

**RESULTS OF SOURCE EMISSIONS CHARACTERIZATION
AT THE HEMPSTEAD, NY REFUSE ENERGY RECOVERY SYSTEM**

Submitted to:

**ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711**

UNDER CONTRACT 68-02-2566

Submitted by:

NORTHROP SERVICES, INC.
ENVIRONMENTAL SCIENCES
P.O. BOX 12313
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

NSi

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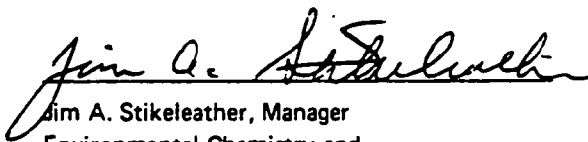
Environmental Chemistry and Emissions Sciences
Northrop Services, Inc.
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DISCLAIMER

This report has been reviewed by Northrop Services, Inc.-Environmental Sciences, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.



FOREWORD

This report presents the results of work performed by Northrop Services, Inc.-Environmental Sciences, under Contract Number 68-02-2566 for the Stationary Sources Emissions Research Branch, Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. The source work was conducted in response to Technical Directive 3.3-52, while the laboratory work was conducted under Technical Directive 3.3-1.

ABSTRACT

In response to a request from Region II of the U.S. Environmental Protection Agency, Northrop Services, Inc.-Environmental Sciences was contracted by the Agency's Environmental Sciences Research Laboratory to conduct source sampling at the Hempstead Resources Recovery Corporation Facility in Hempstead, New York. Source samples were collected from July 24 to July 26, 1979, and extensive laboratory studies were undertaken to validate the results of sample analysis.

Although sampling was hampered by considerable down time at the facility, the measurements for chloride and sulfur oxide emissions indicate low concentration levels for these species. Sampling for organic species yielded an average total organic emission rate in excess of 25 lb/h. The majority of organic emissions consisted of commonly-occurring, innocuous compounds, but several materials posing potential hazards were also detected: substituted phthalate isomers, chlorinated phenols, chlorinated biphenyls and related compounds. The results of additional sample analyses currently in progress will be reported at a later date.

Analysis by ion chromatography of sample fractions from the sulfur oxide sampling train detected the presence of formate and acetate. Laboratory studies indicated that these species were not the result of artifact formation, but rather could be formed by the oxidation of formaldehyde and acetaldehyde via the hydrogen peroxide impinger solutions. However, the possibility that the decomposition or oxidation of other species is responsible for the formate and acetate cannot be ruled out entirely.

Laboratory studies also showed that the collection efficiency of the sampling train for formaldehyde was less than 100%, which means the reported



emission rates may be considered lower limits. Since the aldehyde results are based on one sampling run, their representativeness cannot be determined without additional source testing.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

CCS	-- Controlled Condensation System
D.I. H ₂ O	-- deionized water
DNPH	-- 2,4-dinitrophenylhydrazine
EPA	-- U.S. Environmental Protection Agency
ESP	-- electrostatic precipitator
GC	-- gas chromatography
HCl	-- hydrochloric acid
HCOOH	-- formic acid
HPLC	-- high performance liquid chromatography
IC	-- ion chromatography
Imp	-- impinger
IPA	-- isopropyl alcohol
MeOH	-- methyl alcohol
MS	-- mass spectrometry
MW	-- molecular weight
NSI-ES	-- Northrop Services, Inc.-Environmental Sciences
OAc	-- acetate
PCB's	-- polychlorinated biphenyls
PCP's	-- polychlorinated phenols
PP	-- probe plug
PW	-- probe wash
RDF	-- refuse-derived fuel
RT	-- retention time
XRF	-- x-ray fluorescence
QA	-- quality assurance
RDF	-- refuse-derived fuel
RT	-- retention time
VFR	-- volumetric flow rate
XRF	-- x-ray fluorescence

SYMBOLS

Cl ⁻	-- chloride
CH ₂ O	-- formaldehyde
C ₂ H ₄ O	-- acetaldehyde
C ₂ H ₆ O ₂	-- ethylene glycol
FeCl ₃	-- ferric chloride
HCOO	-- formate
H ₂ SO ₄	-- sulfuric acid
Na ₂ CO ₃	-- sodium carbonate
NaHCO ₃	-- sodium bicarbonate
NaOH	-- sodium hydroxide
Na ₂ B ₄ O ₇	-- sodium borate
SO _x	-- sulfur oxides
SO ₂	-- sulfur dioxide

ACKNOWLEDGMENT

It is with pleasure that we acknowledge the work of Mr. Gary Grotecloss and Mr. Mike Pleasant who conducted the source sampling and participated in the preparation of our initial report. With equal pleasure we acknowledge the assistance of our colleagues, Dr. John Windsor and Mrs. Sandy Parks, for obtaining and interpreting the gas chromatography/mass spectrometry results presented in this report. We also acknowledge the work of our EPA colleagues, Mr. Jim Homolya and Mr. Jim Cheney, for their many helpful discussions.

SECTION 1
INTRODUCTION

Northrop Services, Inc.-Environmental Sciences (NSI-ES) conducted source sampling on Furnace #2 at the Hempstead Resources Recovery Corporation Facility in Hempstead, New York from July 24 to July 26, 1979. The purpose of this sampling was to characterize hydrochloric acid (HCl) and organic emissions produced from the combustion of nonreclaimed refuse. Sampling was also conducted by the U.S. Environmental Protection Agency (EPA) for sulfuric acid (H_2SO_4) and sulfur dioxide (SO_2), while NSI-ES conducted supplementary oxygen monitoring. Since the plant was down (out of operation) for considerable periods of time during the week of sampling, only a few runs were completed.

EPA Region II has requested follow-up laboratory work in order to validate the results obtained from analyses of the Hempstead field samples. This paper reports this work, conducted by NSI-ES and EPA, and gives the results of additional laboratory experiments conducted by NSI-ES.

SECTION 2

CONCLUSIONS

The results of source sampling on Furnace #2 at the Hempstead Refuse Energy Recovery System indicated low concentrations of chloride (Cl^-) and sulfur oxides (SO_x) in the flue gas. Because of the considerable time that the plant was down during the test, sampling performed on July 26, 1979 is considered to be most representative of the plant operation. At an operating capacity of about 75%, the average mass emission rate for total Cl^- was only 28 lb/h (15 lb/h particulate matter (PM), 13 lb/h gas). The mass emission rate of SO_x averaged 51 lb/h (4.5 lb/h PM, 46 lb/h SO_2 gas). Based on past experience with other sources, these levels are not considered environmentally harmful.

Source test results for organic emissions were consistent over three days of sampling, producing an average emission rate of 26 lb/h for total organics. This value must be taken as a lower limit, however, because the absolute collection efficiency of the sampling train has not been determined. The samples were qualitatively analyzed using gas chromatography (GC) and GC/mass spectrometry (GC/MS).

The samples were found to contain several potentially hazardous materials, including substituted phthalates, chlorinated phenols and chlorinated biphenyls. Since the analysis was not quantitative, whether or not these species were present at levels great enough to pose human/environmental risk could not be determined. Additional analyses have been performed on these samples to identify any other species undetectable by GC/MS surveys. These results will be reported at a later date.

SECTION 3

RECOMMENDATIONS

For future field collection of flue gas samples at sources similar to the Hempstead plant, methods development and additional source characterization are recommended within the following framework:

- Development of an organic sampling system designed to collect low molecular weight species quantitatively. This system may be constructed using a cooled resin cartridge and thermal desorption recovery.
- Development and rigorous testing of a source sampling train for aldehyde emissions, possibly using hydrazine impinger solutions with high performance liquid chromatography (HPLC) analysis techniques.
- Additional source testing at the Hempstead plant using the developed systems, and simultaneous testing using the techniques within this study. An effort should be made to sample over an extended period since the composition of the refuse-derived fuel (RDF) and consequent stack emissions may vary substantially.
- Onsite analysis of collected samples, if feasible, when using new or prototype techniques.

Formate (HCOO^-) and acetate (OAc^-) were detected in the hydrogen peroxide (H_2O_2) impinger of the Controlled Condensation System (CCS) by ion chromatography (IC). The identities of these species were verified through numerous laboratory detection methods, confirming that these species are indeed formate and acetate.

NSI-ES proposes that the species present in the flue gas of the Hempstead plant were emitted as formaldehyde (CH_2O) and acetaldehyde ($\text{C}_2\text{H}_4\text{O}$), but were subsequently oxidized to formate and acetate, respectively, in the H_2O_2 impinger of the CCS sampling train. The efficiency of this oxidation process is less than 100%, however. Literature and laboratory studies have not revealed other species which could be responsible for the observed IC peaks, though time constraints did not permit a complete laboratory interference study. Hence the involvement of another species cannot be ruled out.

The lower limits for the mass emissions rates of formaldehyde and acetaldehyde are calculated at 28 lb/h and 28 lb/h, respectively, although these values may not be truly representative since they are based on only one sample.

SECTION 4

PROCESS DESCRIPTION

The Hempstead recovery plant converts municipal refuse into two usable forms: recyclable and combustible materials (The Black Clawson-Parsons and Whittemore Organization 1974). The plant operations described are the recycling processes and the energy recovery processes.

RECYCLING PROCESSES

Raw waste entering the plant is first fed into a solid-waste-type hydropulper, where it is ground, shredded, and eventually pumped away as a water slurry. Unshredded material heavy enough to sink against a countercurrent of water is removed from the pulper. This material is then treated to remove ferrous metals, nonferrous metals and glass. The ferrous metals are removed by a magnet, and the nonferrous metals are removed by a high-speed, overhead, rotating electromagnetic drum. The nonmagnetizable fraction drops into the nonferrous hopper, where it is passed over a grizzly screen that removes large nonrecoverable residue. The smaller items are recycled to the hydropulper for further processing.

The original material carried off by the water is treated to recover glass, aluminum, other nonferrous metals, and an assortment of inorganic materials that includes buttons, stones, pieces of broken china, etc. The heavy inorganic fraction is separated in a liquid cyclone and discharged through an opening in the bottom. This heavy fraction is washed to remove any residual light material (which is returned to the hydropulper), then is rewashed and screened. The over-sized particles are processed again, but the fine particles are dewatered and conveyed to fuel storage.

The plastics and lighter materials are separated from the heavy fraction by surface skimming in a heavy media separator. This light material is conveyed to fuel storage, where it is dried and sized. A magnet removes residual ferrous metals and a shaking table removes aluminum foil. Nonconductors are removed from conductors by high voltage electrodes that permit the nonconductors to fall into a recovery drum. The remaining nonconducting fraction is mostly glass, china, porcelain and occasional small stones. The glass is separated at a transparency sorter and is actually separated by color with the use of colored filters to identify the clear, amber and green fractions.

ENERGY RECOVERY PROCESSES

The energy recovery processes begin with the feeding of the cyclone-treated slurry from the hydropulper to a large surge tank (see Figure 1). The slurry is pumped into a two-stage dewatering press apparatus where the solid content is raised to about 50%. The water discharge is processed and returned to the cycle; the solid is transferred to the fuel storage area for burning (usually within a week). The fuel is burned in two steam-generating furnaces with a nominal capacity of 200,000 lb/h of steam. The maximum fuel feed rate is 90,000 lb/h. The particulate emissions from the furnaces are controlled by the cyclones and electrostatic precipitators (ESP's) listed below:

Cyclones

Manufacturer	FLAKT
Type	12 x CKOB 180
Number of units	12 per furnace

Electrostatic Precipitators

Manufacturer	FLAKT
Type	FAA 323212090-1-SP
Number of units	1 per furnace

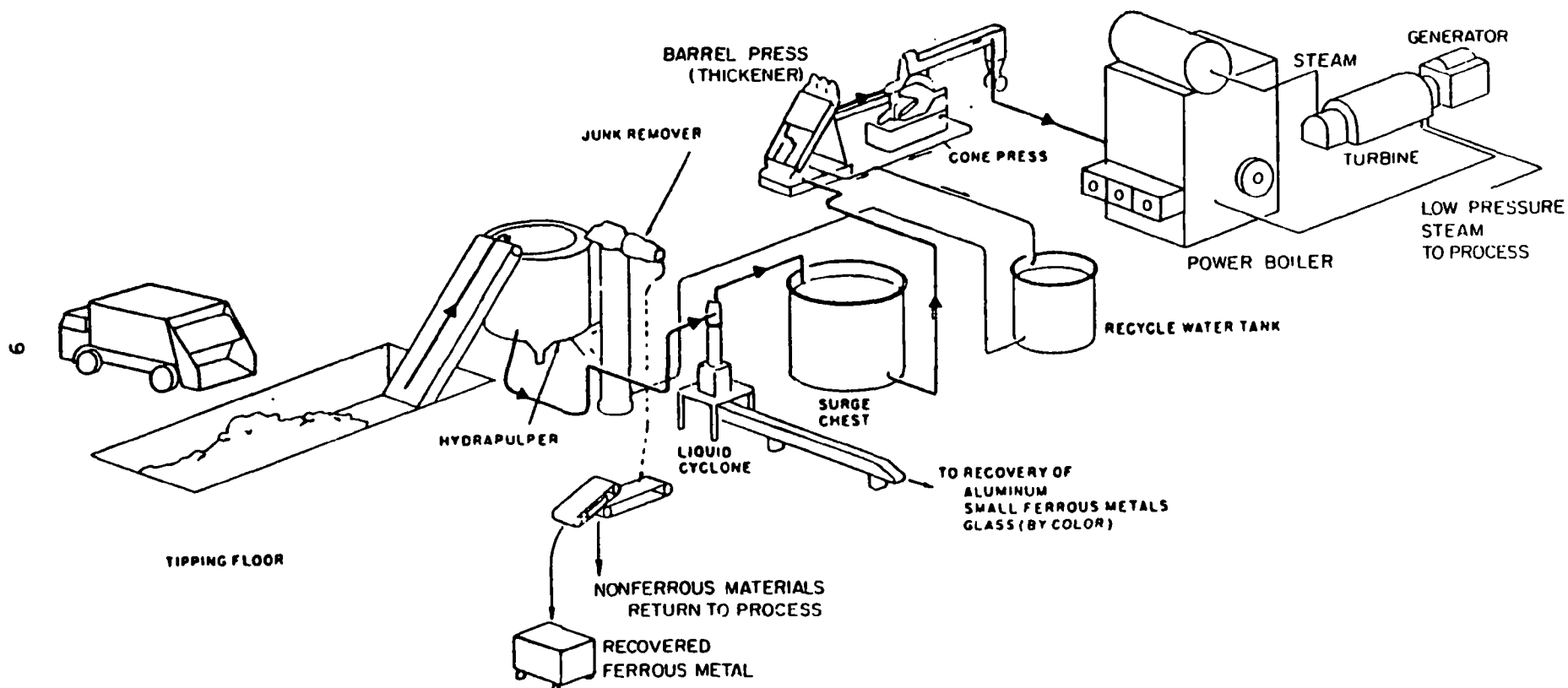


Figure 1. Wet process energy recovery system.

