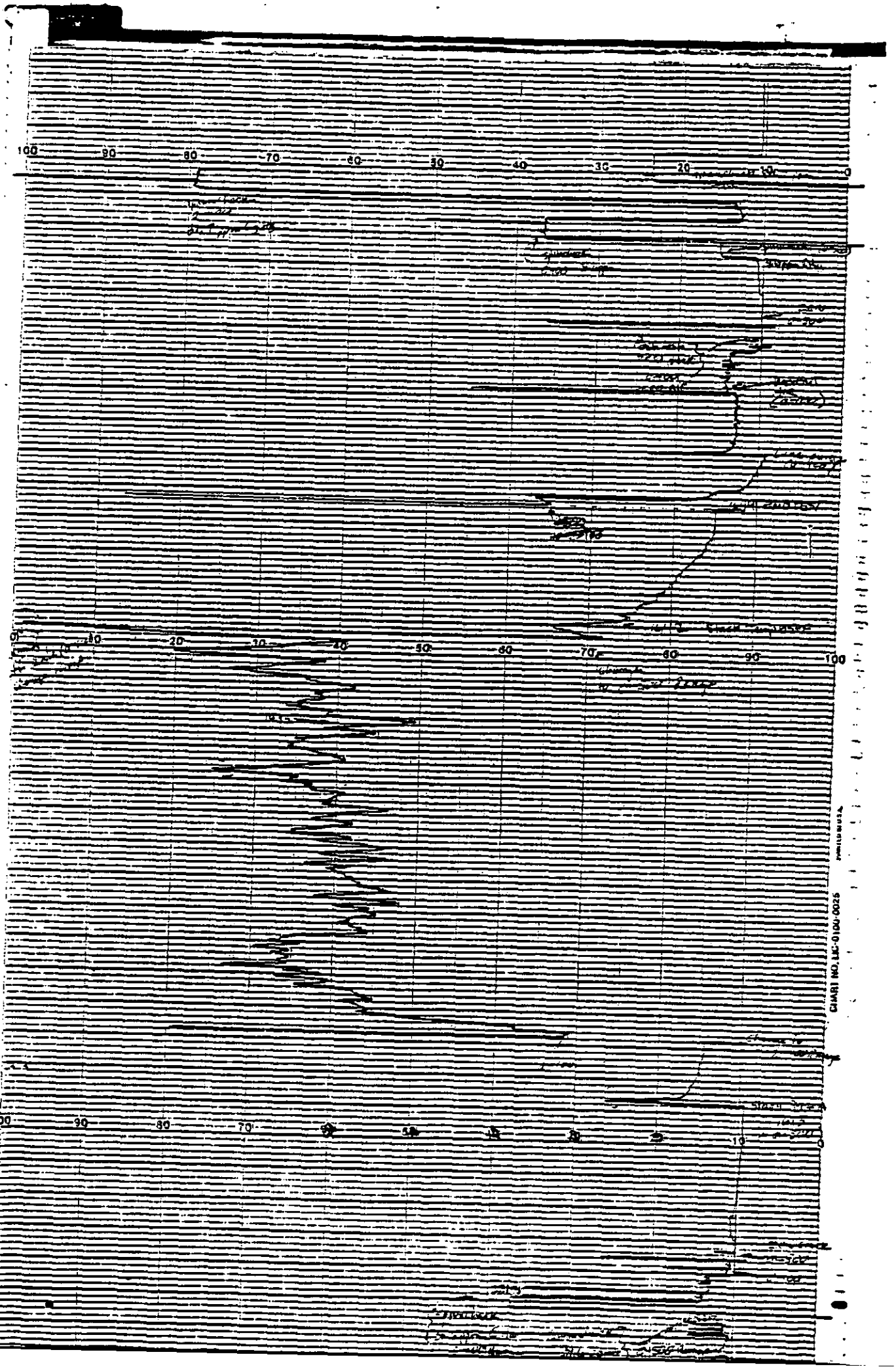
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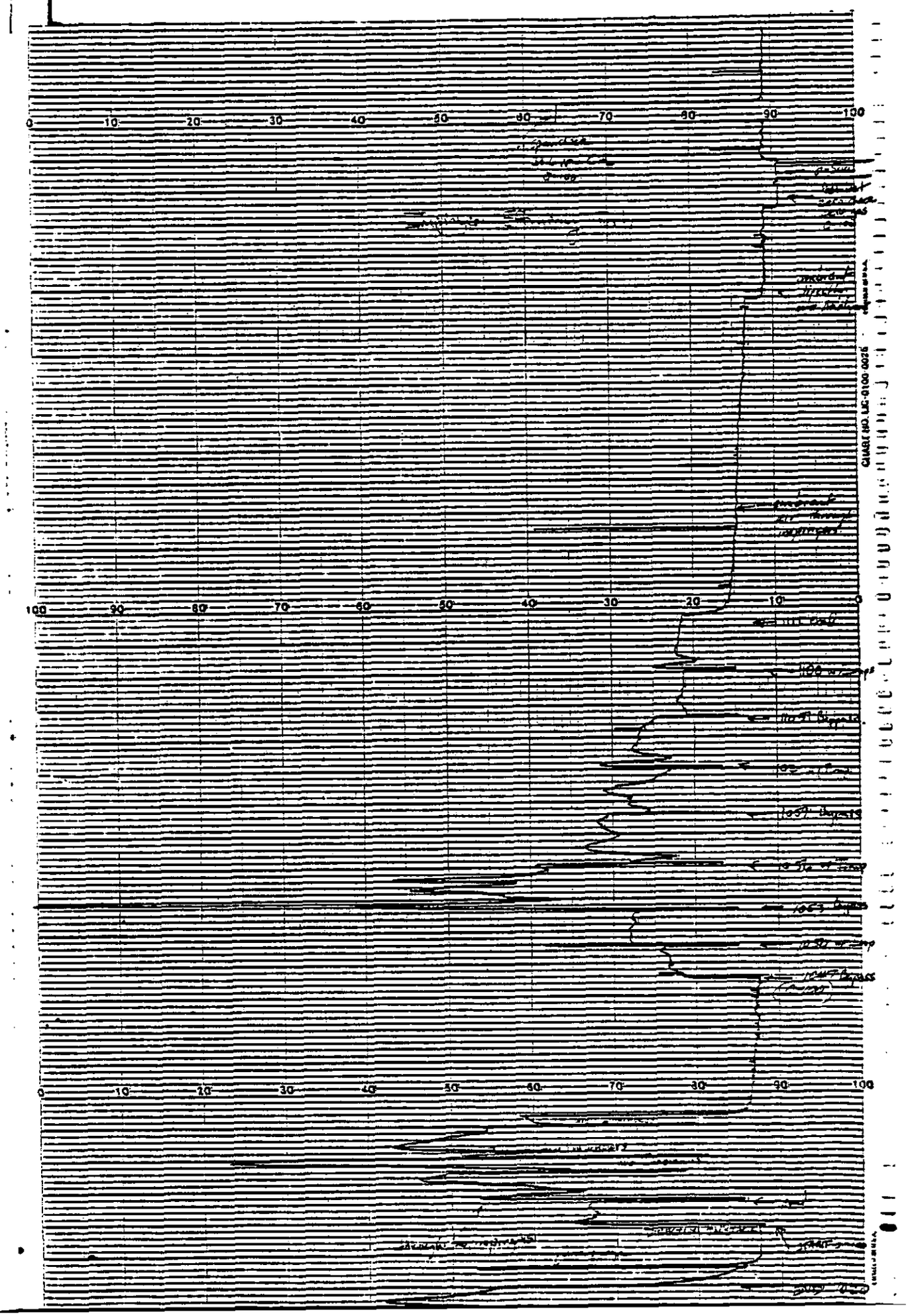