In summary, the solid waste that is burned as fuel contains about 25% moisture, 20% inorganics, and 35% organic combustibles such as paper, wood, plastics and food waste. Additionally, the water used in the process has been treated with a biocide that is certainly retained in the 25% moisture fraction of the fuel.

SECTION 5

RESULTS

In this section the results from the Hempstead study are given in two parts: source testing and laboratory investigations. The first subsection contains all results thus far obtained from Furnace #2 of the plant pertaining to chloride, sulfur oxides, and other organic emissions of higher molecular weight. Since velocity traverses were not made, a volumetric flow rate previously obtained for Furnace #1 (4.4×10^6 SCF/h) was used for calculating mass emission rates (New York Testing Laboratories 1979). Process load data in Tables 1 and 6 are given so that runs can be compared (Ogg, private communication). Results of IC analyses on field samples for the formate and acetate ions are also presented in this section.

Additional studies were requested by EPA to determine the presence of formaldehyde and acetaldehyde in the flue gas. Laboratory investigations into the collection and analysis of these species are presented in the latter subsection.

SOURCE TEST RESULTS

TABLE 1. HEMPSTEAD MASTER SAMPLING DATA

Date	Time	HCl Run #	CCS Run #	HCl-ESP Run #	Organic Run #	% O ₂	% Operating Capacity*
7-24-79	14:30-15:30	1	1			11.5	49
	16:30-17:30				1		49
7-25-79 [†]	09:30-10:30	2					56
	09:30-10:30			1			56
	12:30-12:45						
7-26-79	10:30-11:30	3			2		76
	15:30-17:00	4			3	7.3	74
	16:30-18:00	5			4	9.1	74

* Based on 200,000 lb/h steam generation.

[†] Sampling was interrupted at 10:30 and resumed at 12:30 due to a plant shutdown from 10:00 to 11:50 and from 12:35 to 13:25 on 7-25-79.

TABLE 2. CHLORIDE RESULTS (ppm)

Run #	HCl Sampling Train				
	SCF	PP	PW x 10 ⁻²	Imp x 10 ⁻²	Tot x 10 ⁻²
1	1.874	8.4	1.2	.87	2.1
2	.910	2.5	.00	.00	.025
3	.865	8.2	.37	.31	.77
4	.985	6.5	.29	.30	.66
5	1.331	7.0	.24	.34	.65

HCl-ESP Sampling Train						
SCF	PW	ESP x 10 ⁻²	ESP Filter	NaOH Imp x 10 ⁻²	NaOH Imp	Tot x 10 ⁻²
1	26.241	.63	.55	1.2	2.5	3.2
						3.1

TABLE 3. SULFUR OXIDE RESULTS (ppm)

Run #	HCl Sampling Train				
	SCF	PP	PW	Imp x 10 ⁻²	Tot x 10 ⁻²
1	1.874	.99	.26	1.8	1.8
2	.910	.44	.16	.00	.0060
3	.865	.95	5.5	.45	.52
4	.985	.76	2.5	.46	.49
5	1.331	.94	2.9	.47	.51

CCS Sampling Train						
Run #	Special			IPA	H ₂ O ₂	Tot x 10 ⁻²
	SCF	PW	Filter Plug	Imp	Imp x 10 ⁻²	
1	9.121	.09	.37	.18	.00	1.5

TABLE 4. ORGANIC RESULTS (mg)

Run #	Organics			
	SCF	Imp	XAD-2 Column x 10 ⁻¹	Tot x 10 ⁻¹
1	19.471	*	5.3	5.3
2	21.771	3.5	5.3	5.7
3	19.798	5.4	4.6	5.1
4	23.657	3.1	6.2	6.5

*Sample discarded.

TABLE 5. ACETATE AND FORMATE RESULTS (mg)

Run #	Formate			Acetate		
	IPA Imp	H ₂ O ₂ Imp (x 10 ⁻¹)	Tot (x 10 ⁻¹)	IPA Imp	H ₂ O ₂ Imp (x 10 ⁻¹)	Tot x 10 ⁻¹
1 CCS	1.8	3.6	3.8	2.3	3.3	3.5

TABLE 6. INORGANIC SPECIES MASS EMISSION RATES (lb/h)

Run #	% Operating Capacity	PM Cl ⁻ (x 10 ⁻¹)	Gaseous Cl (x 10 ⁻¹)	Tot Cl ⁻ (x 10 ⁻¹)	PM [*] SO ₄ ⁼	Gaseous SO ₂ (x 10 ⁻²)	Tot SO _x (x 10 ⁻²)
1 HCl	49	5.2	3.5	8.7	1.4	1.4	1.4
2 HCl	56	.11	.00	.11	.66	.00	.0066
3 HCl	76	1.8	1.3	3.1	7.0	.33	.40
4 HCl	74	1.5	1.2	2.7	3.5	.33	.37
5 HCl	74	1.2	1.4	2.6	4.2	.35	.39

* Mass emission rates for oxides of sulfur are based on the analysis of the HCl sampling train.

TABLE 7. ORGANIC SPECIES MASS EMISSION RATES (lb/h)

Run #	% Operating Capacity	CH ₂ O x 10 ⁻¹	C ₂ H ₄ O x 10 ⁻¹	Organics x 10 ⁻¹
1 CCS	49	2.8	2.8	
1 ORG	49			2.6
2 ORG	76			2.5
3 ORG	74			2.5
4 ORG	74			2.7

Figure 2 represents the GC spectrum of the impinger catch of Organic Run #4. Table 8 gives the major peaks in the chromatogram, identified through MS.

TABLE 8. MAJOR GC PEAKS FROM ORGANIC RUN #4

Peak #	Identification
1,3	Polychlorinated phenols (di-, tri-, tetra-, penta-)
2	Phthalates and phthalate isomers

15

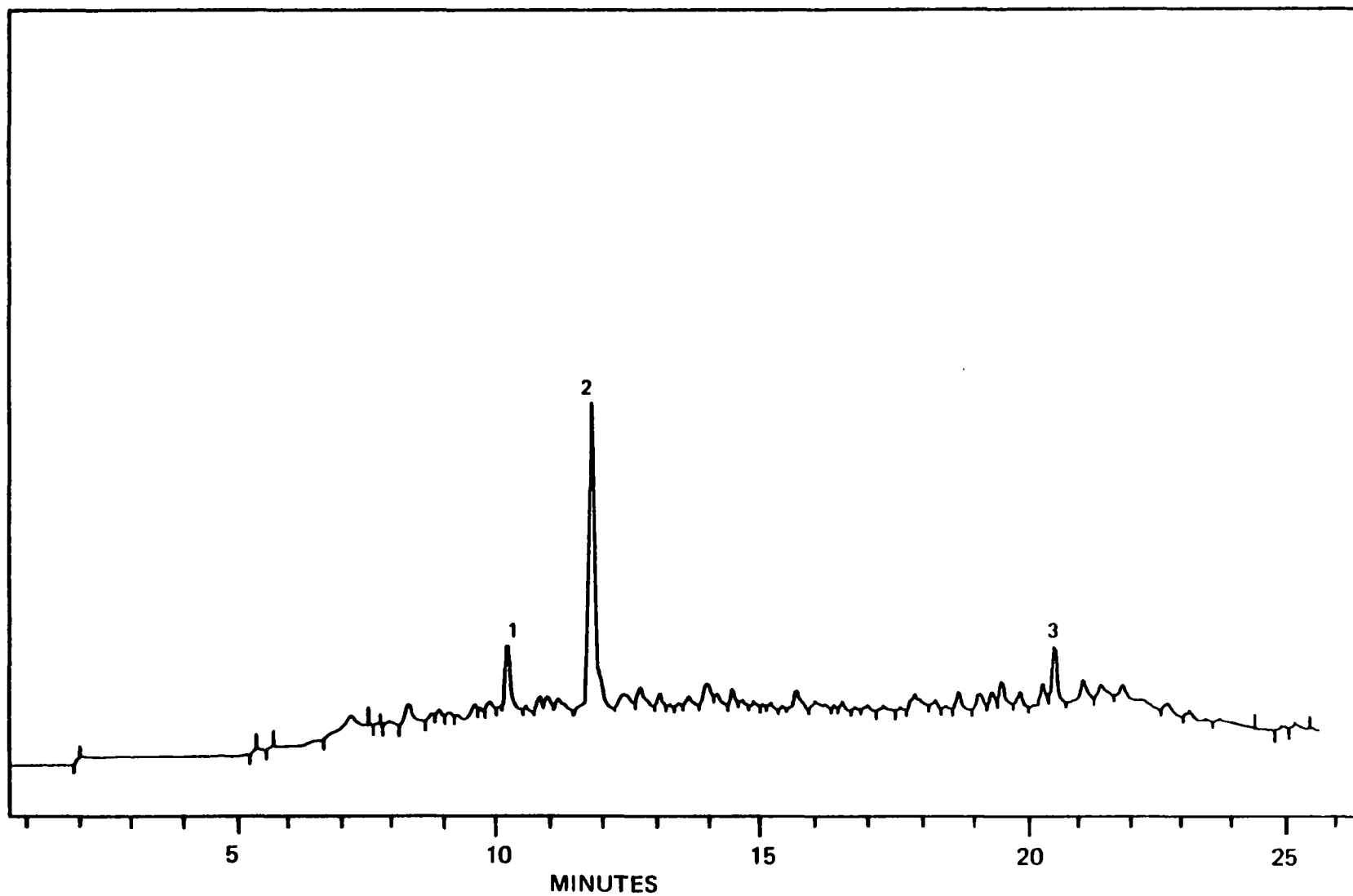


Figure 2. Gas chromatogram of the impinger extract from Organic Run #4.

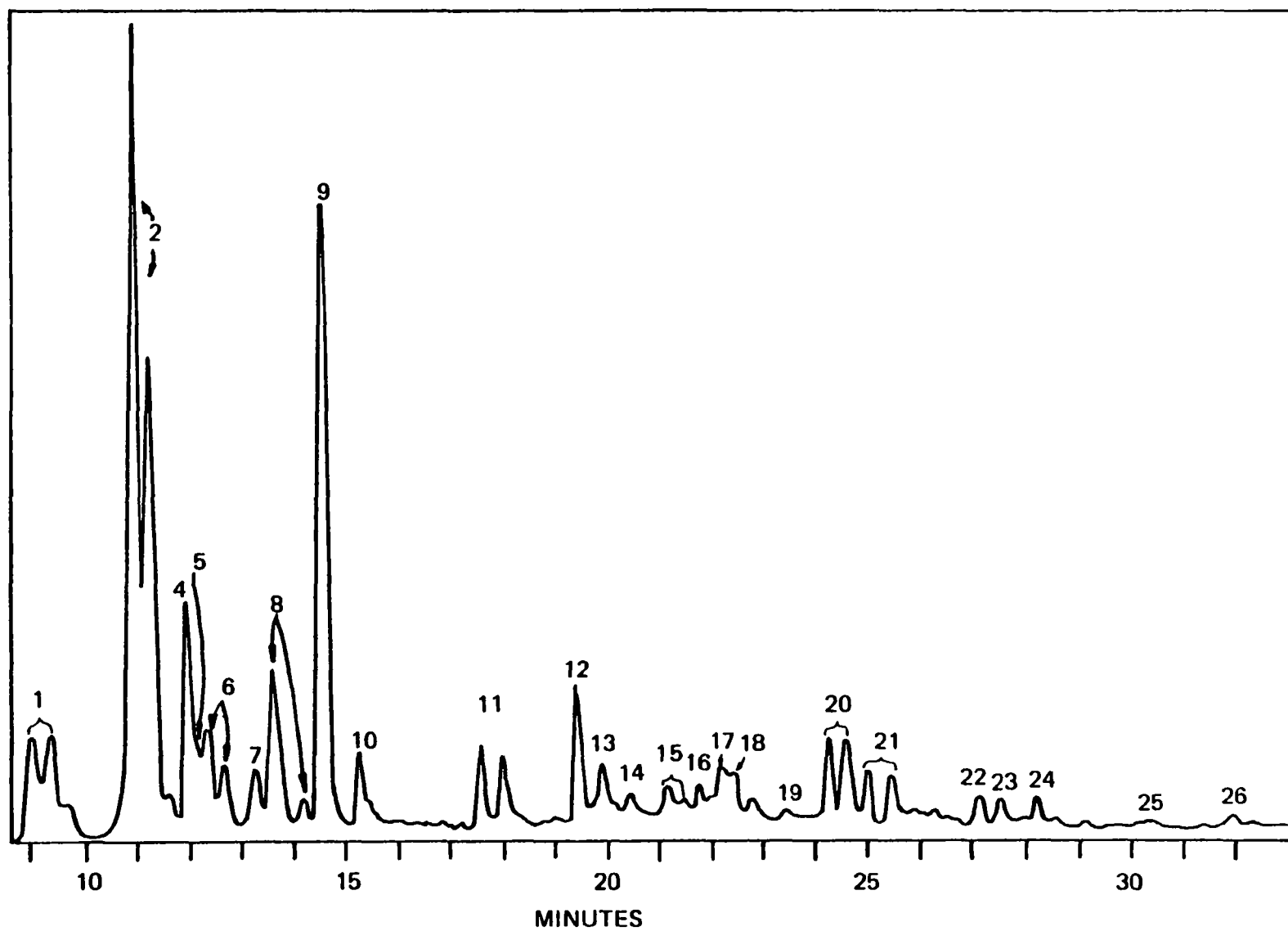


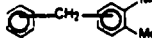


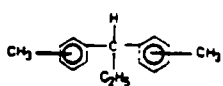
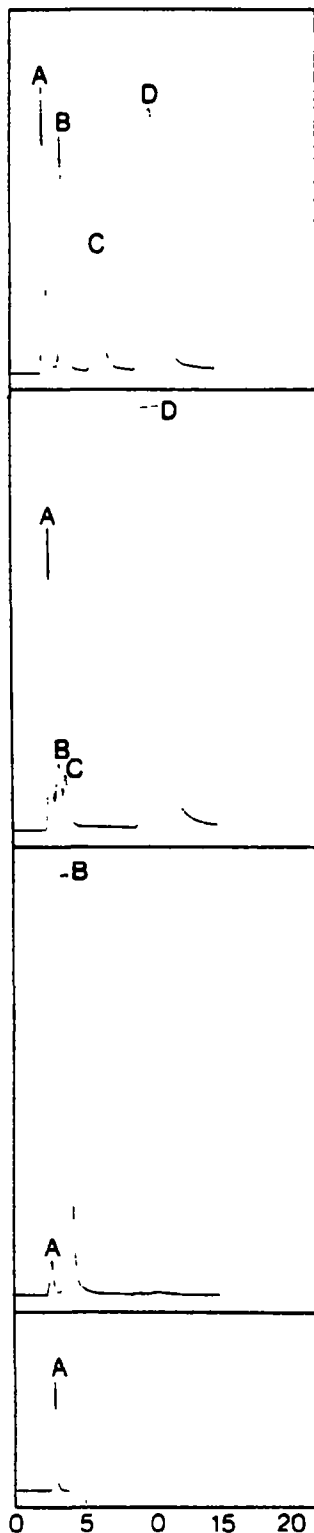


Figure 3. Gas chromatogram of XAD-2 cartridge extract from organic run #4.

TABLE 9. MS IDENTIFICATION OF GAS CHROMATOGRAM OF
XAD-2 CARTRIDGE EXTRACT FROM ORGANIC RUN #4

Peak #	Identification
1	Butylbenzene isomers
2	C ₁₀ H ₁₂ isomers
3	C ₁₁ H ₁₆
4	C ₁₀ H ₁₂
5	Divinyl benzene isomer (tentative)
6	C ₁₁ H ₁₆
7	C ₁₀ H ₁₀ isomer
8	C ₁₂ H ₁₈ isomers
9	Napthalene
10	C ₁₀ H ₁₀ O
11	Methyl napthalenes
12	Biphenyl
13	Ethyl napthalene
14	Methyl biphenyl
15	Alkylated tetrahydronapthalenes
16	Methyl biphenyl
17	C ₁₃ H ₁₆ O ₂ e.g.  (tentative)
18	 isomer
19	 or isomer
20	isomers of 
21	isomers of 
22	C ₁₇ H ₁₀ multialkylated biphenyl isomers e.g. 
23	C ₁₇ H ₁₀ multialkylated biphenyl isomers
24	Anthracene/phenanthrene
25	Methyl anthracene/phenanthrene
26	Dichlorobenzophenone



CALIBRATION STANDARD

A - F^- (5 ppm), 2.50 min
 B - Cl^- (10 ppm), 3.79 min
 C - SO_3^{2-} (30 ppm), 6.43 min
 D - SO_4^{2-} (50 ppm), 10.38 min

CCS-I- H_2O_2 (Hempstead)

A - Unknown, 2.73 min
 B - Unknown, 3.31 min
 C - Cl^- , 3.84 min
 D - SO_4^{2-} , 10.10 min

INSTRUMENTAL CONDITIONS

Columns: 3 x 150 mm pre-column
 3 x 500 mm Separator column
 3 x 6'50 mm Suppressor column
 El Eluent: .006 M Na_2CO_3
 Flow Rate: 130 ml/h (25%)
 Sample Loop: 100 μl
 Meter Setting: 10 $\mu mho/cm$ full scale

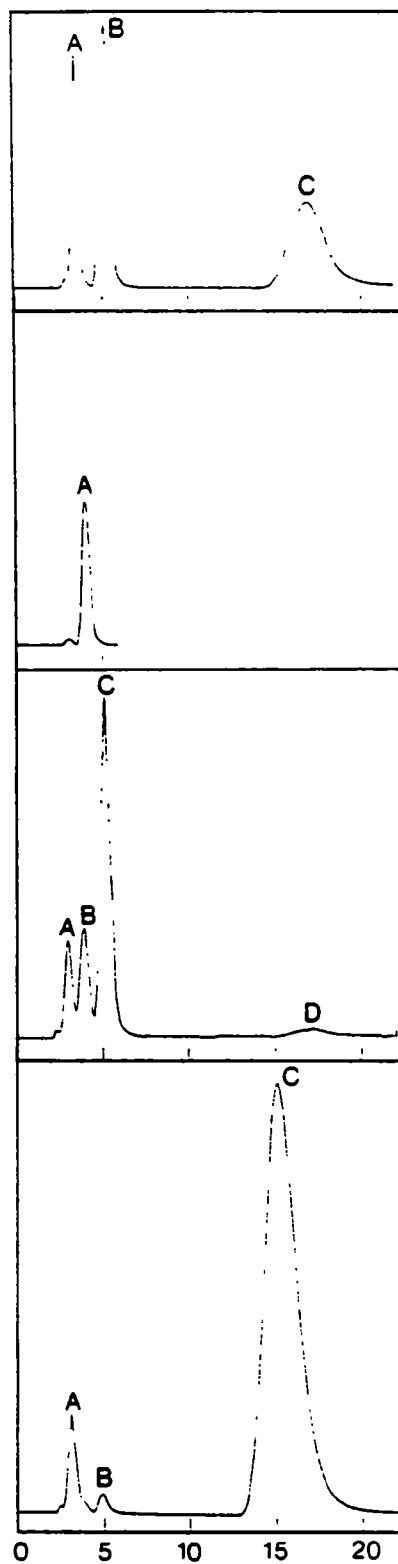
CCS - I - IPA (Hempstead)

A - Unknown, 2.72 min
 B - Cl^- , 3.66 min

CALIBRATION STANDARD

A - $HCOO^-$ (10 ppm), 2.73 min

Figure 4. Original IC analysis of CCS-1-Hempstead sample fractions using a strong eluent system.



CALIBRATION STANDARD

A - F^- (5 ppm), 3.45 min
B - $HCOO^-$ (30 ppm), 5.21 min
C - Cl^- (20 ppm), 16.88 min

CALIBRATION STANDARD

A - OAc^- (40 ppm), 4.04 min

INSTRUMENTAL CONDITIONS

Columns: 3 x 150 mm pre-column
3 x 500 mm Separator column
6 x 250 mm Suppressor column
Eluent: .0015 M $NaHCO_3$
Flow Rate: 103 ml/h (20%)
Sample Loop: 100 μl
Meter Setting: 10 $\mu mho/cm$ full scale

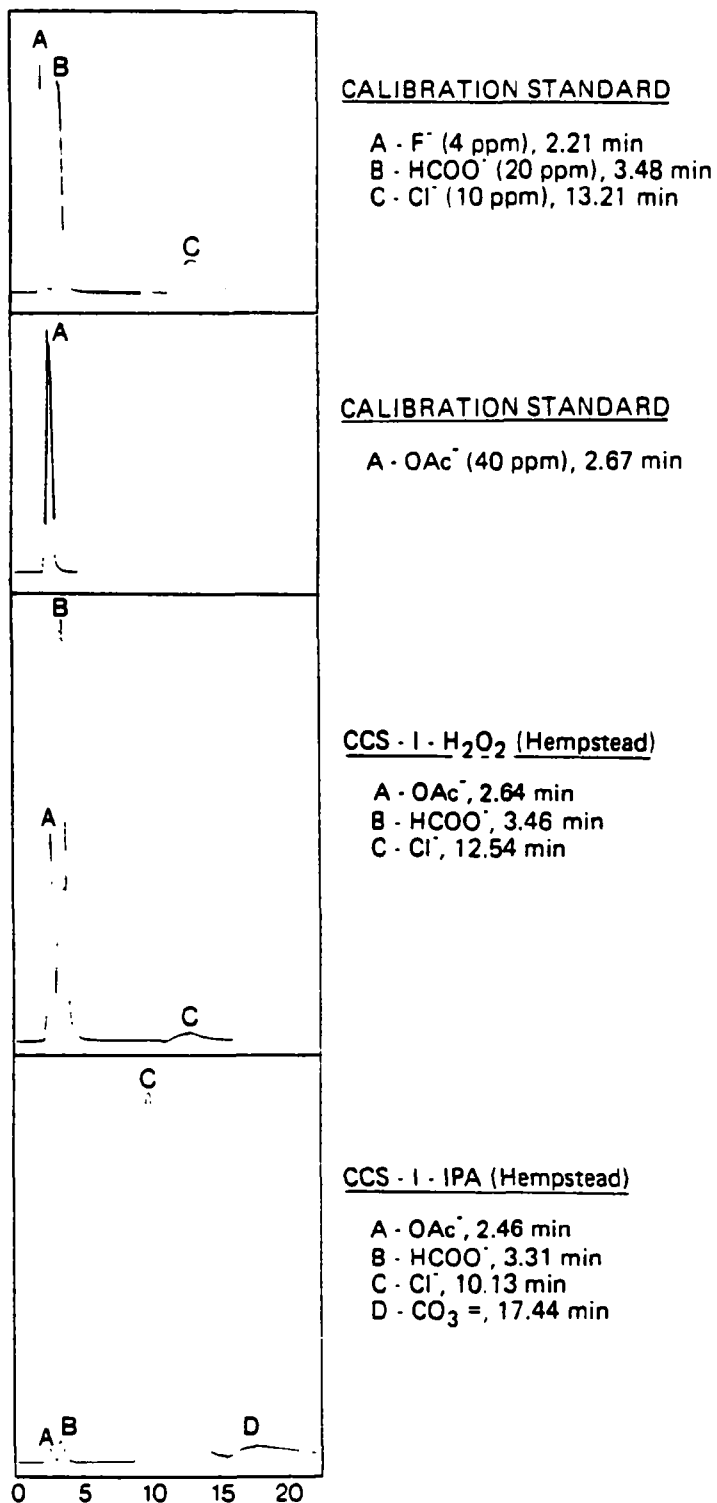
CCS - I - H_2O_2 (Hempstead)

A - CO_3^{2-} , 2.99 min
B - Oac^- , 3.91 min
C - $HCOO^-$, 5.16 min
D - Cl^- , 16.84 min

CCS - I - IPA (Hempstead)

A - CO_3^{2-} , 2.96 min
B - $HCOO^-$, 4.72 min
C - Cl^- , 14.92 min

Figure 5. IC analysis of CCS-1-Hempstead sample fractions using a weak $NaHCO_3$ eluent system.



CALIBRATION STANDARD

A - F⁻ (4 ppm), 2.21 min
B - HCOO⁻ (20 ppm), 3.48 min
C - Cl⁻ (10 ppm), 13.21 min

CALIBRATION STANDARD

A - OAc⁻ (40 ppm), 2.67 min

INSTRUMENTAL CONDITIONS

Columns: 3 x 150 mm pre-column
3 x 500 mm Separator column
6 x 250 mm Suppressor column
Eluent: .005 M Na₂B₄O₇
Flow Rate: 156 ml/h (30%)
Sample Loop: 100 µl
Meter Setting: 10 µmho/cm full scale

CCS - I - H₂O₂ (Hempstead)

A - OAc⁻, 2.64 min
B - HCOO⁻, 3.46 min
C - Cl⁻, 12.54 min

CCS - I - IPA (Hempstead)

A - OAc⁻, 2.46 min
B - HCOO⁻, 3.31 min
C - Cl⁻, 10.13 min
D - CO₃⁼, 17.44 min

Figure 6. IC analysis of CCS-1-Hempstead sample fractions using a weak Na₂B₄O₇ eluent system.