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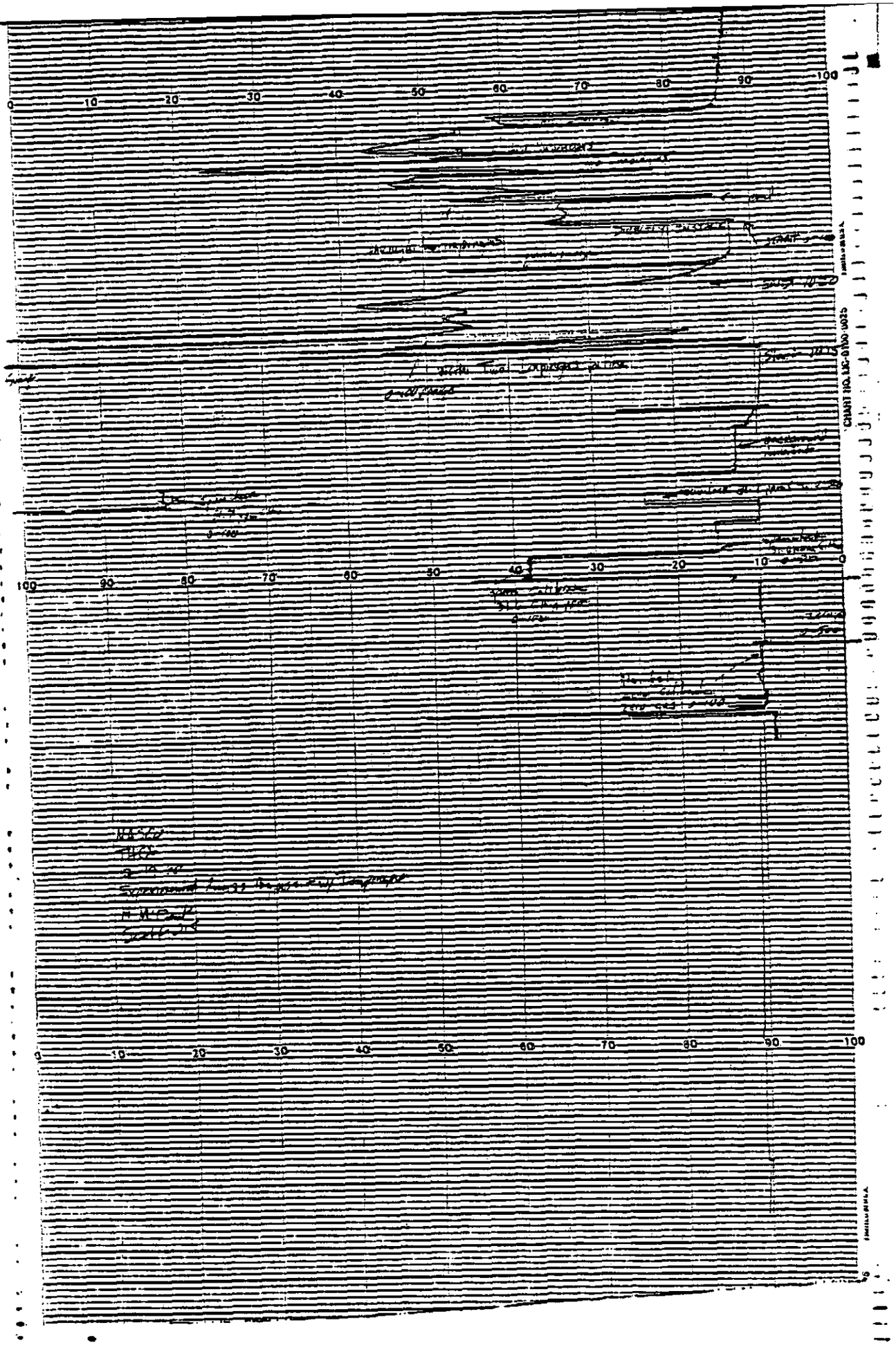
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100 90 80 70 60 50 40 30 20 10 0
0 10 20 30 40 50 60 70 80 90 100