LABORATORY TEST RESULTS

TABLE 10. LABORATORY ALDEHYDE MASTER SAMPLING DATA

Run #	Sampling Train Description	Sample Source
1	standard CCS train: 1st imp - 80% IPA 2nd imp - 3% H_2O_2	ambient air
2	same	formalin (3.7% soln)
3	same	acetaldehyde (liq)
4	modified CCS train: 2nd imp - 3% H_2O_2 /.1N NaOH	formalin (37% soln)
5	modified CCS train: 3rd imp - 3% H_2O_2 /5 ppm Fe^{+3} 4th imp - DNPH/HCl (aqueous soln)	same
6	modified CCS train: 3rd and 4th imp - DNPH/MeOH	formalin (7.4% soln)

TABLE 11. FORMATE AND ACETATE RESULTS - CCS LABORATORY SAMPLES

Sample Description			Analysis for $\text{HCOO}^-/\text{OAc}^-$ *			
Run #	Imp #	Imp Contents	Before Purge		After Purge	
			Untreated	w/added $\text{H}_2\text{O}_2/\text{NaOH}^\dagger$	Untreated	w/added $\text{H}_2\text{O}_2/\text{NaOH}^\dagger$
1	1	80% IPA	-	-	0	0
	2	3% H_2O_2	-	-	0	0
		tot	-	-	0	0
2	1	80% IPA	-	-	0	26.6
	2	3% H_2O_2	-	-	0	14.9
		tot	-	-	0	41.5
3	1	80% IPA	-	-	-	-
	2	3% H_2O_2 (1/24/80)	-	-	8.2	-
	3	3% H_2O_2 (2/29/80)	-	-	169	263
		tot	-	-	-	-
4	1	80% IPA	-	-	-	-
	2	3% H_2O_2 /.1 N NaOH	-	-	137	-
		tot	-	-	-	-
5	1	80% IPA	14.6	547	18.6	566
	2	3% H_2O_2	19.3	201	16.1	214
	3	3% H_2O_2 / 5ppm Fe^{+3}	69.3	199	8.2	74.9
	4	DNPH/HCl (aqueous)	52.7	(52.7)	17.4	(17.4)
		tot	155.9	999.7	60.3	872.3
6	1	80% IPA	-	246	16.3	249
	2	3% H_2O_2	-	68.6	3.8	75.1
	3	DNPH/MeOH	-	-	1.0	(1.0)
	4	DNPH/MeOH	-	-	0.15	(0.15)
		tot	-	314.6	21.3	325.3

* Total mg/10 ft³ sample.† IPA - sample adjusted to 0.6% H_2O_2 (V/V) and .005 M NaOH; H_2O_2 - sample adjusted to .005 M NaOH.

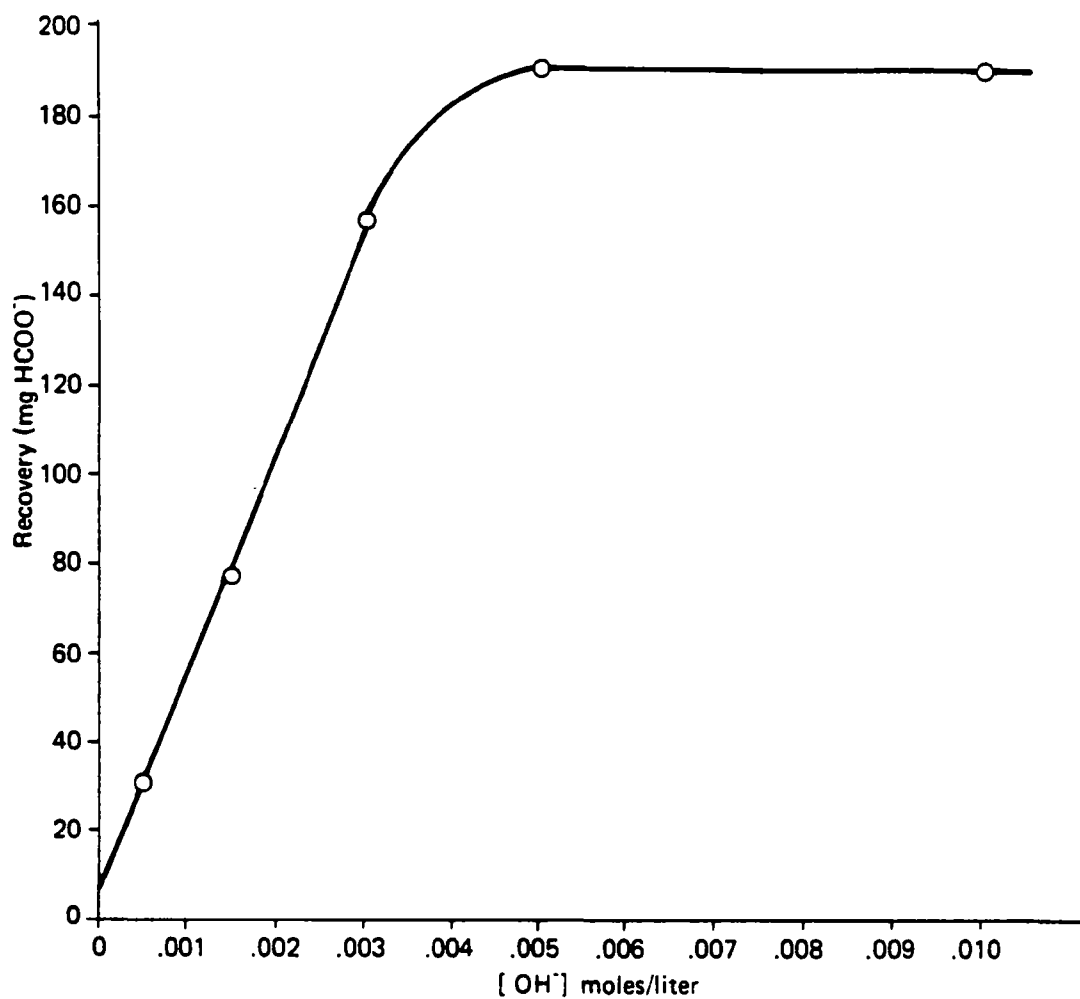


Figure 7. Effect of OH^- concentration on oxidation of CCS-5- H_2O_2 impinger sample.

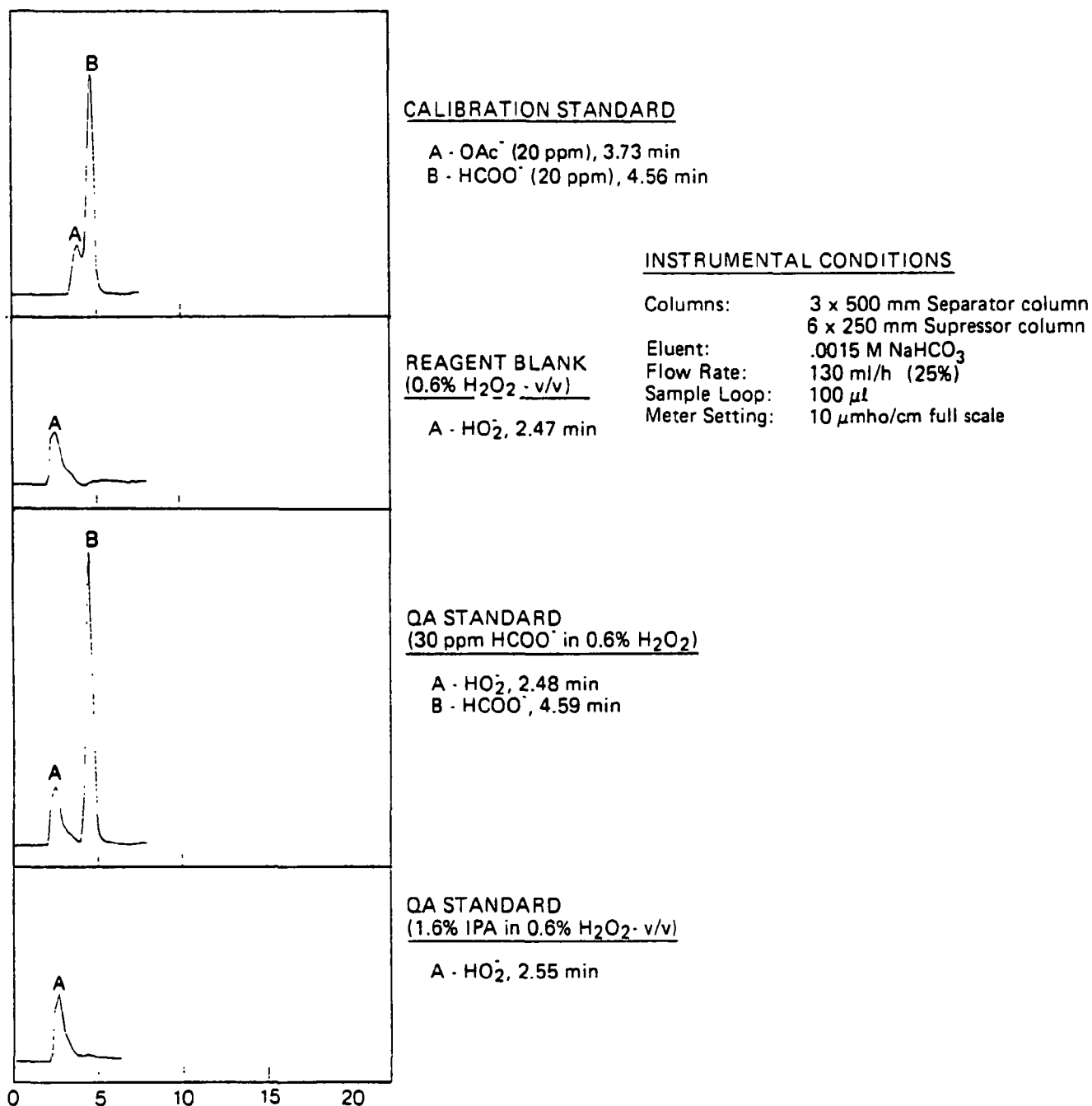
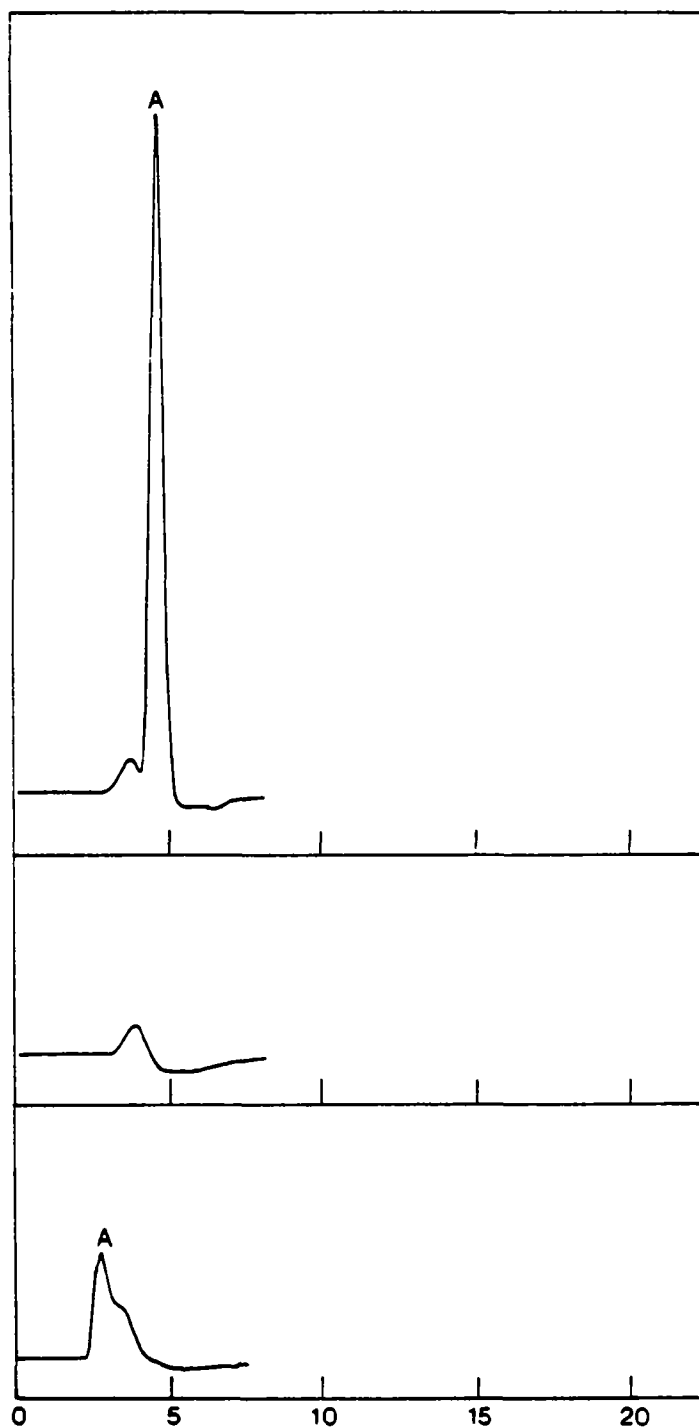


Figure 8. IC analysis of standards in 0.6% H_2O_2 using a weak NaHCO_3 eluent system.



INSTRUMENTAL CONDITIONS

Columns: 3 x 500 mm Separator column
6 x 250 mm Suppressor column
Eluent: .0015 M NaHCO₃
Flow Rate: 130 ml/h (25%)
Sample Loop: 100 µl
Meter Setting: 10 µmho/cm full scale

QA STANDARD
(30 ppm HCOO⁻ in 16% IPA - v/v)

A - HCOO⁻, 4.55 min

QA STANDARD
(16% IPA in D.I. H₂O - v/v)

(peak not detected)

QA STANDARD
(16% IPA/0.6% H₂O₂ - v/v)

A - HO₂⁻ - v/v , 2.53 min

Figure 9. IC analysis of standards is 16% IPA using a weak NaHCO₃ eluent system.

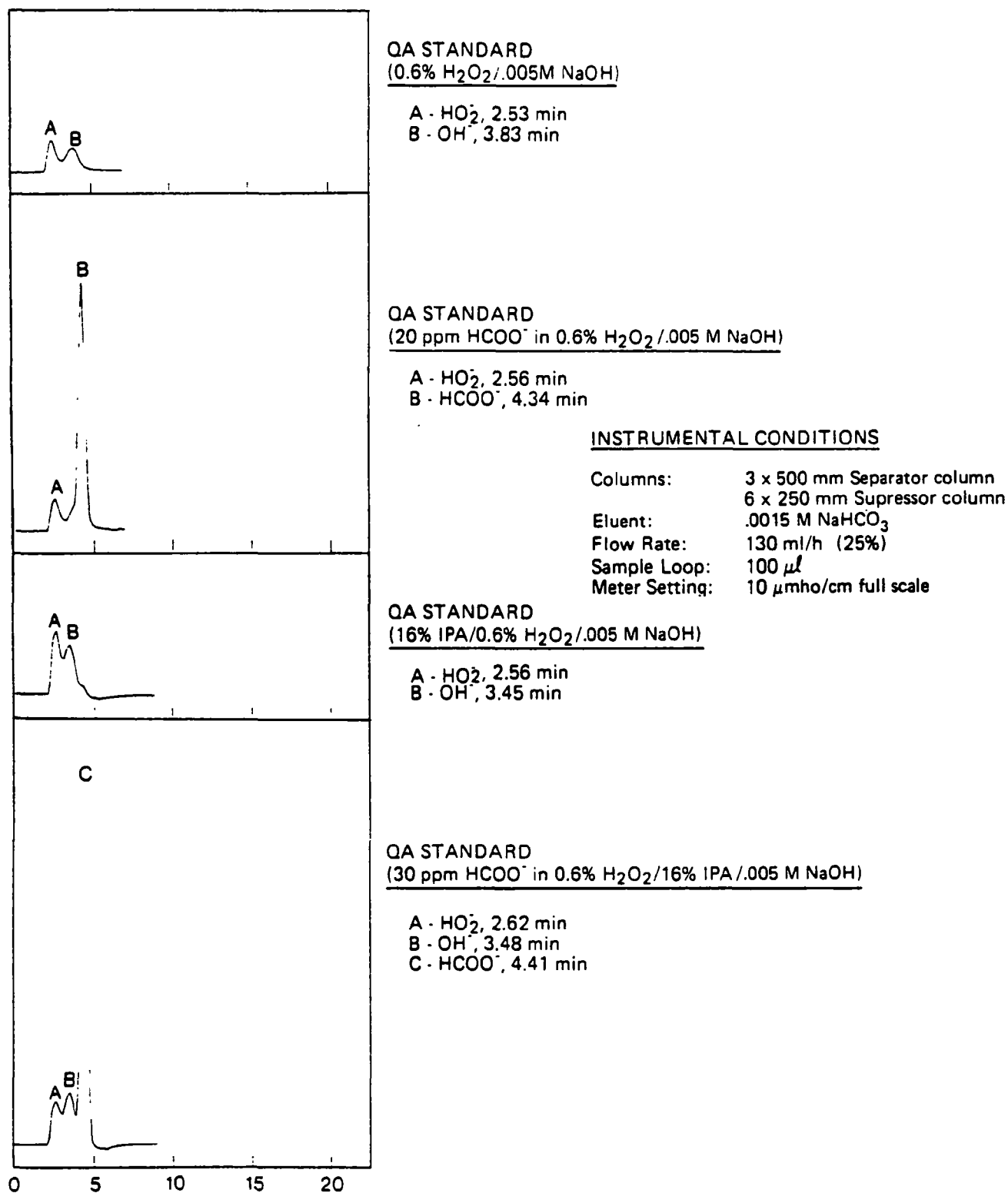


Figure 10. IC analysis of standards treated with H_2O_2 /NaOH using a weak NaOH eluent system.

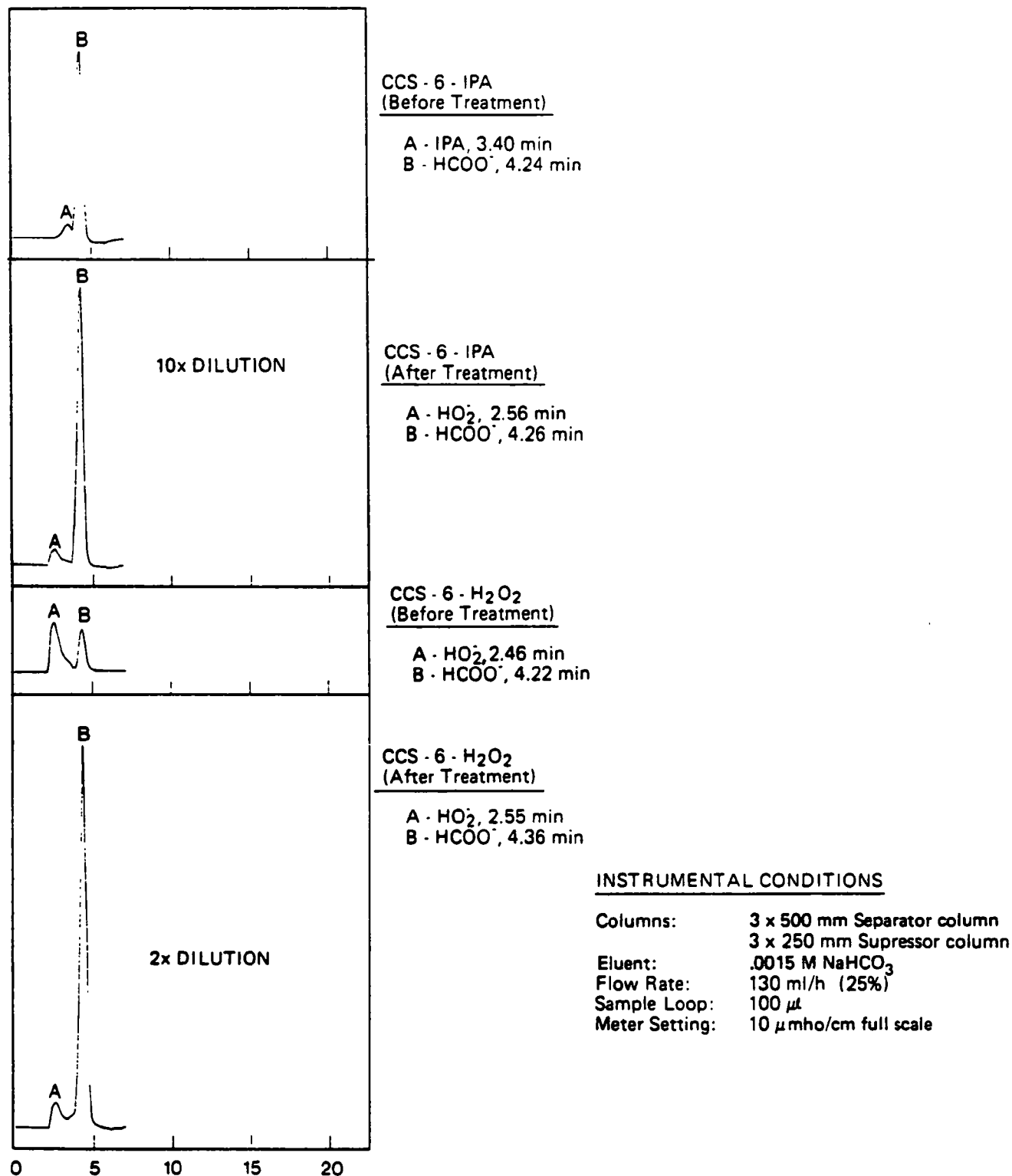


Figure 11. IC analysis of laboratory sample #6 before and after treatment.

TABLE 12. SUMMARY OF CARBONYL INTERFERENCE STUDIES

Sample *	Standard Concentration ($\mu\text{g/ml}$)	Standard RT [†] (min)	Analytical Results					
			After ~24 h			After ~96 h		
			RT (min)	HCOO ⁻ ($\mu\text{g/ml}$)	OAc ⁻ ($\mu\text{g/ml}$)	RT (min)	HCOO ⁻ ($\mu\text{g/ml}$)	OAc ⁻ ($\mu\text{g/ml}$)
formaldehyde	100	4.41	4.35	7.577	-	4.40	22.510	-
acetaldehyde	100	3.61	3.56	-	1.072	3.57	-	9.693
propion- aldehyde	100	3.85	4.34	0.541	-	4.34	4.139	-
acetone	100	-	3.92	-	0.244	3.70 4.28	- 0.318	0.219 -
butyraldehyde	100	3.99	4.31	1.046	-	4.35	2.610	-
benzaldehyde	100	24.01	4.27	0.372	-	3.53 4.38	- 1.380	0.476 -

* 500 mg/ml in 3% H₂O₂ purged 15 min with zero air (sample diluted 4:1 at H₂O prior to analysis).

[†] Standards were prepared solutions of the acid or salt in D.I. H₂O.

TABLE 13. XRF ANALYSIS OF CCS-1-HEMPSTEAD

Element	IPA Imp [*] ($\mu\text{g/ml}$)	H ₂ O ₂ /Imp [*] ($\mu\text{g/ml}$)
Na	138	107
Mg	.11	.09
Al	.17	.01
S	.16	47
K	.14	.09
V	.04	.02
Mn	.09	.08
Co	.14	.11
Cu	.20	.09
Zn	.20	.11
Br	.71	.18
Cd	.015	-
Ba	.02	.01
Pb	.95	.91

* Analysis performed on diluted impinger catches (dilution volume = 100 ml).

TABLE 14. FLUE GAS FORMALDEHYDE CONTENT OF VARIOUS SOURCES BY
FORMATE ANALYSIS OF CCS SAMPLES

Source	Sample	HCOO ⁻ Found (mg) Converted to CH ₂ O in Stack (ppm)			
		Untreated		w/added H ₂ O ₂ /NaOH [*]	
		HCOO ⁻	CH ₂ O	HCOO ⁻	CH ₂ O
refuse-fired boiler (Hempstead)	IPA imp	1.9	3.9	14.0	29.0
	H ₂ O ₂ imp	48.7	101	75.7	157
	tot	50.6	104.9	89.7	186.0
hogged-fuel- fired boiler	IPA imp	2.0	4.4	18.4	40.8
	H ₂ O ₂ imp	349	773	474	1050
	tot	351.0	777.4	492.4	1090.8
coal-fired boiler	IPA imp	0	0	1.0	1.6
	H ₂ O ₂ imp	13.7	22.6	14.3	23.5
	tot	13.7	22.6	15.3	25.1

* IPA imp - sample adjusted to 0.6% H₂O₂ (V/V) and .005 M NaOH, H₂O₂ imp - sample adjusted to .005 M NaOH.

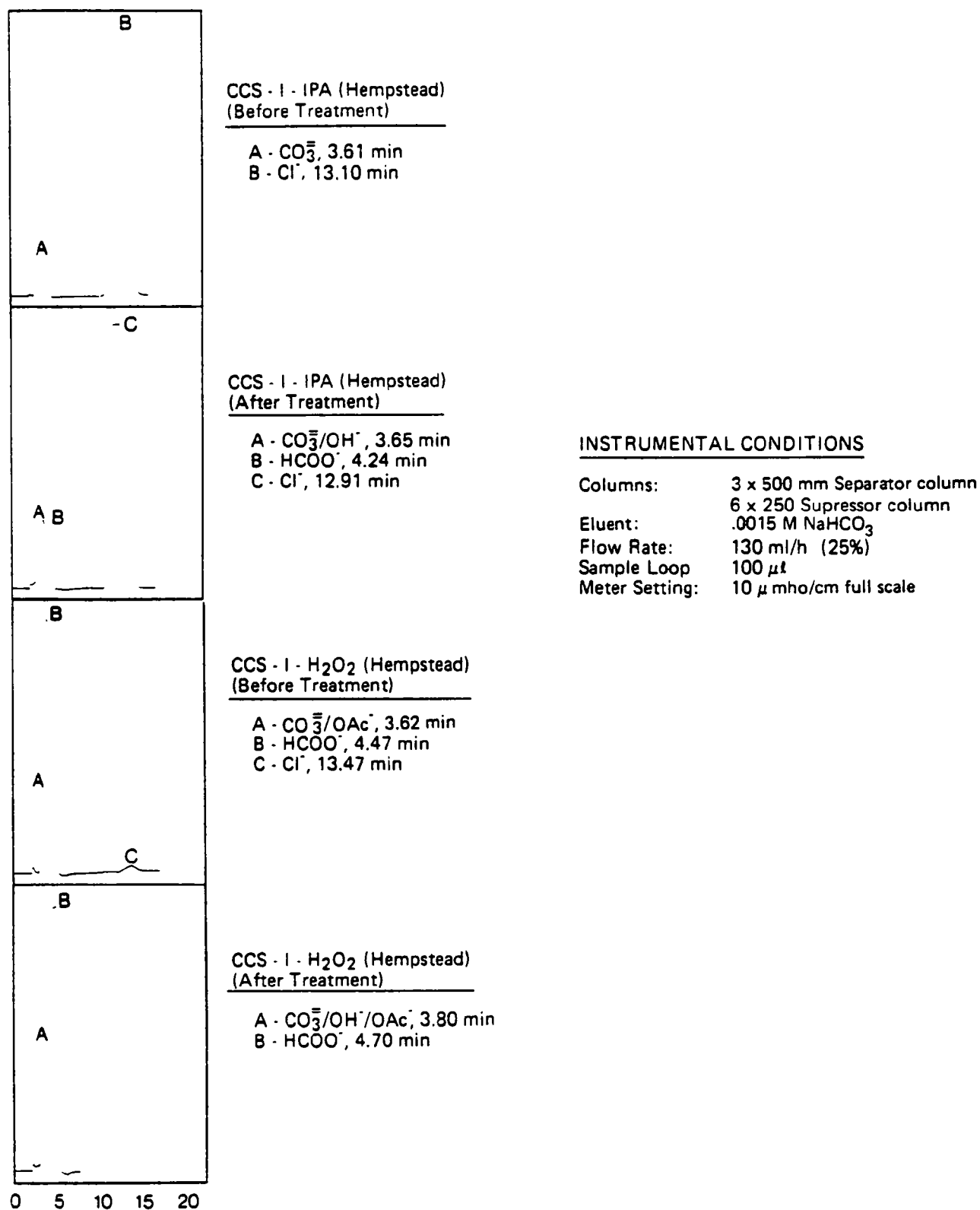


Figure 12. IC analysis of CCS-1-Hempstead sample before and after treatment.