APPENDIX G

HYDROCARBONS LAB DATA

ENGINEERING-SCIENCE

PLANT/LOCATION _____

DATE _____

PARTICULATE WEIGHT, FILTER

Run No./Filter No.					
Filter, Gross Wt., g					
Initial Wt., g					
Net Wt., g					

RESIDUE WEIGHT Acetone Back Half

Run No.	Run 1/G557	Run 2/G559			
Acetone Blank Vol., ml	95.1	95.1			
Acetone Blank Residue, g	0.0006	0.0006			
Acetone Blank Conc., g/l	0.0063	0.0063			
Wash Volume, ml	206.0	201.0			
Gross Residue Wt., g	0.0156	0.0091			
Blank Wt., g	0.0013	0.0018			
Net Residue Wt., g	0.0143	0.0073			

RESIDUE WEIGHT Acetone Probe Wash

Run No.	Run 1/G556	Run 2/G558			
Acetone Blank Vol., ml	95	95.1			
Acetone Blank Residue, g	0.0006	0.0006			
Acetone Blank Conc., g/l	0.0063	0.0063			
Wash Volume, ml	71.4	112.3			
Gross Residue Wt., g	0.0082	0.0297			
Blank Wt., g	0.0045	0.0071			
Net Residue Wt., g	0.0037	0.0226			

ENGINEERING-SCIENCE

PLANT/LOCATION _____

DATE _____

PARTICULATE WEIGHT, FILTER

Run No./Filter No.					
Filter, Gross Wt., g					
Initial Wt., g					
Net Wt., g					

RESIDUE WEIGHT, TCE Back Half

Run No./Beaker No.	Run 1/G541	Run 2/G542			
TCE Blank Vol., ml	58.5	58.5			
TCE Blank Residue, g	0.0007	0.0007			
TCE Blank Conc., g/l	0.0120	0.0120			
Wash Volume, ml	94.4	162.3			
Gross Residue Wt., g	0.0054	0.0123			
Blank Wt., g	0.0011	0.0019			
Net Residue Wt., g	0.0043	0.0104			

Extractions - Neutral

Run No./Beaker No.	Run 1/G541	Run 2/G544
DH_2O Blank Vol., ml	148.6	148.6
DH_2O Blank Residue, g	0.0018	0.0018
DH_2O Blank Conc. g/l	0.0121	0.0121
Wash Volume, ml	185.0	199.0
Gross Residue Wt. g	0.0049	0.0037
Blank Wt., g	0.0022	0.0024
Net Residue Wt. g	0.0027	0.0000

Extraction - Acid

	Run 1/G542	Run 2/G545
Acid Blank Vol, ml	148.6	148.6
Acid Blank Residue, g	0.0008	0.0008
Acid Blank Conc. g/l	0.0054	0.0054
Wash Volume, ml	185	199.
Gross Residue Wt. g.	0.0003	0.0022
Blank wt, g	0.0010	0.0011
Net Residue Wt. g.	—	0.0011

ANALYSIS Post wt. SOLVENT Acetone, TCE ANALYSIS STARTED _____ FINISHED _____

PROJECT NUMBER 3346 PROJECT NAME Secondary #1 PROJECT MANAGER L. Grenoble ITEM WEIGHED Beakers

TARE WEIGHT

DATE		12-17	12-17	12-18	18-Dec 00			
R.H. (%)		20	26	24	20			
TEMP (°F)		68	66	66	66			
Std. Wt.		100.0000gm	100.0000	100.0000gm	100.0000gm			
ANALYST		CC	LC	CC	VP			
NUMBER	FIELD SAMPLE NUMBER	1st Wt.	2nd Wt.	3rd Wt.	4th Wt.	5th Wt.	6th Wt.	FINAL TARE Wt. (g)
G 555	Blank Beakers	98.2620	98.2603	98.2615	98.2614			98.2615
G 556	Run1 Probe wash Beakers	94.2432	94.2413	94.2417				94.2415
G 557	Run1 Back Half Beakers	95.8436	95.8427	95.8431				95.8429
G 558	Run2 Probe wash Beakers	93.6510	93.6499	93.6506	93.6501			93.6504
G 559	Run2 Back Half Beakers	96.1710	96.1699	96.1701				96.1700
G 560	Blank TCE	96.2044	96.2031	96.2036				96.2034
G 561	Run1 Back Half TCE	95.9929	95.9918	95.9922				95.9920
G 562	Run2 Back Half TCE	98.2571	98.2567					98.2569
G 563		93.9140		93.9145				93.9143

FINAL WEIGHT

DATE	Jan 15	Jan 15	Jan 16					
R.H. (%)	28	28	27					
TEMP (°F)	70	72	70					
Std. Wt.	100.0000gm	100.0000	100.0000					
ANALYST	CC	MK	MK					
NUMBER	1st Wt.	2nd Wt.	3rd Wt.	4th Wt.	5th Wt.	FINAL SAMPLE Wt. (g)	TARE Wt. (g)	DIFFERENCE (g)
G 555	98.2620	98.2621				98.2621	98.2615	0.0006
G 556	94.2487	94.2498	94.2496			94.2497	94.2415	0.0082
G 557	95.8571	95.8585	95.8585			95.8585	95.8429	0.0156
G 558	93.6791	93.6803	93.6798			93.6801	93.6504	0.0297
G 559	96.1788	96.1793				96.1791	96.1700	0.0091
G 560	96.2039	96.2042				96.2041	96.2034	0.0007
G 561	95.9972	95.9976				95.9974	95.9920	0.0054
G 562			98.2694			98.2692	98.2569	0.0123