SECTION 6

DISCUSSION

For clarity, the results of source and laboratory testing have been divided by compound class: (1) inorganics, (2) organics of high molecular weight, and (3) formate and acetate. The inorganic work has been completed; additional analysis of the organic samples is under way and will be reported at a later date. Because of the pertinence to source samples collected at Hempstead, results of a limited laboratory study on the collection and analysis of aldehydes are also reported here.

INORGANIC DETERMINATIONS

The results presented in Tables 2, 3 and 6 (pp. 12-14) indicate that the emission levels of chloride and sulfur oxides are indeed quite low in comparison to power plants and other incinerators that have been characterized (Jahnke et al. 1977, Homolya et al. 1976). The average total chloride concentration emitted as stack effluent at Hempstead was only 120 ppm, while the average gas phase concentration was only 73 ppm.

The results from Run #1 of the HCl train appear inconsistent with the results obtained in Runs #3, 4 and 5 on July 26, 1979. The results of both Run #1 of the HCl-ESP train and Run #2 of the HCl train appear to be anomalously low. (Since these runs were interrupted by plant down time, they cannot be considered representative of the source emissions.) In addition, the results obtained from all runs made on July 24 appear to be inconsistent with the runs completed on July 26. Although thorough checking of the process data revealed that the plant was operating under a steady load, the percent operating capacity

was only 49% and the % O_2 was a high 11.5. Run #1 may thus not be representative of the source. If we can exclude the above samples, we obtain average total chloride and gaseous chloride concentrations of 69 ppm and 32 ppm, respectively.

The CCS sampling of SO_x was performed only on July 24. Concentrations were very low, with SO_2 measured at 150 ppm and H_2SO_4 at only 18 ppm. Again, the results obtained on July 24 and 25 are not taken as representative of plant operation. Past simultaneous sampling efforts with the HCl and CCS train have shown that the total sulfur oxides collected agree quite well. If Runs #3, 4 and 5 of the HCl train for sulfur oxide analysis are assumed valid, an average sulfur oxide concentration of 51 ppm is obtained.

Although the existence of irregularities in the samples taken on July 24 (interruption in sampling) and July 25 (apparent disagreement with July 26 samples) has been emphasized, these differences observed during the three days of sampling may be due to the varying composition of the RDF. Since many parameters may be affecting the source sampling, no one sample should be construed as fully representative of the source emissions.

ORGANIC DETERMINATIONS

The results of sampling for organic emissions are presented in Tables 4, 7, 8 and 9 (pp. 13-14, 17). The total amounts reported for all four samples are quite consistent, and yield an average mass emission rate of 26 lb/h. The samples were collected in two fractions: species condensable at $0^\circ C$, and species trapped in the Amberlite XAD-2 cartridge at ambient temperature.

Preliminary GC/MS analysis of Organic Run #4 indicated that polychlorinated phenols (PCP's) and phthalates were the primary components of the impinger catch. Small quantities of polychlorinated biphenyls (PCB's) were also collected in the cartridge; all other compounds detected were relatively innocuous species. The occurrence of these species in small quantities is not

unexpected, considering the chemical makeup of the RDF and the similar findings at other incinerators that have been reported (Eiceman et al. 1979). The source of the chlorophenols was thought to be the biocide used in treating the refuse (Betz CSD), until an investigation proved this chemical to be a chlorohydantoin, which could not directly form the chlorophenols. Alternatively, the chlorophenols may be formed by pyrolysis of phenolic polymers (Bakelite and Formica) and subsequent chlorination by a chlorinating agent, such as chlorohydantoin.

The presence of chlorophenols is of prime concern, since these compounds have been reported to undergo condensation to form dioxins under the proper conditions (Buser 1978, Gribble 1974). Additional analyses performed on these samples will be reported at a later date.

FORMATE AND ACETATE

During the course of routinely analyzing CCS samples for sulfate, a major unidentified peak was observed in both the IPA and H_2O_2 impingers at a retention time of 2.73 min (see Figure 4, p. 18). A minor peak of similar retention time had also been observed in an earlier run, and formate was suggested as being the species present. Analysis of a formate standard gave the same retention time as the unknown peak in the Hempstead sample. Since the original eluent system was not suitable for analysis of fast-eluting species, a weaker eluent system was devised for running the samples. Results for both a weak bicarbonate ($NaHCO_3$) and a weak borate ($Na_2B_4O_7$) eluent system are presented in Figures 5 and 6 (pp. 19-20). Since the samples were initially prepared in a carbonate eluent (in order to eliminate the water dip which would interfere with analyses of chloride), a reagent blank was run first. This blank did not include peroxide because previous experience has shown that most of the peroxide either reacts or is thermally and photochemically destroyed in field samples before analysis can be performed. The retention times for $CO_3^{=}$ in the $NaHCO_3$ and $Na_2B_4O_7$ eluent systems were 2.98 and 19.54 min, respectively, and therefore did not interfere in the $HCOO^-/OAc^-$ analysis. In addition, dilute IPA solutions have been found to shorten the retention times of all ions. The argument of retention times is actually very good when all the eluent systems

are considered, and more firmly identifies these peaks as formate and acetate. Quantitative results are reported in Table 5 (p. 13) and mass emissions rates in Table 7 (p. 14).

The formate and acetate were not detected, nor expected, in the NaOH impinger of the HCl train, since these species are acids or salts that would not be collected in a basic solution. Due to the oxidizing nature of H_2O_2 and the ease of oxidation of aldehydes, however, a logical source for the species would be the parent compounds formaldehyde (CH_2O) and acetaldehyde ($\text{C}_2\text{H}_4\text{O}$). The presence of these species has been reported in low-temperature, inefficient combustion sources (Harrenstien et al. 1979). The fact that the % O_2 for the CCS run was relatively high may indicate less efficient combustion during this period of operation and further supports the aldehyde hypothesis.

Collection Efficiency Studies

Due to recent concern over the possible carcinogenicity of formaldehyde, NSI-ES was requested by EPA to validate the source samples through additional laboratory testing. The first phase of this testing was to determine the possibility of artifact formation in the sample train and the collection efficiency of the train for formaldehyde and acetaldehyde. A description of six laboratory runs of the CCS system and the sample source is presented in Table 10 (p. 21). Table 11 (p. 22) lists the analysis results. No results are listed for analysis of the probe wash, filter and special plug sample fractions, since no HCOO^- or OAc^- was detected in any of these fractions. Run #1 consisted of a blank in which ambient air (laboratory) was sampled to test for artifact formation. In other runs, formaldehyde (g) was generated by bubbling air through an impinger containing formalin. Acetaldehyde (g) was generated and sampled in Run #3. Initially, no formate or acetate was detected in the blank or in the formaldehyde run, and only small quantities of acetate were detected in the acetaldehyde run.

The initial results of these tests indicated either that: (1) a very small amount of CH_2O was being generated, even with use of the 37% formalin

solution; (2) the IPA and H_2O_2 impingers have a very poor collection efficiency for CH_2O ; (3) the CH_2O is collected by the impinger solutions, but is only very slowly oxidized to HCOO^- ; or (4) some combination of the above.

Of the four possibilities, collection of CH_2O with slow oxidation to HCOO^- appeared to be most likely. Consequently, a test was conducted to determine the effect of acid, base, and transition-metal ions on the oxidation of CH_2O in a 3% H_2O_2 solution. A test solution containing a small amount of 37% formalin in 3% H_2O_2 was prepared, and three aliquots of this solution were treated individually: one with HCl , another with NaOH , and the third with ferric chloride (FeCl_3), maintaining an untreated aliquot as a control. The samples were analyzed on the following day, with the result that the degree of oxidation of CH_2O to HCOO^- was reduced by a factor of 2 upon treatment with HCl , but was increased by a factor of 15 upon treatment with both NaOH and Fe^{+3} . Since treatment of samples with Fe^{+3} involves addition of the Cl^- ion (a slowly-eluting ion in weak eluent systems) to the sample, NaOH was used to speed oxidation.

A test was conducted to determine the concentration of OH^- ion required to ensure complete oxidation of CH_2O to HCOO^- in 0.6% H_2O_2 solution. Using the 3% H_2O_2 impinger catch from CCS Run #5 (after dilution to 1 liter with D.I. H_2O) as a control, aliquots of the sample were treated with additions of .5 N NaOH such that the OH^- concentration ranged from .0005 to .01 M. The samples were allowed to stand overnight prior to analysis for the HCOO^- ion. The results of this test, presented in Figure 7 (p. 23), indicate that a OH^- ion concentration of .005 M is sufficient for complete oxidation of CH_2O .

Based on these findings, the laboratory samples were routinely treated with NaOH and analyzed for HCOO^- . Treatment of the IPA impinger with NaOH yielded a slight increase in the amount of HCOO^- detected, but when these samples were also treated with H_2O_2 (0.6%), the increase in HCOO^- was quite dramatic (Table 11, p.22). Reanalyses of the system blank samples (Run #1) after the treatment described above yielded no formate or acetate in either impinger catch. Reanalysis of Run #2 samples after treatment showed the

presence of HCOO^- , whereas none was detected in the original analysis. More than 1 month after the original analysis, testing of the H_2O_2 impinger catch from Run #3 showed that of the total acetate detected in the treated sample, 64% was detected in the untreated sample, and only 3% of the total acetate was detected in the original analysis of January 24, 1980.

At this point we may conclude that neither formate nor acetate is the result of artifact formation in the sample train. Both formaldehyde and acetaldehyde are collected in IPA and peroxide impingers and are converted to their corresponding acids by the action of 3% hydrogen peroxide, but this reaction is not complete. Thus more aldehyde is collected than is apparent in analysis of the samples as received from the field. The collection efficiency of the train was evaluated by using treated impinger solutions and backup impingers to collect breakthrough.

With the exception of the impinger solutions, Runs #4 and 5 were carried through the same conditions as Runs #1, 2 and 3. Addition of NaOH to the H_2O_2 impinger in Run #4 produced a large increase in the amount of formate detected relative to the untreated samples. Run #5 indicated that 75% of the formate was collected in the IPA and H_2O_2 impingers as configured in the CCS train at Hempstead.

In Run #6 an attempt was made to duplicate the level of formate detected in the H_2O_2 impinger at Hempstead (80 mg) to more accurately evaluate its collection efficiency. For this run a collection efficiency of nearly 100% was attained by the first two impingers, compared to 75% for Run #5 where considerably more formaldehyde was generated. Apparently the saturation point was attained in Run #5, beyond which the collection efficiency dropped rapidly.

Interference Determinations

Formaldehyde and acetaldehyde are collected in the sampling train with efficiency near 100%, but cannot be detected by IC with the same efficiency

until subjected to the stronger oxidation of the $\text{NaOH}/\text{H}_2\text{O}_2$ solution. The final task of our study was then to determine the potentially-interfering compounds (i.e., other species) that may have been converted to formate and acetate by the action of the H_2O_2 solution.

A thorough search of the literature revealed few potentially-interfering species. Only ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) was clearly documented to be converted to formate by the action of dilute H_2O_2 (Miner and Dalton 1973). A brief mention in the older literature of CO_2 reduction by peroxide to produce formaldehyde or formic acid (HCOOH) was not confirmed or even mentioned elsewhere (Fry and Payne 1930). Only the aldehydes appeared to be rapidly oxidized to their acid forms. The breaking of a carbon-carbon bond would be necessary to produce formic acid, for which enough energy does not seem available in the system.

Throughout this laboratory study, the following steps were taken to test for possible artifact formation and/or interferences to the analytical technique due to sample preparation and treatment: (1) routine preparation of control standards containing the same amounts of each constituent as in the samples being analyzed, (2) consistency in handling procedures, and (3) analysis of each sample under the same conditions on the same day. An example of such a control standard would be a sample prepared to contain 16% IPA (V/V), 0.6% H_2O_2 (V/V) and .005 mole/liter NaOH in D.I. H_2O , and then allowed to stand overnight. This standard would be analyzed along with an IPA impinger sample (200 ml 80% IPA diluted to 1 liter) that had been treated with H_2O_2 and NaOH . Figures 8-10 (pp. 24-26) are representations of chromatograms of typical laboratory samples and control standards generated in this study. Figure 11 (p. 27) represents chromatograms of a laboratory sample before and after treatment. Analysis of control standards containing $\text{IPA}/\text{H}_2\text{O}_2$ and $\text{IPA}/\text{H}_2\text{O}_2/\text{NaOH}$ of various representative concentrations indicated no oxidation of IPA to HCOO^- or OAc^- . The presence of OH^- ion results in a positive interference to OAc^- determinations with the NaHCO_3 eluent (but not with the $\text{Na}_2\text{B}_4\text{O}_7$ eluent); however, this problem was not too serious since the laboratory work mostly involved analysis of HCOO^- ion.

Tests were conducted to determine the possibility of interference to HCOO^- due to either oxidation by H_2O_2 of compounds other than CH_2O , or oxidation by H_2O_2 of compounds yielding products having the same retention time as the HCOO^- ion. Laboratory samples of acetone and various aldehydes of higher molecular weight were prepared at a concentration of 500 $\mu\text{g/ml}$ in 3% H_2O_2 (as compared to ~400 $\mu\text{g/ml}$ HCOO^- in 3% H_2O_2 for CCS-1- H_2O_2 , Hempstead), then purged for 15 min using a cylinder of zero air, and allowed to stand overnight. Prior to analysis, aliquots of the samples were diluted 4:1 with D.I. H_2O , again duplicating the actual sample recovery procedure. The samples were analyzed a second time approximately 4 days after the initial preparation using the procedure outlined above.

The results of these tests and the retention times of the corresponding acids are given in Table 12 (pp. 28). Any confusion with formate or acetate resulting from conversion of these aldehydes to their corresponding acid should be very slight. In most cases, a slow appearance of peaks did seem to occur that could possibly be misinterpreted as formate or acetate, though the degree of interference is probably negligible. Nonetheless, benzaldehyde also yielded a peak at the acetate retention time! Under no circumstances could benzaldehyde be oxidized by dilute H_2O_2 to form acetaldehyde, leading us to conclude that the observed peaks are due to formaldehyde and acetaldehyde impurities in the chemicals.

The fact that the retention times of the acids of these aldehydes are significantly different from the retention times of formate and acetate, and the fact that the original Hempstead sample identification was confirmed in borate eluent, lead NSI-ES to propose that oxidation of other aldehydes is not responsible for the results obtained at Hempstead. Borate could not be used to analyze these samples due to the interference of H_2O_2 in freshly-prepared samples.

Since the flue gas of a combustion source contains a relatively large amount of carbon dioxide (~10%), tests were conducted to determine the possibility of the reduction of CO_2 to formic acid in the CCS impinger train. Using

a cylinder of CO_2 (5%) in air, a sample was collected in which the IPA impinger was treated with HCl and the H_2O_2 impinger with H_2SO_4 . This step was taken to duplicate the time-averaged concentrations of Cl^- and $\text{SO}_4^{=}$ that were determined in analyses of the IPA and H_2O_2 impinger catches of the CCS-1-Hempstead sample, respectively. A second sample was collected under the same conditions as the first, except that both impingers were spiked with vanadium (0.1 ppm), and the IPA impinger with zinc (1 ppm). Selection of these two metals was based on analysis of the actual field samples by X-ray fluorescence spectrometry (XRF). (The results are presented in Table 13, p. 28.) Analysis of these samples for HCOO^- yielded negative results in all cases, as well as verified that no reduction of CO_2 occurs under these conditions.

Relative Impinger Distributions of HCOO^- and OAc^-

The only major discrepancy between the results of analyses of the laboratory samples and those of the actual field samples is the relative distribution of HCOO^- and OAc^- in the impingers. The two impinger samples from the field test were, of course, reanalyzed using the $\text{H}_2\text{O}_2/\text{NaOH}$ pretreatment procedure. The values of both HCOO^- and OAc^- were found to be significantly greater in both samples; however, the amount found in the IPA impinger catch remained quite low with respect to the amount found in the H_2O_2 impinger catch. Our studies have not shown this condition to be attributable to artifact formation or interferences in the analytical method.

Any plausible explanation for changes in the formate and acetate concentrations must take into account the highly reactive nature of aldehydes. An IPA impinger catch obtained from an actual source test necessarily contains a complex mixture of both organic and inorganic species. It has a relatively long residence time in its concentrated form prior to dilution and subsequent analysis. Conversely, an IPA impinger catch obtained from a laboratory-generated sample remains an essentially pure solution, and it has a relatively short residence time in its concentrated form prior to dilution and subsequent analysis. Thus, in the absence of a suitable oxidizing agent such as H_2O_2 and given sufficient time, reactions involving a large percentage of any

aldehyde species condensed in the IPA solution will probably occur that decrease their original concentration significantly.

As an example of the above, aldehydes are known to be reduced in the presence of a zinc catalyst in acid solution (Morrison and Boyd 1979). XRF analysis detected zinc at 20 ppm; IC analysis detected the presence of the chloride ion, which, as HCl, is sufficient to make the solution acidic. Thus this reaction would not be unexpected. Assuming this explanation of aldehyde chemistry to be valid, the calculated collection efficiency of the various impingers of the CCS train based on the laboratory tests cannot be considered strictly representative of the efficiency of the system in actual field use.

Concluding Remarks

A complete interference study could not be accomplished within our allotted time period, but the compounds we considered the most likely candidates to cause interference were proven to pose none. We do not discount that another species may be responsible for the formate and acetate peaks, but we do feel that formaldehyde and acetaldehyde are the most likely candidates, if only from the standpoint that they are the most likely combustion products exhibiting the observed properties. Other studies have shown that formaldehyde is a key intermediate in low-temperature combustion sources and is the major emitted aldehyde (Harrenstien et al. 1979). In fact, formaldehyde may be formed from thermal decomposition of phenolic polymers, which may be responsible for the observed chlorophenols.

If another species is responsible for the observed results, then it must have the following properties: 1) oxidization to formate and/or acetate by 3% H_2O_2 , 2) no appreciable solubility in IPA/ H_2O_2 or great enough reactivity to be destroyed before analysis, and 3) no appreciable solubility in basic solution (no formate or acetate was observed in the NaOH impingers of the HCl train) or great enough reactivity to be destroyed before analysis. Clearly, a systematic survey of all compounds exhibiting these properties would be a major undertaking.

As a final point of reference, we analyzed other samples available for formate and acetate production. These sources included a hogged-fuel-fired boiler, and a coal-fired power plant. These results along with the Hempstead results are summarized in Table 14 (p. 29). The results both before and after treatment are given, and in Figure 12 (p. 30) representations of chromatograms of the Hempstead sample before and after treatment are shown. Since treatment with NaOH may possibly oxidize other species besides aldehydes, the untreated value should be considered a lower limit for the formaldehyde content of the flue gas. Table 14 readily illustrates that the lowest values were obtained for the coal-fired boiler, and by far the highest values for the hogged-fuel-fired boiler. Considering the relative efficiency of the combustion processes, the order of formaldehyde emissions would not appear to be unreasonable.

A means of verifying these results would be comparison of our sampling apparatus to another type of aldehyde train. Problems with this approach are that aldehydes are difficult to collect and stabilize, and other aldehyde trains are known to have numerous interfering compounds (Smith et al. 1972). Unique, undocumented problems may also exist with the Hempstead-type of emissions source.

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APPENDIX A

SAMPLING AND ANALYTICAL PROCEDURES

This section describes the sampling and analytical procedures implemented in characterizing selected source emissions at the Hempstead Resources Recovery Corporation Plant in Hempstead, New York, from July 24 to July 26, 1979. Also presented are the procedures followed during the course of follow-up laboratory investigations.

HYDROCHLORIC ACID DETERMINATIONS

The method used for chloride measurement was designed to collect gaseous and particulate chlorides emitted from stationary sources. The method employs a midget impinger sampling train to collect HCl in the flue gas via passage through a series of impingers containing 0.1 N NaOH; the chloride collected is then analyzed using IC.

Apparatus

The apparatus consisted of a heated quartz-lined probe, midget impinger sampling train immersed in an ice bath, a pump, and a dry gas meter.

Sampling

The train was prepared by loading 15 ml of 0.1 N NaOH into the first two midget impingers and 15 ml of 3% hydrogen peroxide (H_2O_2) into the third impinger. The fourth impinger remained empty. A piece of Pyrex glass wool was inserted into the inlet of the probe to filter out particulate matter. Impinger solutions were allowed to equilibrate in the ice bath and the system

was leak checked. Each sample was pulled for approximately 1 h at a flow rate of about 1 liter/min. The probe was allowed to cool prior to sample recovery.

Sample Recovery

Recovery of the sampling train entailed collecting three separate fractions: (1) the probe plug wash, (2) the probe wash, and (3) the combined 0.1 N NaOH impinger catches. Each fraction was recovered and stored in a separate 125 ml Nalgene polypropylene sample bottle.

Sample Analysis

All samples were quantitatively transferred to appropriately-sized volumetric flasks, proportionally diluted, and subsequently analyzed using IC. The IC employed a 3 x 500 mm column in combination with a 3 x 150 mm precolumn. Samples were analyzed on the 10 $\mu\text{mho/cm}$ range using 0.006 M sodium carbonate (Na_2CO_3) as the eluent. Results were reported in total milligrams per sample.

HYDROCHLORIC ACID — ELECTROSTATIC PRECIPITATOR DETERMINATIONS

The current method for characterizing chloride emissions draws the sample first through a glass wool filter plug and then through a solution capable of retaining HCl. Recent studies indicate that significant amounts of HCl can be retained by the glass wool filter media. In an attempt to alleviate this inherent source of bias, an electrostatic precipitator (ESP) was utilized (Cheney, personal communication).

An integrated sampling system was developed implementing both an ESP to remove particulate chlorides, and impingers containing 0.1 N NaOH to remove HCl. The flow rate required for efficient operation of the ESP necessitated the use of a larger Greenberg-Smith impinger train.

Apparatus

The equipment consisted of a heated quartz-lined probe, an electrostatic precipitator, a sampling module, a sampling pump, and a dry gas meter. The sampling module contained an ice bath for the Greenburg-Smith impingers, along with voltage controls to heat the probe and filters.

Sampling

Sampling preparations involved loading 200 ml of 0.1 N NaOH into the first impinger; 200 ml of 3% H_2O_2 into the second impinger; and filling the last impinger with silica gel. All components were allowed to reach operating temperature and the impinger train was leak checked.

The flow controller was adjusted to a flow rate of approximately 15 ft³/h for a sampling time of 2 h. After concluding a run, the probe and ESP were allowed to cool prior to sample recovery.

Sample Recovery

Recovery of the sampling train required the collection of five different fractions: (1) the probe wash, (2) the ESP wash, (3) the ESP filter, (4) the 0.1 N NaOH impinger catch, and (5) the 3% H_2O_2 impinger catch. Fractions were recovered and stored in separate polypropylene sample bottles. Cooled fractions from the ESP were rinsed with three 15-ml portions of distilled deionized water. The washings were saved and stored in a separate polypropylene sample bottle. The ESP filter was stored in a plastic petri dish.

Sample Analysis

All samples were quantitatively transferred to appropriately-sized volumetric flasks and diluted to the mark with distilled deionized water. Solutions were analyzed using an IC employing a 3 x 500 mm column combined with a 3 x 150 mm precolumn. Samples were analyzed on the 10 $\mu\text{H}/\text{cm}$ range using 0.006 M Na_2CO_3 as the eluent. Results were reported in total milligrams per sample.

SULFUR OXIDE DETERMINATIONS

The sampling method utilized for the measurement of sulfur oxides was the Controlled Condensation System (CCS) (Cheney and Homolya 1979), designed to separate and collect the various sulfur oxides from stationary sources. Using a Goksøyr-Ross type condensation approach, a heated quartz filter, and a Greenburg-Smith impinger train, the CCS was designed to collect and separate sulfur oxides belonging to four main categories: (1) particulate sulfates and sulfites, (2) sulfuric acid, (3) sulfur trioxide gas, and (4) sulfur dioxide gas.

Apparatus

The apparatus utilized in the CCS system consisted of a heated quartz-lined probe, a glass filter holder, a glass plug holder, a sampling module, a sampling pump, and a dry gas meter (see Figure A-1). The sampling module contained an ice bath for the Greenburg-Smith impingers, along with a water bath for the plug holder, and voltage controls for heating the probe and filter.

Sampling

The system was prepared for sampling by measuring 200 ml of 80% IPA into the first impinger and 200 ml of 3% H_2O_2 into the second impinger; the last impinger was filled with silica gel. All components were allowed to reach operating temperature and the impinger train was leak checked. During sampling all temperatures were monitored and readjusted as necessary.

The flow controller was adjusted to maintain a flow rate of 10 liter/min for a sampling time of 0.5 h. Following the conclusion of each run, the impingers were purged for 15 min at a 10 liter/min flow rate. The probe and filter were allowed to cool before sample recovery.

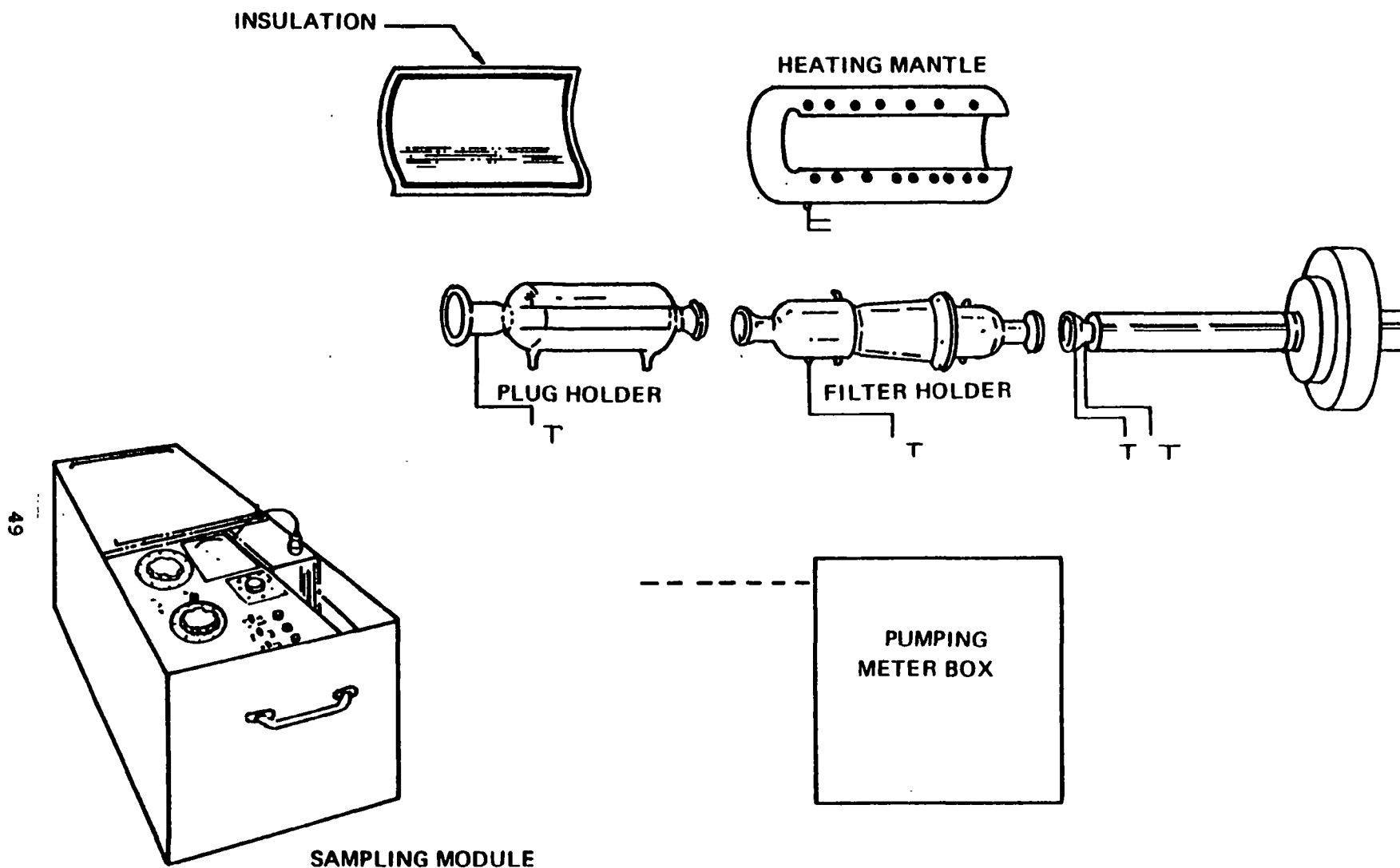


Figure A-1. Schematic drawing of manual acid condensation system. A sampling pump and dry gas meter are contained within the pumping meter box.