[redacted] SOLVENT Eth/DCM/Comp ANALYSIS STARTED [redacted] FINISHED [redacted]

PROJECT NUMBER 3346 9114 PROJECT NAME Secondary Fiberglass A1 PROJECT MANAGER R. Stiver/L. Grenoble ITEM WEIGHED [redacted]

TARE WEIGHT

DATE		Dec 17	Dec 18	Dec 22, 80	Dec. 29, 80			
R.H. (%)		20%	24	30 16	37			
TEMP (°F)		68	68	66	69			
Std. Wt.		100.0000 g	100.0000 g	100.0000 g	100.0000 g			
ANALYST		cc	cc	cc	cc			
NUMBER	FIELD SAMPLE NUMBER	1st Wt.	2nd Wt.	3rd Wt.	4th Wt.	5th Wt.	6th Wt.	FINAL TARE Wt. (g)
G 548	FIELD BLANK ACID EXTRACTION	95.5364	95.5366					95.5365
G 539	DH2O Blank Neutral Extract	91.8032	91.8037					91.8034
G 540	DH2O Blank Acid Extraction	94.5560	94.5565					94.5562
G 541	Run 1 IMPINGER NEUTRAL EXTRACTION	95.0684	95.0694	95.0679	95.0684			95.0681
G 542	Run 1 IMPINGER ACID EXTRACTION	97.6533	97.6543	97.6538				97.6540
G 543	R [redacted]	100.9520	100.9532	100.9510	100.9521			—
G 544	Run 2 IMPINGER NEUTRAL EXTR.	91.6435	91.6445	91.6446				91.6445
G 545	Run 2 IMPINGER ACID EXTRACTION	94.9410	94.9415					94.9412
G 546	FIELD BLANK NEUTRAL EXTRACTION	94.8823	94.8830	94.8819	94.8815			94.8817

FINAL WEIGHT

DATE	Jan 15, 1981	Jan 15, 1981	Jan 16					
R.H. (%)	28	28	27					
TEMP (°F)	70	72	70					
Std. Wt.	100.0000 g	100.0000	100.0000					
ANALYST	cc	MKT	MKT					
NUMBER	1st Wt.	2nd Wt.	3rd Wt.	4th Wt.	5th Wt.	FINAL SAMPLE Wt. (g)	TARE Wt. (g)	DIFFERENCE (g)
G 539	91.8028	91.8028				91.8028	91.8034	—
G 540	94.5565	94.5580	94.5578			94.5579	94.5562	0.0017
G 541	95.0718	95.0730	95.0729			95.0730	95.0681	0.0049
G 542	97.6540	97.6545				97.6543	97.6540	0.0003
G 543							—	
G 544	91.6449	64.6454				91.6452	91.6445	0.0007
G 545	94.9420	94.9432	94.9435			94.9434	94.9412	0.0022
G 546	94.8822	94.8833	94.8837			94.8835	94.8817	0.0018
G 548	95.5363	95.5372	95.5373			95.5373	95.5365	0.0008

ANALYSIS Part WT SOLVENT — ANALYSIS STARTED _____ FINISHED _____

PROJECT NUMBER 3346 PROJECT NAME Secondary Al. PROJECT MANAGER L. Genoble ITEM WEIGHED Quartz fiber

TARE WEIGHT

DATE		13Dec80	13Dec80					
R.H.(%)		34	40					
TEMP(°F)		72	69					
Std.Wt.		30.0000	30.0000					
ANALYST		WKF	WKF					
NUMBER	FIELD SAMPLE NUMBER	1st Wt.	2nd Wt.	3rd Wt.	4th Wt.	5th Wt.	6th Wt.	FINAL TARE Wt. (g)
Q766		26.9646	26.9645					
Q767		29.7489	29.7493					
Q768		31.2882	31.2881					
Q769		32.2735	32.2736					
Q770	SCRUBBER RUN 3A	28.3037	28.3037					28.3037
Q771	SCRUBBER RUN 3B	31.9450	31.9451					31.9451
Q772	BAGHOUSE RUN 1	33.0767	33.0770					33.0769
Q773	BAGHOUSE RUN 2	31.9160	31.9164					31.9162
Q774		31.9392	31.9396					
Q775		32.0643	32.0646					