Sampling Recovery

The sampling train was recovered as five fractions in separate bottles: (1) probe wash, (2) filter, (3) plug wash, (4) 80% IPA impinger catch and (5) 3% H_2O_2 impinger catch. Each fraction was recovered and stored in a polypropylene sample bottle. The filter was stored in a plastic petri dish.

Sample Analysis

All samples were quantitatively transferred to volumetric flasks and diluted to a known volume. The samples were analyzed by IC, employing a 3 x 500 mm column, combined with a 3 x 150 mm precolumn. Samples were analyzed on the 10 $\mu\text{mho/cm}$ range using 0.006 M Na_2CO_3 as the eluent. Results were reported in total milligrams per sample.

ALDEHYDE DETERMINATIONS

While analyzing the CCS-1- H_2O_2 sample fraction for sulfur oxides by IC, a large peak was detected at a retention time of ~2.70 min in the .006 M Na_2CO_3 element system. This retention time does not correspond to those of standards used for calibration (F^- , Cl^- , etc.). Investigations were conducted to determine the identity of this unknown species by using standard solutions of various ions. The peak was thus tentatively identified as the formate ion (HCOO^-).

Verifications of the peak's identity was achieved by analysis of the sample in two eluent systems using sodium formate reference standards. One system consisted of a 0.0015 M NaHCO_3 element at a flow rate of 130 ml/h in conjunction with a 3 x 150 mm precolumn, a 3 x 500 mm anion separator column, and a 6 x 250 mm suppressor column. Samples were analyzed on the 10 $\mu\text{mho/cm}$ range using an external standard method of analysis. The second system consisted of 0.005 M $\text{Na}_2\text{B}_4\text{O}_7$ element at a flow rate of 156 ml/h in conjunction with a 3 x 150 mm precolumn, a 3 x 500 min anion separator column, and a 6 x 250 mm

suppressor column. Samples were analyzed on the 10 μ mho/cm range using an external reference method of analysis.

With the much greater resolution of fast-eluting ions attributable to using these weak eluents, the unknown peak originally detected as a solitary peak by the strong eluent (.006 M Na_2CO_3) was resolved into two peaks. These peaks were positively identified as formate and acetate. All aldehyde determinations reported were based on analysis of samples collected using the CCS.

LABORATORY ALDEHYDE DETERMINATIONS

This section describes the sampling and analytical procedures implemented in the laboratory to examine the reliability of using the CCS for aldehyde emissions characterization.

Apparatus

The apparatus utilized in the laboratory consisted of a sampling train identical to the system utilized in field for the sampling of sulfur oxide. The system consists of a heated quartz-lined probe, a glass filter holder, a glass plug holder (condenser), a sampling module, a sampling pump, and a dry gas meter. The sampling module contains an ice bath for the Greenburg-Smith impingers, a constant temperature water bath for the glass plug holder, voltage controls for heating the probe and filter, and a thermocouple meter for monitoring the temperature of the various components of the system.

Sampling

In conducting the laboratory studies, care was taken to duplicate as nearly as possible the operating parameters used in the field when sampling with the CCS. During sampling the probe and filter were maintained at a temperature of 520° F, the plug holder at 140°F, and the impinger was immersed in an ice bath. Sampling was conducted for a period of 30 min at a sampling rate of 10 liter/min.

The system was prepared for sampling by measuring 200 ml of 80% IPA into the first impinger and 200 ml of 3% H_2O_2 into the second impinger. For the blank run, three impingers were used, with the third containing dried silica gel. This arrangement duplicates the impinger train as utilized in the Hempstead sampling. In other runs conducted, the solutions contained within the third and fourth impingers depended upon the particular experiment being performed. All components were allowed to reach operating temperature and the impinger train was leak checked. During sampling all temperatures were monitored and readjusted as necessary.

Following each run, the impingers train was purged for 15 min at a 10 liter/min flow rate. The probe and filter were allowed to cool before sample recovery.

Formaldehyde gas was generated and sampled by connecting a .5 in Tygon line to the probe liner on one end with a teflon connector, and to the outlet of a Greenburg-Smith impinger with a ground glass joint connector on the other end. The impinger was then changed with 200 ml of a formalin solution in a hood at ambient temperature. Sampling was conducted by pulling ambient air through the impinger solution and into the heated probe of the CCS train. The initial blank run consisted of pulling laboratory air through the Tygon line and into the heated probe.

Acetaldehyde gas was generated and sampled in a similar manner, except that the Greenburg-Smith impinger was filled with pure acetaldehyde (~30 ml) to a level below the glass center tube in the impinger. The incoming air was therefore passed over the liquid surface, rather than bubbled through the liquid.

In selected sample runs, 10-ml aliquots of the IPA and H_2O_2 impinger solutions were extracted for separate analysis after the conclusion of the sample run and prior to the 15 min purge of the impinger train.

In order to determine the effects of high carbon dioxide concentrations (~10% CO_2 in stock concentration) in air sampled by the CCS train, a cylinder containing 5% CO_2 in air was employed to collect samples using one 80% IPA impinger, followed by one 3% H_2O_2 impinger. The impingers were immersed in an ice bath and the cylinder gas was bubbled through the impinger train at a rate of 10 liter/min for 30 min.

Sample Recovery

Each sample run was recovered in four separate fractions as follows: (1) the probe wash, (2) the filter, (3) the glass-wool plug wash, and (4) the impinger train (collected separately), each impinger being rinsed with D.I. H_2O . Except for storage of the filter in a plastic petri dish, all sample fractions were placed in polypropylene sample bottles.

Sample Analysis

All samples were diluted to a known volume (impinger catches to 100 ml, all other fractions to 100 ml) with D.I. H_2O , and then analyzed for formate and/or acetate ions using a Dionex Model 10 IC. The IC method of analysis consisted of a 0.0015 M NaHCO_3 eluent in conjunction with a 3 x 500 mm anion separator column and a 6 x 250 mm anion suppressor column. The samples were analyzed using the 10 $\mu\text{mho/cm}$ range of the instrument with the eluent flow rate adjusted to 120 ml/h. An external standard method of analysis was employed using standards prepared from stock standard sodium formate and sodium acetate solutions.

During the course of the study, selected samples were pretreated with H_2O_2 and/or NaOH prior to analysis. Known amounts of standard stock H_2O_2 and/or NaOH solutions were added to a 50-ml aliquot of the sample and mixed thoroughly, then allowed to stand overnight prior to analysis.

The sample, consisting of 10-ml aliquots of the IPA and H_2O_2 impinger extracted prior to purging, were diluted to 50 ml with D.I. H_2O , thereby monitoring the 4:1 dilution ratio used for the individual impinger catches (i.e., 200 ml were diluted to 1000 ml).

Analysis of the DNPH/HCl impinger catch (CCS Run #9) was performed gravimetrically; analysis of the DNPH/MeOH impingers (CCS Run #11) was performed by a colorimetric technique (Lappin and Clark 1951).

ORGANIC DETERMINATIONS

The sampling method utilized for the measurement of total organic emissions from stationary sources was a prototype sampling system. The method was designed to retain the organic emissions in an Amberlite XAD-2 column. Samples were analyzed using GC and GC/MS.

Apparatus

The apparatus utilized in this system consisted of a heated quartz-lined probe, an Amberlite XAD-2 column, a Greenberg-Smith impinger train, a pump, and a dry gas meter.

Sampling

The sampling train was prepared by inserting the Amberlite XAD-2 column (8 in long x 1/2 in diameter) between the first and second impinger. The first impinger was left empty to condense out water. The second impinger contained 200 ml of 3% H_2O_2 . Silica gel was used in the last impinger.

The impinger solutions were allowed to equilibrate in an ice bath. The system was leak checked prior to each run. Each run consisted of pulling a gas sample through the heated probe, which contains a glass-wool probe plug, and through the impingers and Amberlite XAD-2 column. The sample was pulled at a rate of approximately 25 ft³/h for 1 h.

Sampling Recovery

Recovery of the sampling train entailed the collection of two separate fractions (1) the first impinger catch, (2) the Amberlite XAD-2 column catch.

The contents of the first impinger were transferred to a one-liter glass sample bottle. The impinger was rinsed several times with distilled-deionized water. The washes were stored in the glass sample bottle along with the original impinger catch. The ends of the Amberlite XAD-2 column were sealed with glass ball and socket joints.

Sample Preparation and Analysis

All samples were extracted using methylene chloride. The extracts were quantitatively transferred to 100-ml volumetric flasks and diluted to the mark using methylene chloride. The sample fractions were concentrated down to approximately 1 ml. The samples were transferred to individual, clean, tared 5-ml glass vials with teflon liners. The sample fractions were completely dried under a nitrogen environment. The vials were reweighed and the mass of organic residue in each vial was recorded for the calculation of mass emission rates.

Samples were then diluted, using methylene chloride, to a concentration of 15 to 20 µg of organic residue per microliter of methylene chloride. Sample fractions were analyzed by a Hewlett-Packard Model 5985A GC/MS under the following operating parameters:

	Maximum Cut-off Temp	Desired	Actual
Temperature, initial °C	350	50	51
Temperature, final °C	350	275	275
Injection port temperature, °C	400	275	275
FID temperature, °C	400	300	300
TCD temperature, °C	300	275	275
AUX temperature, °C	300	275	274
Rate, °C/min	6.00		
Chart speed	1.00		
Zero	10.0		
Attenuation, 2T	4		
FID Signal	+B		
Slope sensitivity	0.10		
Area reject	1000		
Flow A, ml/min	8.1		
Flow B, ml/min	41.2		

Purification of XAD-2/Resin

The Amberlite XAD-2 resin was purified prior to sampling using the following procedure:

- (1) The resin was washed in a 2-liter roundbottom flask with two 1-liter portions of distilled-deionized water. Care was taken to ensure that the mixture was well shaken.
- (2) Next, the resin was refluxed with 1 liter of reagent-grade methanol for 7 h.
- (3) After removing the methanol, 1 liter of "glass distilled" methylene chloride was added to the mixture, which was then allowed to sit for 17 h. The mixture was refluxed for 7 h and the methylene chloride decanted.
- (4) Step 3 was repeated.
- (5) Finally, the resin was dried in the oven in a glass container at 80° C for 1 h.
- (6) The resin was stored in a sealed, all-glass container until ready for use.

APPENDIX B

CALCULATIONS

$$\text{Standard Cubic Feet (SCF)} = K \times \sigma \times V_{\text{dgm}} \times P_{\text{bar}}/T_{\text{dgm}} \quad (\text{Eq. B-1})$$

where $K = 17.636 \text{ }^{\circ}\text{R/in Hg}$,
 $\sigma = \text{dry gas meter calibration factor}$,
 $V_{\text{dgm}} = \text{dry gas meter volume}$,
 $P_{\text{bar}} = \text{barometric Pressure, in Hg, and}$
 $T_{\text{dgm}} = \text{dry gas meter temperature, }^{\circ}\text{R}$.

$$\text{Parts Per Million (PPM)} = \frac{K_1 \times \text{mg}}{\text{MW} \times \text{SCF}} \quad (\text{Eq. B-2})$$

where $K_1 = 849.52 \frac{\text{PPM} \times \text{g} \times \text{ft}^3}{\text{mg}}$
 $\text{mg} = \text{number of milligrams of pollutant}$,
 $\text{MW} = \text{molecular weight of pollutant, and}$
 $\text{SCF} = \text{standard cubic feet of sample}$.

$$\text{Mass emissions rate (lb/h)} = K_2 \times \text{mg} \times \text{VFR/SCF} \quad (\text{Eq. B-3})$$

where $K_2 = 2.205 \times 10^{-6} \text{ lb/mg}$
 $\text{mg} = \text{number of milligrams of pollutant}$,
 $\text{VFR} = \text{volumetric flow rate of stack, } 4.4 \times 10^6 \text{ SCF/h}$
 $\text{SCF} = \text{standard cubic feet}$.

The percent operating capacity was calculated based on a steam generation rate of 200,000 lb/h, equivalent to a 100% operating capacity.

A volumetric flow rate (VFR) for the stack had to be assumed in calculating the mass emission rates. The value used, 4.4×10^6 SCF/h, was the average value calculated from three tests (Method 5) performed on Furnace #1 by New York Testing Laboratories, Inc. (1979), from April 30 to May 1, 1979 while the unit was operating at 96% capacity. The results in this report are based on samples collected from Furnace #2.

The mass emission rates for sulfur oxides are based on the analysis of sulfur oxides collected in the HCl sampling train.

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