FINAL WEIGHT

DATE	Jan 6	Jan 7	1/9/81	1/9/81				
R.H.(%)	24	28	22	22				
TEMP(°F)	70	68	62	60				
Std.Wt.	30.0000 gm	30.0000 gm	30.0000	30.0000				
ANALYST	CL	CL	WKF	WKF				
NUMBER	1st Wt.	2nd Wt.	3rd Wt.	4th Wt.	5th Wt.	FINAL SAMPLE Wt. (g)	TARE Wt. (g)	DIFFERENCE (g)
Q770	28.4706	28.4701				28.4704	28.3037	0.1667
Q771	32.1054	32.1058				32.1056	31.9451	0.1605
Q772	33.0648	33.0682	33.0646	33.0641		33.0643	33.0769	—
~~Q773~~	~~33.0648~~							
Q773	31.9137	31.9139				31.9138	31.9162	—

ANALYSIS _____ SOLVENT _____ ANALYSIS STARTED _____ FINISHED _____

PROJECT NUMBER 3346 PROJECT NAME Secondary A1 PROJECT MANAGER L. Genoble ITEM WEIGHED Quartz Filters

TARE WEIGHT

DATE		13 Dec 80	13 Dec 80					
R.H. (%)		34	40					
TEMP (°F)		72	69					
Std. Wt.		30.0000	30.0000					
ANALYST		MKS	MKS					
NUMBER	FIELD SAMPLE NUMBER	1st Wt.	2nd wt.	3rd wt.	4th. wt.	6th wt.	6th wt.	FINAL TARE Wt. (g)
Q 776		27.5795	27.5795					
Q 777	SCRUBBER RUN 4A	30.7391	30.7395					30.7393
Q 778	SCRUBBER RUN 4B	33.3879	33.3880					33.3880
Q 779		33.7831	33.7831					2
Q 780		30.8593	30.8597					
Q 781		31.5354	31.5358					
Q 782		30.3080	30.3033					
Q 783	SCRUBBER RUN 3A	27.6365	27.6362					27.6364
Q 784	SCRUBBER RUN 3B	30.7395	30.7391					30.7393
Q 785		29.1697	29.1696					

FINAL WEIGHT

DATE	Jan 6	Jan 6	1/9/81	1/9/81	1/12/81			
R.H. (%)	24	28	22	22	24			
TEMP (°F)	70	68	62	60	65			
Std. Wt.	30.0000gm	30.0000gm	30.000	30.000	30.000			
ANALYST	CC	CC	MKS	MKS	MKS			
NUMBER	1st Wt.	2nd Wt.	3rd wt.	4th wt.	6th wt.	FINAL SAMPLE Wt. (g)	TARE Wt. (g)	DIFFERENCE (g)
Q 777	31.2521	31.2517				31.2519	30.7393	0.5126
Q 778	33.8921	33.8989	33.8870	33.8869		33.8870	33.3880	04990
Q 783	27.8294	27.8307	27.8265	27.8298	27.8294	27.8296	27.6364	0.1932
Q 784	" ~~31.3102~~	31.2102				31.2102	30.7393	0.4709

ENGINEERING-SCIENCE

PLANT/LOCATION _____

DATE _____

PARTICULATE WEIGHT, FILTER

SCRUBBER | Baghouse

Run No./Filter No.	Run 1A/Q783	Run 3A/Q770	Run 4A/Q777		Run 1/Q772
Filter, Gross Wt., g	27.8296	28.4704	31.2519		33.0643
Initial Wt., g	27.6364	28.3037	30.7393		33.0769
Net Wt., g	0.1932	0.1667	0.5126		—

PARTICULATE WEIGHT, FILTER

SCRUBBER | BAGHOUSE

Run No./Filter No.	Run 2B/Q784	Run 3B/Q771	Run 4B/Q778		Run 2/Q773
Filter, Gross Wt., g	31.2102	32.1056	33.8870		31.9138
Initial Wt., g	30.7393	31.9451	33.3880		31.9162
Net Wt., g	0.4709	0.1605	0.4990		—